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PETROLOGY, GEOCHEMISTRY
AND
TECTONIC SETTING
OF
SOME FLYSCH DEPOSITS

by

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Thesis submitted for the degree of
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Unless otherwise acknowledged, all data and interpretations in this thesis are my own.

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ABSTRACT

The Paleozoic flysch sequences of eastern Australia show large variations in their mineralogical and geochemical compositions. On the basis of detrital mineralogy, the following five graywacke suites are recognized : Tamworth, Hill End, Hodgkinson, Bendigo and Cookman. The graywackes exhibit increasing maturity from the Tamworth to Cookman suites, characterised by an increase in quartz content and a decrease in lithic and feldspar grains. The graywacke suites are derived from dominantly andesitic, dacitic, crystalline, meta-sedimentary and sedimentary source rocks, respectively. The associated mudrocks are also characterized by variations in abundances of phyllosilicates and tectosilicates (feldspar and quartz). Three broad groups of mudrocks are recognized : tectic type (Tamworth suite); phyllo-tectic type (Hill End and Hodgkinson suites); and phyllic type (Bendigo and Cookman suites).

With the increase in mineralogical maturity, increasing geochemical differentiation is observed in the sedimentary suites, in the form of enrichment of Si and Zr in graywackes, and enrichment of large cations (K, Rb, Ba), Al-group (Al, Ga) and ferromagnesian elements (Cr, Ni, Zn) in mudrocks, and loss of small cations (Ca, Na, Sr) in solution. A close similarity is observed between the Th, U, Nb, La/Y, Zr, Sc/Ni, Ni/Co, La/Yb and rare earth element characteristics of graywacke suites and orogenic andesites from various tectonic settings. On this basis, the Tamworth suite is assigned to an oceanic island arc; the Hill End suite to a continental island arc; and the Hodgkinson suite to an Andean type tectonic setting. The Bendigo and Cookman suite graywackes are characterised by their highly quartzose nature and highly fractionated chemistry, suggesting their recycled nature and possibly a passive margin type of tectonic setting.

The major element geochemistry of arenites can be used to infer the provenance type and tectonic setting of sedimentary basins. In general, there is a progressive decrease in total Fe as Fe_2O_3+MgO;TiO_2; Al_2O_3/SiO_2 and an increase in K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ in arenites as the tectonic setting changes from oceanic island arc to continental island arc to Andean type to passive margins.

The trace element characteristics of sedimentary rocks show excellent signatures of provenance types and tectonic settings. The most useful elements are those which are relatively immobile, fractionate only in the clastics and have low residence times in sea water, e.g., Th, U, Nb, Zr, REE, Y, Sc and Co. Optimum discrimination of oceanic island arc, continental island arc, Andean type and passive margin tectonic settings is achieved by La-Th; Ti/Zr-La/Sc; La/Y-Sc/Cr; La-Th-Sc; Th-Sc-Zr/10; Th-Co-Zr/10; and Rb-V-Zr plots, for arenites. The trace elements in mudrocks also show characteristics of the tectonic setting and the most discriminating parameters are Th, Nb, U, Nb/Y, Th/U, Zr/Th and La/Sc.

The bulk oceanic island arc sedimentary composition is similar to the composition of the total crust, whereas the average Andean type-passive margin sedimentary composition is comparable to the upper continental crustal composition. The continental island arc sedimentary composition is intermediate. The change from oceanic island arc to continental island arc to Andean type and passive margin sedimentary compositions is similar to the change in the average compositions of sedimentary rocks from Archean through Proterozoic to Phanerozoic. This suggests a gradual mafic to felsic transition in crustal composition through geological time.

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CHAPTER 1
INTRODUCTION

1.1 SEDIMENTATION AND TECTONICS

It has long been recognized that the filling and structural evolution of geosynclines follow in an orderly fashion and that tectonics is the ultimate sedimentary control. With the advent of the plate tectonic theory, the relationship between the nature of the sediments and the tectonic cycles became apparent. However, "classical" geosynclinal terminology was found inadequate to categorise sedimentary basin types in the light of actualistic models of basin evolution (Dickinson, 1974a).

1.2 SEDIMENTARY COMPOSITION AND NEW GLOBAL TECTONICS

The question of how plate tectonics can explain the diversity and distribution of sedimentary rocks, has an important bearing on various geological problems. Krynine (1940 and later) outlined a definite relationship between sandstone petrography and tectonics. He divided sandstones into "quartzite", "graywacke" and "arkose" series, solely on the mineralogical basis and related them to the peneplanation, geosynclinal and post-orogenic stages respectively. Krynine's teacher, M.S. Shvetsov (1934) of the USSR probably influenced these ideas but it was this work which set the stage for the development of sedimentary tectonics.

However, soon after Krynine proclaimed these ideas, it was recognized that geosynclines could differ remarkably in their nature and thus show great variability in their sediment fill (Kay, 1951). This was followed by a great number of attempts to classify sandstones into various generic types. Hückenholz (1963) showed that the "arkose" and "graywacke" of the type areas can not be distinguished on the basis of rock fragments, or "clay matrix". Many of the classifications proposed were hypothetical and were never used other than by those who proposed them.

Recent attention towards sediments of the arc-trench system has contributed significantly to the understanding of the petrogenesis of sandstones (Dickinson, 1970a,b; Dickinson and Rich, 1972; Ingersoll, 1978a; etc.). Crook (1974) and Schwab (1975) showed that plate tectonics govern the relationship between sandstone composition and tectonic setting. According to them, quartz-poor arenites are indicative of magmatic island arc, and the quartz-rich types are indicative of passive continental margin (Atlantic-type). Quartz-intermediate types are associated with the Andean-type (tectonically mobile) continental margin. Reading (1974) also arrived at similar conclusions. This concept has been further expanded by Dickinson and Suczek (1979). The following three major groups of provenances (and several subgroups) and derivative sandstone suites have been recognized on the basis of triangular plots of framework grains:

1 Continental Block:- sources are on the shield, platforms and faulted basement blocks

2 Magmatic Arc:- sources are within the island arc orogen and the active continental margin

3 Recycled Orogen:- sources are deformed and uplifted sequences in subduction zones, along collision orogens or within foreland fold thrust belts.

Insights gained from the study of modern sediments of known tectonic settings have generally substantiated the above conclusions. Studies along these lines have been carried out by Potter (1978) on modern big river sands, and by Dickinson and Valloni (1980) and Valloni and Maynard (1981) on deep sea sands. Evidences for the plate tectonic theory are very well documented in the Mesozoic-Cenozoic record. The composition of sedimentary rocks make important contributions in interpreting the pre-Mesozoic plate settings because the provenance regions have been destroyed and the only record lies in the sediments derived from them. Thus, the relationship between sedimentary composition and plate tectonics provides a powerful tool for recognizing the nature of ancient continental margins. An example is the study carried out by Schwab (1981) on sedimentary rocks of the western Alps.

1.3 SEDIMENTARY ROCKS AND CRUSTAL EVOLUTION

Sedimentary rocks contribute significantly to the understanding of processes of crustal evolution. Continental glaciers traverse large areas of the crust and chemical alterations are minimal in these processes. The composition of the glacial beds has been used to estimate the composition of the continental crust (Goldschmidt, 1954). Similarly, many flysch sequences are emplaced with minimal chemical weathering and thus can provide a good estimate of the crustal composition of the region during sedimentation. The rare earth elements (REE) in sedimentary rocks have also been used to estimate crustal composition and growth (Taylor, 1979).

The presence of sedimentary rocks throughout the geological column, makes them an excellent candidate in deciphering secular trends in the composition of the crust. Studies along these lines have been done by Ronov and co-workers, who have collected massive data on the chemical composition of sedimentary rocks of the Russian Platform (Ronov, 1968;1972; Ronov and Migdisov, 1971; Ronov et al. 1974). Similar studies using different methods have also been done by Schwab (1978) and McLennan (1981a). Attempts have also been made to decipher the secular variation in the composition of individual lithologies, e.g. on carbonates (Veizer and Compston, 1974, 1976; Veizer, 1978; Veizer and Garret, 1978); on mudrocks (van Moort, 1973; Garrels and Mackenzie, 1971; Ronov and Migdisov, 1971) and sandstones (Ronov and Migdisov, 1971).

Very few studies relating the geochemical composition to the tectonic setting of the sedimentary basins, have been done. Middleton (1960) and Blatt et al. (1980) have suggested that taphrogeosynclinal sandstones are rich in K_20, eugeosynclinal sandstones are rich in Na_20 and exogeosynclinal sandstones are rich in Fe_20_3 + Mg0. Recently, Maynard et al. (1980) have also investigated the major element composition and tectonic setting of some modern deep sea sands. Pettijohn et al. (1972) have also suggested a broad geochemical classification of sandstones.

1.4 AIM AND SCOPE OF THE PRESENT INVESTIGATION

The above review clearly indicates that data on the geochemistry of sedimentary rocks are very meagre. The scheme for discrimination of the tectonic setting is dependent on the framework grains. The nature of the framework grains could be obliterated or destroyed by post-depositional alteration. A large part of the matrix in the older arenites may have formed due to the degradation of lithic grains (Cummins, 1962; Hawkins and Whetten, 1969). Moreover, such grains are almost impossible to correctly identify in metamorphic rocks. Geochemical studies can throw significant light in such cases.

Mudrocks, though forming a substantial part of sedimentary sequences, have remained neglected in lithogenetic studies. This has been because of their fine grain size and supposed monotonous mineralogical compositions. A detailed study of the mineralogy and geochemistry of mudrocks, complimentary to that of arenites, is most desirable. Estimates of the average geochemical composition of mudrocks and various types of arenites, like arkose, graywacke, lithic arenites, are very old and poorly constrained (Clarke, 1924; Middleton, 1960; Pettijohn, 1963). Nevertheless they have very frequently been used in literature. There is an urgent need to revise these estimates in the light of the tectonic setting discrimination of sedimentary rocks, and to systematise the variability of composition of sedimentary rocks within each tectonic setting and between different tectonic settings (Veizer, 1979).

It is apparent that many more data on clastic rocks on a global scale are needed in order to understand the evolutionary trends occurring on the crust. Ronov (1972) and Pettijohn et al. (1972) have emphasised the need for a more precise quantitative global estimation of volumes, masses, proportions and compositions of rocks of all geological systems in the light of the modern plate tectonic theory in order to get a clearer picture of long term trends over the whole history of the earth.

A large number of factors such as provenance, transportation, deposition, climate and diagenesis, control the composition of sedimentary rocks. The necessity of averaging and comparing petrological and geochemical data of like facies has been pointed out by Pettijohn et al. (1972) and Crook (1978). Inferences about sedimentary tectonics and crustal evolution can best be modeled on basins where transportation, depositional environment and diagenesis are subordinate to the provenance factor (Ingersoll and Suczek, 1980). Flysch forms the most suitable facies for such an exercise because "the detrital material from which it is constituted becomes homogenized in transit and is implaced and buried under hydraulic and geomorphic conditions which largely preclude further mineralogical and chemical differentiation" (Crook, 1978).

The Phanerozoic flysch sedimentary rocks of eastern Australia provide an unique opportunity for such a study because large variations are seen in the composition of the graywackes. The sedimentary basins studied are : the Tamworth Trough (New South Wales); the Hill End Trough (New South Wales); the Bendigo Trough (Victoria) and the Hodgkinson Basin (Queensland) (Figure 1.1).

The purposes of the present investigation are summarized below:

1 To differentiate various compositional suites of graywackes and mudrocks and to understand the relationship between mineralogy, geochemistry, grain size and facies.

2 To understand the relationship between tectonism and other factors which control the geochemical composition of sedimentary rocks and to propose a model of geochemical differentiation in sedimentary assemblages.

3 To propose criteria to discriminate tectonic settings on the basis of major and trace element characteristics of sedimentary rocks.

4 To examine the rare earth element (REE) geochemistry of sedimentary rocks in relation to their tectonic setting and to compare the REE compositions of tektites and various sedimentary rock types.

5 To estimate the bulk composition of the sedimentary assemblages in each tectonic setting and to compare these with crustal compositions.

6 To constrain the provenance of Archean sedimentary rocks by comparing their geochemical characteristics to those of sedimentary rocks of known provenance and tectonic setting.

7 To examine aspects of the secular variation in the composition of sedimentary rocks, the evolution of geosynclinal material and crustal growth.

1.5 TERMINOLOGY

Confusion exists in literature on the definition of the terms "flysch", "graywacke" and "turbidite". These terms have sometimes been used synonymously. The term "flysch" has been defined by various authors (Hsü, 1970; Stanley, 1970; Reading, 1974; Jipa, 1980; Crook, 1974). In the present work, Reading's (1974) definition of the term flysch as "any thick succession of alternations of sandstone, calcarenite or conglomerate with shale or mudstone, interpreted as having been largely deposited by turbidity currents or mass-flow in a

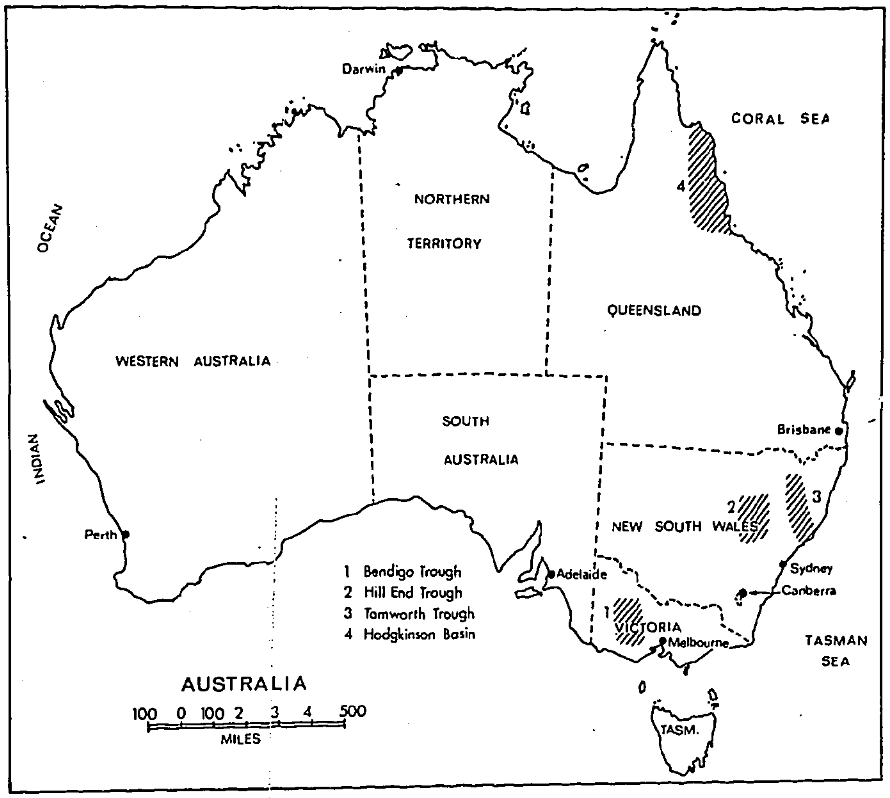


Figure 1.1 Location map of sedimentary basins. The Bendigo Trough has also been referred to as the Ballarat Trough in the literature.

deeper water environment within a geosynclinal belt", has been adopted. This definition fits in with the plate tectonic constraints on basin evolution. Jipa's (1980) definition differs in including some continental, specially large lacustrine type deposits, within flysch. Though many sedimentation units in flysch are emplaced as turbidites, they are by no means synonymous terms (Kuenen, 1967). Other emplacement processes can also contribute significantly to the accumulation of flysch sequences.

The term "graywacke" has been used in much more variable ways and no unanimity exists for its precise definition. The term "graywacke" has been defined by various authors on the basis of matrix content, lithic grains or sedimentary structures. In the present work, the term "graywacke", as generally used in Australia for the suite of rocks showing sedimentary features of the flysch type, has been adopted. This will fit into most definitions of wackes and graywackes in literature (Crook, 1974). The term "arenite" has also been used in a general sense for clastic sediments and sedimentary rocks of sand grain size (Folk, 1974). The terms "mud" and "mudrock" have been used to denote fine grained clastic sediments and sedimentary rocks, respectively. However, on many occasions the term "shale" as used by the original authors (e.g. Average Archean Shale (AAS)), has been retained.

1.6 SAMPLES AND ANALYTICAL TECHNIQUES

The sampling, preparation and analytical methods used in the present work are described in detail in Appendix A. The location of the samples subjected to geochemical analyses, is given in Appendix B. Multivariate statistical techniques were used on various data sets throughout this work. An introduction to these methods along with details of the computer programs used is presented in Appendix C.

CHAPTER 2
GEOLOGICAL SETTING OF THE SEDIMENTARY BASINS

2.1 INTRODUCTION

The Paleozoic rocks of the eastern third of the Australian continent constitute the Tasman Geosyncline. The geosyncline has been divided into various troughs and highs, each with a distinctive geological history (Packham 1960; Crook and Powell, 1976) (Figure 2.1). The western region has an Early Cambrian to Early Carboniferous history and is called the Lachlan Fold Belt. The eastern part with mainly a post-Silurian history is called the New England Fold Belt (see inset in Figure 2.2). The Hodgkinson Basin of northern Queensland does not form part of the Tasman Geosyncline _senso stricto_. However, Day et al. (1978) and Withnall et al. (1980) consider it to form the northern extension of the Tasman Geosyncline.

The geological history of the region has been described in detail by Brown et al. (1968), Scheibner (1976, 1978) and Crook and Powell (1976). The granitoids constitute an important lithology of the region and have been studied in detail by Chappell and White (1974) and White and Chappell (1977).

In this chapter the geological setting of the sedimentary basins studied, has been described in brief. The characteristic features of each basin are tabulated in Table 2.1.

2.2 TAMWORTH TROUGH

2.2.1. General Geology

The Tamworth Trough constitutes the western part of the New England Fold Belt and is separated from the Lachlan Fold Belt by the Permian-Triassic platform cover sediments of the Sydney Basin. The western boundary of the trough is now under this cover and the Great Serpentine Belt forms its eastern margin (Figure 2.2). The stratigraphy of the area seems to be complicated, probably because the same rock formations have been given different names in different regions (this is common in geosynclinal sequences). A simplified stratigraphic scheme has been adopted (after Crook and Powell, 1976) for the present work (Table 2.2). The areas constituting the Upper Horton and Barraba

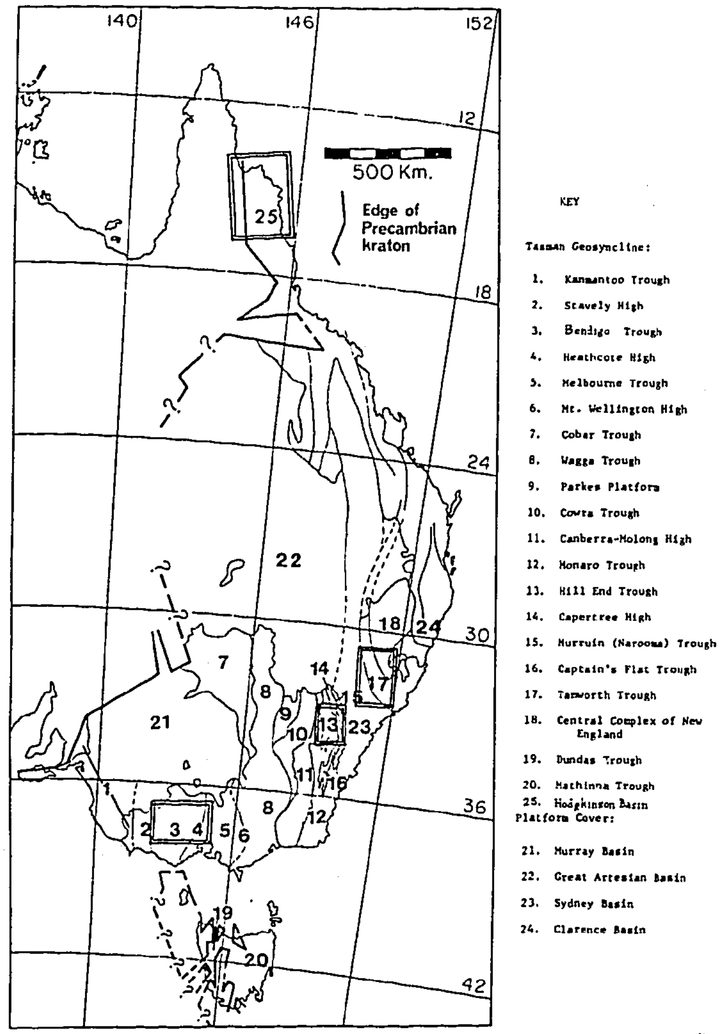


Figure 2.1 Generalised distribution of tectonic units in eastern Australia (After Crook and Powell, 1976)

Table 2.1. Summary of the characteristics of the sedimentary sequences studied in detail.

Basin	Age	Dominant Detrital Grains	Source Rocks	Paleogeographic Setting	Diagenesis-Metamorphism
Tamworth Trough	Devonian-Carboniferous	Andesitic RF, feldspar	Andesites	Fore-arc	Prehnite-pumpellyite
Hill End Trough	Silurian-Devonian	Dacitic RF, quartz, feldspar, Sed. RF	Dacites and sedimentary rocks	Inter-arc	Chlorite-biotite
Bendigo Trough	Ordovician	Quartz	Meta- Sedimentary rocks	Marginal basin	Lower chlorite
Hodgkinson Basin	Devonian	Quartz, quartzose RF, feldspar	Crystalline rocks	Retro-arc ?	Upper chlorite

RF - rock fragments

districts have been studied extensively by Dr. B.C. McKelvey and students of the University of New England and classified under the northern sector. All other parts of this trough have been classified under the southern sector. Structural, stratigraphical and sedimentological aspects of this region have been discussed in detail by a number of authors (Crook, 1959a,b; 1960a,b; 1961a,b,c; 1963, 1964; Marsden, 1972; McKelvey, 1974; Leitch, 1974 and Ellenor, 1975).

The limestones, chert and mudstones constituting the Trelawney and Uralba Beds form the oldest sedimentary strata of the sequence. These rocks are very limited in their geographical distribution and have yielded Cambrian-Ordovician trilobites, brachiopods, corals and conodonts (Cawood, 1976). The overlying Lower-Middle Devonian Tamworth Group sequence is developed only in the southern sector. These rocks are about 3000 metres thick and are rudites, arenites, radiolarian argillites and some lenticular biostromal limestones (Ellenor, 1975). The limestones are well developed in the Yarrimie Formation. The environment of deposition of this group is controversial. According to Crook (1964), the terrigeneous rocks were deposited by turbidity currents in deep water, but Marsden (1972) and Ellenor (1975) suggested that the sediments were deposited in relatively shallow-water. Local uplift of the basin has been envisaged to explain the deposition of carbonates concurrently with deep water turbidites (Brown et al. 1968). However Crook (1980b) suggested that the sequence was deposited in a complex terrain of varying water depths, much of it greater than 1 km below sea level. According to this explanation, the carbonate banks were accumulated along the small topographic highs, and were isolated from the deeper water.

The thick and monotonous sequence of volcanic rudites, graywackes and mudrocks constitutes the Parry Group of the Upper Devonian-Lower Carboniferous age. This group has been differently divided into various formations/beds in the northern and southern sectors (Table 2.2). The sequence shows typical features of turbidites and a westerly source has been inferred on the basis of paleocurrent studies (Crook, 1964; White, 1965). The Crow Mountain Creek beds (?Upper Carboniferous) are observed near the Woodreef area but their geographical extent and age is uncertain (Price, 1973). The sediments of the Parry Group pass upwards into the Kuttung Group with the shallowing of the basin and

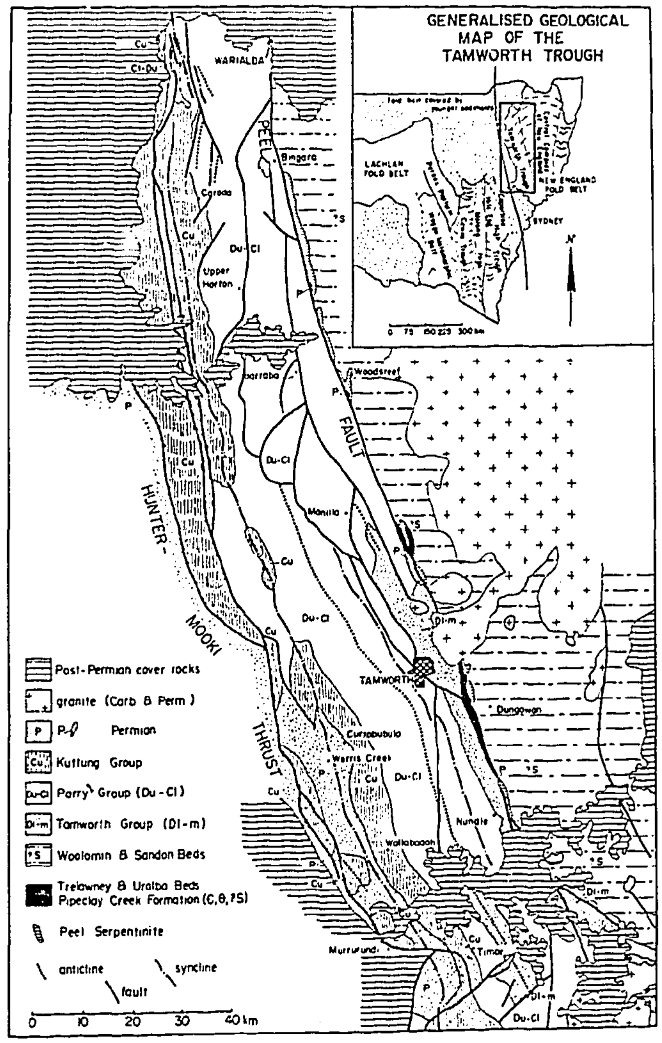


Figure 2.2 Generalised geological map of the Tamworth Trough (after Crook and Powell, 1976).

Table 2.2. Stratigraphy of the Tamworth Trough (after Crook and Powell, 1976)

			northern sector		southern sector	
Permian			Ironbark Ck. Arenite		Koogah Formation Werrie Basalt Temi Formation	Andersons Flat Beds
Carboniferous	upper	Kuttung Group	Lark Hill Formation Rocky Ck Conglomerate Plagyan Rhyolite Clifden Formation Ermelo Andesite Tuff Spion Kop Conglomerate Caroda Formation	Crow Mt. Ck Beds	Currabubla Formation Coeypolly Conglomerate Merlewood Formation	
Carboniferous	lower	Parry Group	Namoi Formation Luton Formation Mandowa Mudstone Keepit Conglomerate		Namoi Fm Tulcumba Sst Tangaratta Fm Mandowa Mudst Keepit Congl	Goonoo Goonoo Mudstone Boiling Down Sst Mem Gowrie Sst Mem Garoo Congl Mem Scrub Mtn Congl Mem Kiah Lst Mem
Devonian	upper		Eungai Mudstone Lowana Formation Noumea Beds		Baldwin Fm	Baldwin Formation
Devonian	middle lower	Tamworth Group			Yarrimie Formation Moore Ck Limestone Member Silver Gully Formation Loomberah Limestone Member Wogarda Argillite Drik Drik Formation Nemingha Limestone Member Copes Ck Keratophyre	
Camb. to Sil.			Uralba Beds (O)		Pipeclay Ck Formation (Є & O) Hawksnest Beds (O-S?) Trelawney Beds (O)	

consist of mainly sandstones, diamictites and mudrocks deposited in fluvial, glacio-fluvial and glacio-lacustrine environments. Some calc-alkaline andesites and rhyolites are also interbedded with the sediments of the Kuttung Group.

The detrital assemblage is mainly composed of andesitic rock fragments and feldspar grains, with very little quartzose grains. The sequence mainly exhibits zeolite to prehnite-pumpellyite facies of burial metamorphism.

2.2.2. Paleogeography

The paleogeography of this trough has been discussed by a number of the authors mentioned earlier. On the basis of mineralogical and chemical data of the graywackes, a tholeiitic andesitic provenance has been assigned to these rocks (Crook, 1960a,b; 1974; Chappell, 1968; Leitch, 1974). According to Leitch (1975), Scheibner (1976) and Crook (1980a) the Tamworth Trough sediments were deposited in a fore-arc basin having a volcanic arc in the west and a subduction complex in the east (Figure 2.3). Recent advances in the study of turbidite facies have greatly increased our understanding of deposition in deep-water basins (see recent reviews by Walker, 1978, Cas, 1979; Ingersoll, 1978b; Mutti and Ricci-Lucchi, 1978). Data on the turbidites and associated facies of the Tamworth Trough are insufficient, and more field studies are needed for a definite interpretation of the ancient fan morphology in the area. However, some preliminary observations are worth noting.

The sediments of the Tamworth Trough show typical features of turbidites, such as sole marks of various types. However, the well known graded bedding of the flysch sequences is often missing. Instead, the graywackes are generally thick bedded and massive. As such, in studying the facies, Bouma's (1962) sequence as modified by Cas (1979) was followed. The Tamworth sequence generally shows beds arranged in the a_2e, a_2a_2......; a_2bcde, a_2bce; bce; eee; manner. The Yarrimie Formation sequence is thin bedded, mudrock dominated, distal and characterizes the lower fan facies. It shows a coarsening upward feature into the turbidites of the Parry Group which are more proximal, exhibit a thickening of graywackes and a thinning of mudrocks, and characterise the mid-fan facies. The upper part of the Parry Group and the lower part of the Kuttung Group contain abundant conglomerate, pebbly and massive graywacke beds. An infilled

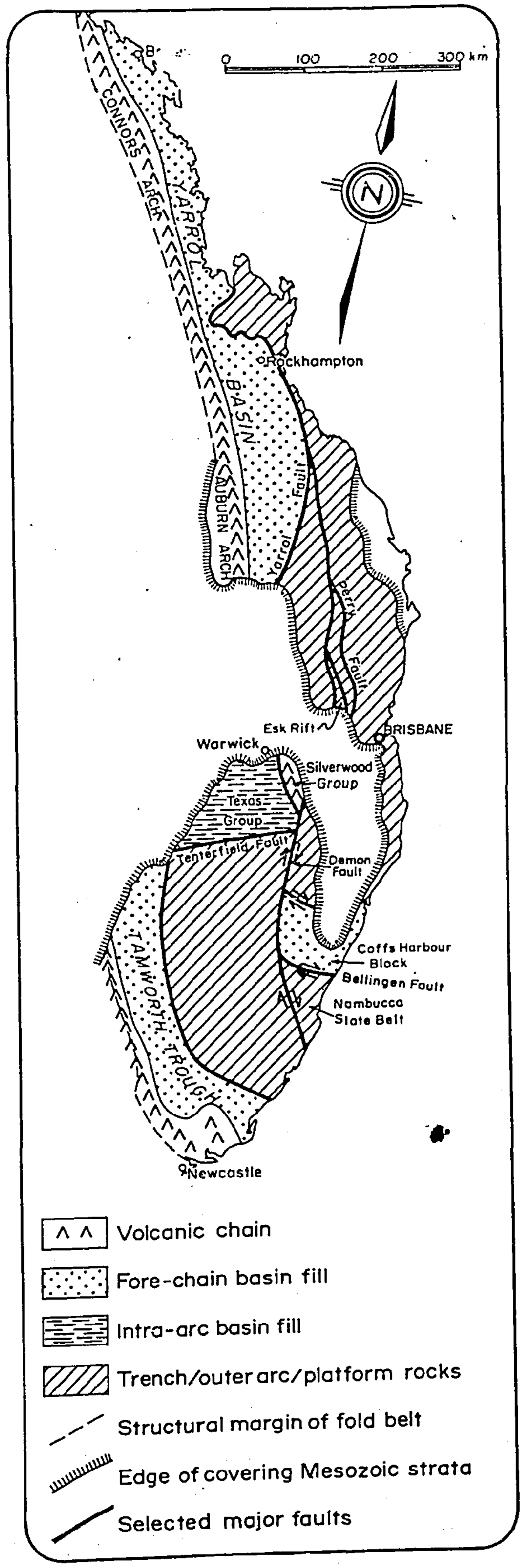


Figure 2.3 Tectonic interpretative map of the New England Fold Belt (after Leitch, 1975).

submarine paleocanyon, stimulating sedimentation in the upper fan, has been described in the Parry Group west of Barraba (McKelvey, 1974; Crook and Powell, 1976). Several unconformities have been reported in the sequence (White, 1965). These are of the infra-flysch type and occur due to paleocanyon fill (Crook, 1959). Thus the Tamworth Trough exhibits an overall coarsening upward sequence, indicating a change from lower through middle to upper fan facies, and can be interpreted as a complete progradation of a submarine fan.

2.3 HILL END TROUGH

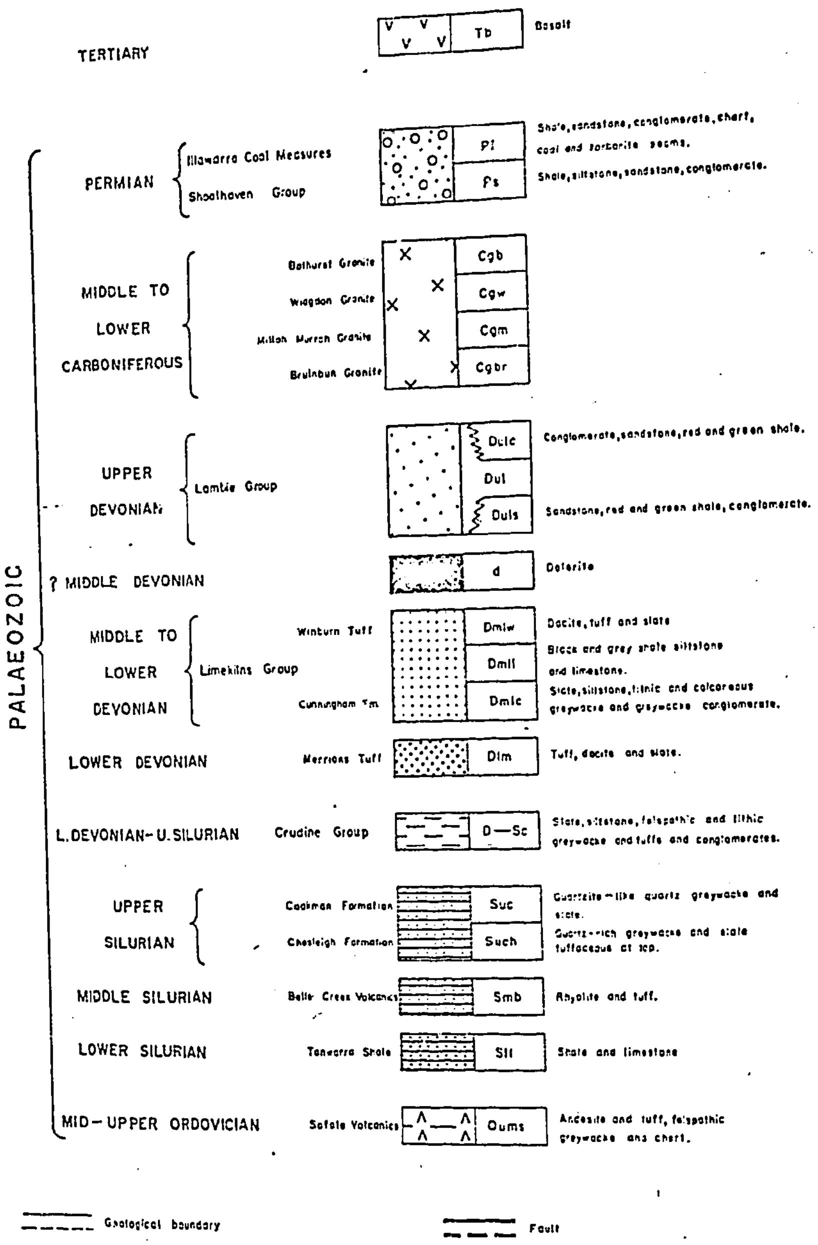
2.3.1. General Geology

The Hill End Trough (Silurian-Devonian) is one of the best studied basins in New South Wales. Significant contributions have been made in recent years on the stratigraphy, structure and evolution of this basin (Packham, 1960, 1968; Crook and Powell, 1976; Cas, 1977, 1979; Cas and Jones, 1979; Powell et al. 1977). The trough is flanked by coeval and older volcanics, limestones and other shallow water deposits of the Molong High in the west and of the Capertee High along the Wiagdon thrust in the east.

The Hill End Trough sequence is about 5000 meters thick and has been divided into various formations by Packham (1968, 1969; Figure 2.4). The Ordovician Sofala Volcanics are seen near the eastern margin of the trough and consist of mainly mafic lavas and minor volcaniclastics, limestones and chert beds.

The Chesleigh Formation is the oldest unit of the Hill End Trough flysch sequence and is about 1050 m thick. The lower 600 m consist only of thick bedded massive graywackes. The rest of the portion is made up of interbedded graywackes and mudrocks. There are a few tuffacious horizons in the lower portion of the Chesleigh Formation, particularly near the Hill End township.

The overlying Cookman Formation is about 450 m thick in the type section near Sofala and consists of an interbedded sequence of quartzose graywackes and mudrocks. Turbidite structures are common. Graywacke beds are generally from a few cm to 50 cm thick but beds upto a metre thick are also seen. The Turondale Formation, consisting of an interbedded sequence of about 600 m of graywackes (sometimes tuffaceous) and mudrocks, forms the lower part of the Crudine Group.



Legend for Figure 2.4

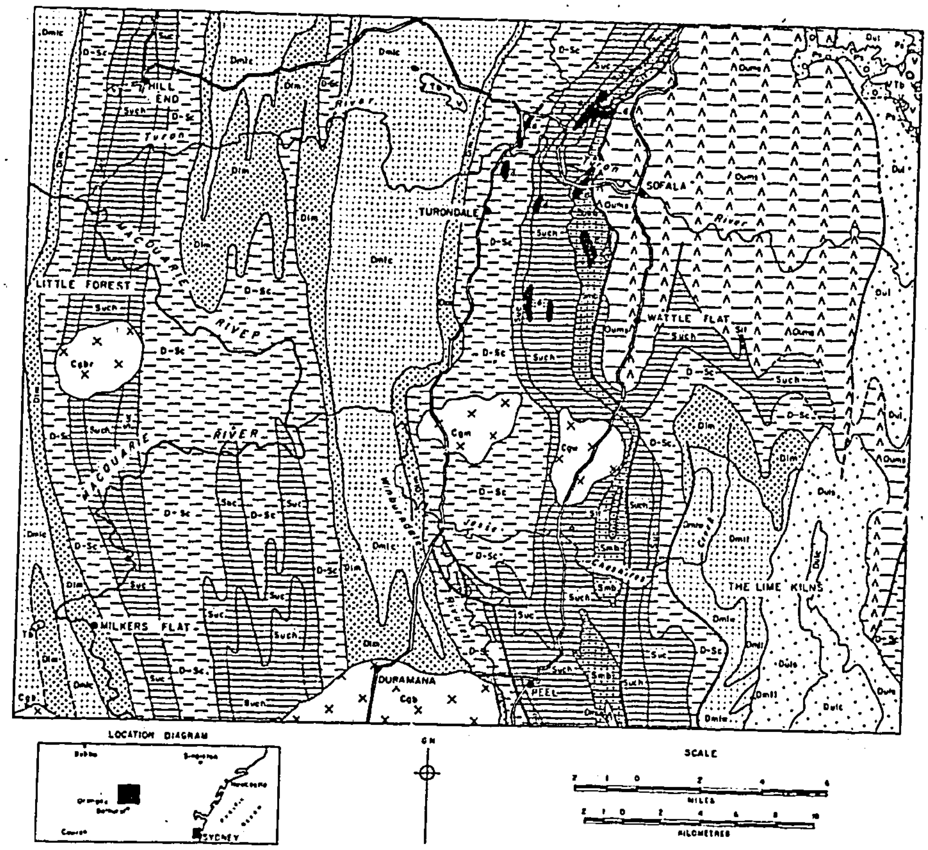


Figure 2.4 Generalised geological map of the Hill End Trough and surrounding regions (after Packham, 1969). See opposite page for the legend.

The Turondale Formation sequence has been broadly divided into three parts (Packham, 1968). The lower 250 m are mainly composed of thick bedded, amalgamated and massive tuffaceous graywackes and conglomerates. The clastics are mainly derived from a felsic volcanic source but some sedimentary rock fragments are also encountered. The overlying sequence, approximately 175 m thick, is generally fine grained and dominantly consists of mudrocks with a few interbedded graywacke beds. Graded bedding from graywackes to mudrocks is often seen. At places, small scale cross-bedding and ripple laminations are also observed. The upper 175 m thick portion of the Turondale Formation contains common tuffaceous beds similar to those of the lower portion but the beds are generally thin with a higher proportion of mudrocks.

The Waterbeach Formation forms the upper part of the Crudine Group, and consists of a 515 metre thick sequence dominated by mudrocks with minor intercalations of graywackes. Packham (1968) considers that the characteristic feature of this sequence is the absence of volcanic material. However, the graywackes do have a volcanic component, as revealed by the presence of felsic volcanic fragments though their proportion is considerably less, when compared with the Turondale Formation. Excellent turbidite structures such as graded bedding, parallel laminations, load casts, groove casts etc are commonly seen.

The Merrions Tuff has been considered as a marker unit in elucidating the history of the Hill End Trough. The formation is widespread and consists of equal proportions of volcaniclastics and silicic lavas. The volcaniclastics are generally massive, thick bedded and of felsic composition (Cas, 1977, 1978). Size grading is seen only where sedimentary units are thin. Amalgamated beds are very common. A "cold-state" subaqueous mass-flow origin within a deep basin on a relatively even basin-floor has been suggested to explain the emplacement of the Merrions Tuff (Cas, 1979).

The Cunningham Formation consists of a 1000 m thick sequence of interbedded graywackes and mudrocks and differs from the Merrions Tuff sequence in the absence of lavas and tuffs. It resembles clastics of the Waterbeach Formation, except that coarse grained material is more evident in the Cunningham Formation. The thinner beds show graded bedding. Turbidite and slump structures are common.

The Hill End Trough sequence is folded into a north-south trending synclinorium. The age of deformation was thought to be Middle Devonian, concurrent with the Tabberabberan orogeny (Packham, 1968). Recent work suggests that the major regional deformation occurred in the Early Carboniferous (Powell et al. 1977; Crook and Powell, 1976). The Turon River section (type area) forming the eastern part of the trough is metamorphosed to the chlorite grade, and the western part (near the Hill End township) to the biotite grade of the greenschist facies. Despite this metamorphism and deformation, the original clastic fabric is well preserved, especially in the chlorite grade, allowing recognition of the premetamorphic texture and structure.

2.3.2. Paleogeography

Scheibner (1973) suggested that the Hill End Trough originated in the Middle Silurian as an inter-arc basin of wholly intraoceanic type. However, Cas and Jones (1979) found a close similarity in the characteristics of the Hill End Trough and the southern apex of the modern inter-arc basin of the Havre Trough, where it impinges on the north island of New Zealand. According to these authors "........the Hill End Trough was, at most, an embryonic interarc basin, or the embryonic part of the arc, generated by the foundering and limited extension of a crust of continental or transitional, but not oceanic, character. The potential void thus created was filled by the products of active silicic volcanism and epiclastic sediments, partly of continental derivation". The paleogeography of the Hill End Trough during the Upper Silurian-Lower Devonian, as envisaged by Cas and Jones (1979) is shown in Figure 2.5.

Except for Merrions Tuff, the data on the sedimentary facies of the Hill End Trough are not sufficient to make an unequivocal assessment of the paleotopographical conditions that existed during the Silurian-Devonian. The thick sequence, measuring about 5000 metres, and the absence of any characteristics which are indicative of shallow-water conditions within the trough, suggest a marine and deep-water environment of deposition. Sedimentary structures such as graded bedding, flute casts, groove casts, small scale cross-bedding, ripple laminations and slump structures are commonly seen. The well known graded bedding of the flysch sequences is replaced by the massive and thick nature of coarse clastics, particularly in the Turondale Formation

Figure 2.5 Schematic paleogeographic reconstruction of the Hill End Trough-Canberra Magmatic Province during the Silurian-Devonian times (after Cas and Jones, 1979).

and Merrions Tuff. Turbidity currents and mass flows have been envisaged as the major processes of emplacement of the sediments in the Hill End Trough. Using the criteria as enumerated by Walker (1978), Ingersoll (1978b), Cas (1979) and Mutti and Ricci-Lucchi (1978), probably, a dominant lower fan to mid fan and minor upper fan facies can be recognized in the Hill End Trough sequence. However, a definite interpretation of the fan morphology during the Silurian-Devonian in the Hill End region requires detailed work on facies associations.

2.4 BENDIGO TROUGH

2.4.1. General Geology

The Bendigo Trough of Victoria comprises a thick fossiliferous sequence of quartzose graywackes and mudrocks. On the basis of abundant graptolites and brachiopods a Lower to Upper Ordovician age has been assigned to these rocks. Mount William Fault marks the eastern margin and the Wedderburn line marks the western margin of this trough (Figure 2.6). The Bendigo-Ararat zone together has also been referred to as the Ballarat Trough in literature (Brown et al. 1968; Crook and Powell, 1976). The Middle to Late Cambrian volcanics along with minor volcaniclastics, shale and chert beds of the Heathcote Axis lie near the eastern margin of this trough (Van den Berg, 1978). Black shales are abundant in the lower part of the Bendigo Trough sequence. Biostratigraphic zonations have been achieved on the basis of graptolite occurrences, however, no rock stratigraphic units have been defined. A definite esimate of the thickness of the sequence is lacking but a thickness of around 4,400 m (4000 m - Lower Ordovician and 400 m - Middle Ordovician) has been suggested (Brown et al. 1968). Deformation is thought to have occurred sometime between the Late Ordovician and Middle Devonian (Crook and Powell, 1976). The rocks generally exhibit a low chlorite grade of metamorphism.

2.4.2. Paleogeography

On the basis of the similarity of the facies, the sediment movement pattern and on scale perspective, a paleogeographic reconstruction similar to the modern Bengal Fan-Irrawaddy delta complex of the Indian Ocean has been suggested for the Ordovician of the Tasman Geosyncline by Cas et al. (1980). The paleotopographic reconstruction for the Late Ordovician is made up of a continental shoreline and shelf in western

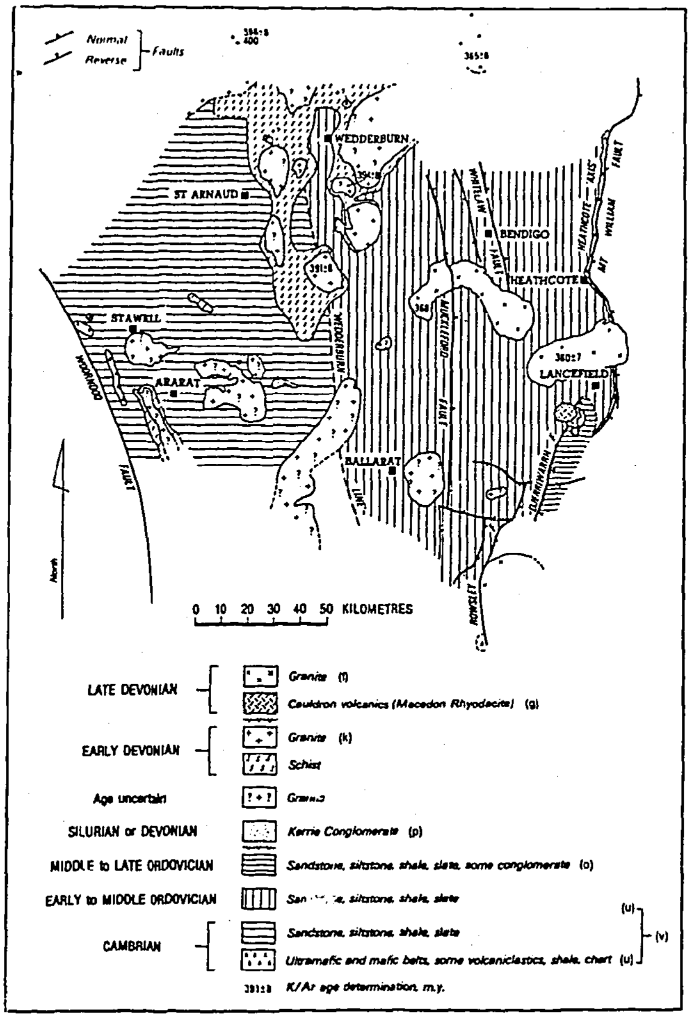


Figure 2.6 Generalised geological map of the Bendigo Trough and surrounding regions (after VanderBerg, 1978). In the present work Sandstones and all fine grained lithologies shown on this map are called graywackes and mudrocks respectively.

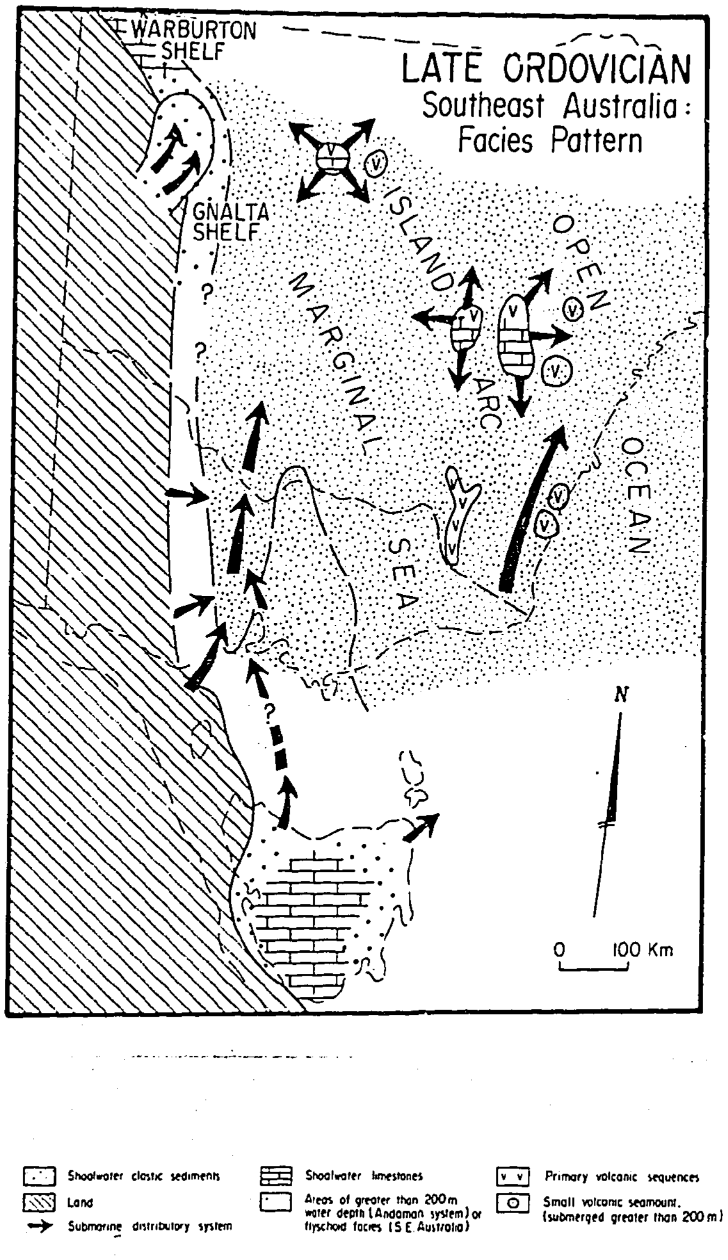


Figure 2.7 Paleogeographic map of southeastern Australia during the Ordovician (after Cas et al. 1980).

New South Wales, Victoria and Tasmania, a marginal sea in central New South Wales and Victoria (the Bendigo Trough), and a line of volcanic centres in New South Wales (Figure 2.7). Crook (1980b) has postulated a gradual migration of flysch deposition towards the east during the Ordovician period, and thus paleogeographic implications, as inferred for the Upper Ordovician by Cas et al. (1980), are also applicable for the Lower to Middle Ordovician of Victoria. The paleocurrent directions of dominantly northwesterly, northerly and northeasterly have been inferred for the Late Ordovician flysch sequence of Victoria.

The general occurrence of graded bedding and other turbidite structures, the wide extent of the sequence and the absence of shallow water structures suggest that the Bendigo Trough sediments were emplaced in a deep water environment. The graptolites are assumed to have been killed by the turbid water in the upper parts of the turbidity currents and then captured by the flow and settled down with the finer fraction (Douglas and Ferguson, 1976). Detailed facies studies of the area are lacking. However, the beds are dominantly fine grained and there is a complete absence of conglomerate beds. The beds are generally arranged in an eee manner in the lower part and a_3e, a_3be patterns in the upper part of the sequence, probably suggesting deposition in the lower to mid fan region.

2.5 HODGKINSON BASIN

2.5.1. General Geology

The Hodgkinson Formation is the most extensive unit of the Hodgkinson Basin of northern Queensland and covers an area of about 39000 square kms (Figure 2.8). The formation grades into its metamorphic equivalent - the Barron River Metamorphics towards the ~~southwest~~ northeast. The rocks are highly folded and thus the true thickness can not be accurately estimated. The eastern section of the Dasailly Range, on the Mulligan Highway, is estimated to measure between 7,500 and 10,000 m (de Keyser and Lucas, 1968).

The thick and highly folded sequences of interbedded mudrocks and graywackes with minor chert, conglomerates and volcanics constitute the Hodgkinson Formation. The mudrock is the most dominant lithology. The clastic rocks are conspicuous by the presence of abundant detrital muscovite and gneissic clasts. The volcanic rocks near the Daintree

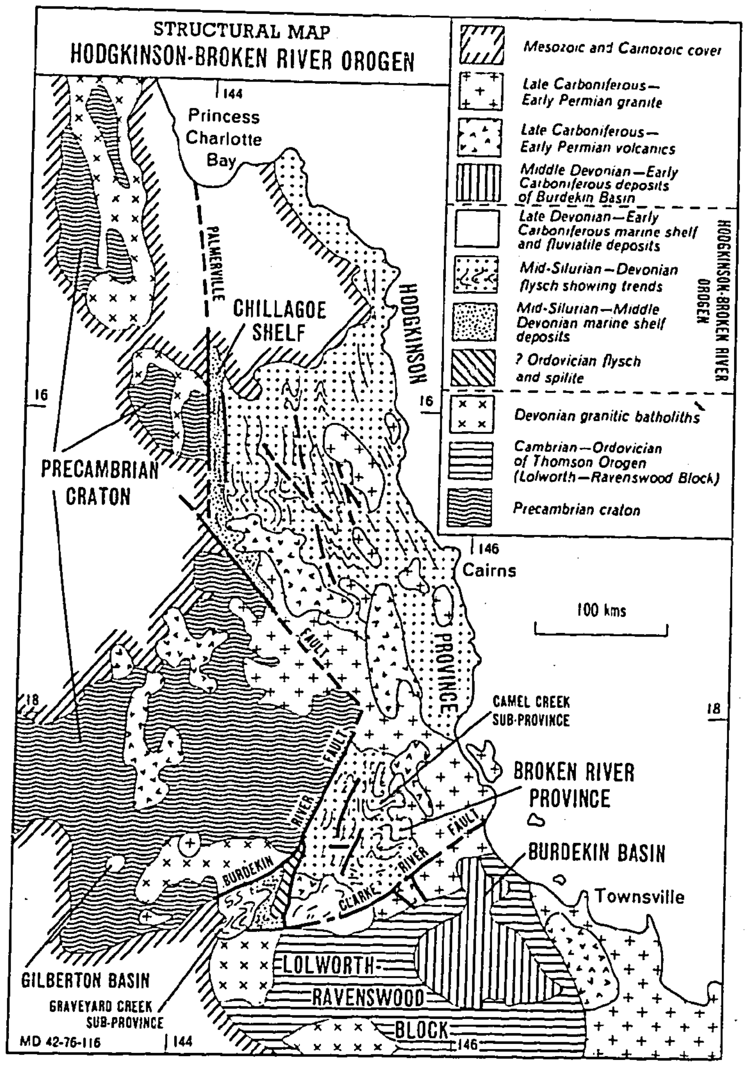


Figure 2.8 Generalised geological and structural map of the Hodgkinson-Broken River provinces (after Day et al. 1978).

River are mainly basic, and metamorphosed to the greenschist facies. Chemically they are close to spilites (de Keyser and Lucas, 1968). Volcanics exposed in the Dasailly Range are altered keratophyres or quartz keratophyres. Recent geochemical work has shown that the spilitised basalts of the Hodgkinson Basin have a close affinity with ocean floor tholeiites (Fawckner and Gregory, 1978).

Various fossil evidences summarized by de Keyser and Lucas (1968) clearly indicate a Devonian age for the Hodgkinson Formation.

The Hodgkinson Formation shows a chlorite grade of the greenschist facies of metamorphism but reaches the biotite grade in places. The intensity of deformation and metamorphism decreases from the northeast to the southwest, as is shown by the gradation from high grade Barnard Metamorphics through the Barron River Metamorphics and strongly folded but unmetamorphosed Hodgkinson Formation and finally to the milder regime of broad folding and faulting in the cratonic block region.

2.5.2. Paleogeography

Many problems still remain to be solved towards inferring the paleogeographic evolution of this basin. On the basis of the monotonous and extensive thickness of the formation, and the common occurrence of turbidite structures, the sequence can be assigned to the flysch facies. The presence of coralline limestone and the occurrence of plant remains suggest proximity to the coast and a shallow depth of the sea near the southwest part of the basin. Abundant detrital crystalline grains and rock fragments are seen in the graywackes of the Hodgkinson Formation. According to de Keyser and Lucas (1968) the Precambrian basement, probably exposed for a short time in geanticlines, formed the source rocks, whereas Crook (1967) suggested that the sediments have been derived from the adjacent epeirogenic cratonic region. A marginal basin developed by rifting near the edge of a continental margin, in which the sediments are from both these sources, has been favoured by Fawckner and Gregory (1978). Graded bedding, characteristic of flysch turbidites is extensively developed in the graywackes. Besides this, bottom structures like flute casts and load casts are commonly seen. Ripple cross laminations and parallel laminations are observed at a few places. Due to repeated folding, the structure of the area is complicated. Detailed work on the facies is lacking. However, the nature of bed thickness and sedimentary structures, suggest coarsening upward

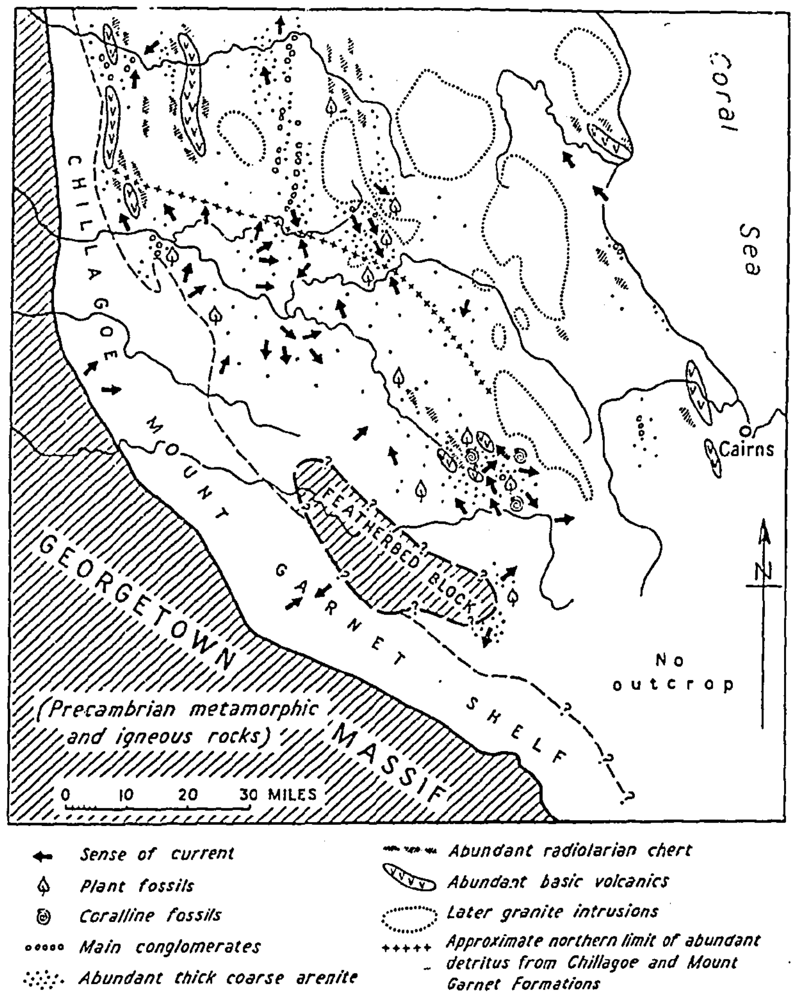


Figure 2.9 Paleocurrent directions in the Hodgkinson Basin. (after de Keyser and Lucas,1968)

sequence in Daisally Range (Mulligan Highway) and Mount Molloy sections, indicating that the sediments probably were emplaced in the lower to mid fan paleotopographic system.

An apparent discordance has been recorded in the current directions indicated by sole marks and cross-laminations (Figure 2.9; de Keyser and Lucas, 1968). This has been explained as due to either the non-contemporaneity of the strata in which the sedimentary structures occur or due to complex folding.

CHAPTER 3
DETRITAL AND DIAGENETIC CHARACTERISTICS OF GRAYWACKES

3.1 INTRODUCTION

Detailed textural, mineralogical and petrographic descriptions along with the model analysis data on graywackes of various stratigraphic horizons are presented in Appendix D. In this chapter, detrital characteristics, parameter associations and diagenetic features of various graywackes are highlighted.

3.2 GRAIN PARAMETERS

A large variation is observed in the grain characteristics of graywackes. The method of modal analysis is described in Appendix A. Various types of lithic grains were distinguished using the criteria of Dickinson (1970a), Wolf (1971), Graham et al. (1976) and Dickinson et al. (1979). Detrital parameters used for modal comparison are given in Table 3.1 and briefly defined below:

(1) Total quartzose grains (Q) include monocrystalline quartz grains (Qm) and polycrystalline quartzose lithic fragments (Qp). The polycrystalline component includes:

   a. chert grains which are microcrystalline and monomineralic silica aggregates

   b. meta-sandstone grains showing planar fabric

   c. aggregate quartz having intergrown crystalline quartz without preferred planar fabric.

(2) Total feldspar (F) includes plagioclase (P) and K-feldspar (K) grains.

(3) Unstable polycrystalline lithic fragments (L) are of the following types:

   a. Volcanic, metavolcanic and hypabyssal lithic grains (Lv). These are of various textural types but can be broadly classified into microlitic and felsitic types (Dickinson et al. 1979). Microlitic types show visible microlites or laths of plagioclase crystals displaying disoriented or fluidal fabric whereas felsitic types show a porphyritic to fine grained mosaic of quartz and feldspars.

Table 3.1 Detrital Grain Parameters

Q = Qm + Qp where	Q = total quartzose grains
	Qm = monocrystalline quartz grains
	Qp = polycrystalline quartzose grains
F = P + K where	F = total feldspar
	P = plagioclase feldspar
	K = K-feldspar
L = Lv + Ls where	Lv = volcanic-metavolcanic - hypabyssal lithic grains
	Ls = aphanitic sedimentary - metasedimentary lithic grains
	L = total aphanitic lithic grains
Lt = L + Qp where	Lt = total lithic fragments

b. Aphanitic sedimentary and metasedimentary rock fragments (Ls). These include grains of shale, slate, argillites, and murky and fine-grained schistose fragments. These fragments form a gradation of generally fine grained textures and fabric and contain abundant phyllosillicates.

3.3 DETRITAL CHARACTERISTICS OF GRAYWACKES

The average modal compositions of various graywacke groups are presented in Table 3.2. The terms quartz-poor, quartz-intermediate and quartz-rich are used in a broad sense for graywackes having boundaries at ≅ 15% and ≅65% of modal QFL quartz, respectively (Crook, 1974).

3.3.1 Tamworth Trough

The Tamworth Trough graywackes are fine to coarse grained volcaniclastics, composed of debris mainly derived from contemporaneous volcanic eruptions nearby. The framework grains are dominantly microlitic volcanic rock fragments, and volcanic feldspar which is almost all plagioclase. Quartz grains generally form less than 5% of the modal composition but clinopyroxene grains are common and form about 5% of the whole rock. Some graywacke beds are extremely rich in feldspar which can make up to 60% of the whole rock. These beds may have formed due to the reworking of detritus in the proximity of the source terrain. The dominant lithic nature of the detritus is common in graywackes of all stratigraphic horizons of the Tamworth Trough. The only exception is the slightly more quartzose nature of the Crow Mountain Creek Beds, which constitute a very small proportion of the Tamworth Trough. These graywackes are rich in quartz and feldspar and depleted in microlitic volcanic rock fragments compared to typical Tamworth Trough graywackes and thus are derived from felsic source rocks.

3.3.2 Hill End Trough

The Hill End Trough graywackes show large variation in mineral composition. Graywackes belonging to the Turondale, Waterbeach, Merrions Tuff and Cunningham Formations constitute the dominant part of the sequence and are mainly quartz-intermediate in nature. The dominant detrital grains are quartz, volcanic and sedimentary rock

Table 3.2 Average Modal Composition of Graywackes*

	Tamworth Trough**	Hill End Trough (1)†	(2)†	Hodgkinson Formation	Bendigo Trough
Quartz	7.7	33.7	73.1	49.8	60.5
Feldspar	28.9	9.8	0.8	12.9	2.1
Volcanic Rock Fragments	21.9	11.9	0.4	2.9	0.0
Sedimentary Rock Fragments	0.3	7.4	11.0	4.7##	2.5
Muscovite	0.1	0.5	1.8	4.8	14.7
Biotite	0.6	1.1	6.4	0.0	0.1
Accessories	1.1	0.9#	0.5#	2.9#	1.9#
Epidote	3.8	6.4	0.0	0.0	0.0
Pyroxene	2.9	0.0	0.0	0.0	0.0
Calcite	6.7	3.9	0.6	0.6	0.0
Opaques	2.9	1.5	0.9	0.7	0.1
Chlorite	3.4	1.5	0.1	0.4	3.1
Matrix	20.2	19.7	5.1	20.2	15.2

* Data from Tables D1-D5

** Includes Crow Mountain Creek Beds

\# Heavy Minerals (zircon, tourmaline & rutile)

†† Include Metamorphic Rock Fragments

†(1) Hill End suite (see Section 3.3)

†(2) Cookman suite (see Section 3.3)

fragments and feldspar. The quartz grains are mainly monocrystalline and of both volcanic and non-volcanic affinity. The volcanic rock fragments are mainly of the felsitic type. The feldspar is dominantly plagioclase. Sedimentary rock fragments are quite common and form up to 10% of the whole rock. The Turondale graywackes are slightly more feldspathic than others. The graywackes almost show a continuous gradation from volcanic rich to sedimentary rich detritus.

The graywackes of the Cookman Formation show quite different characteristics from the dominant graywackes of the Hill End Trough. They are quartz-rich and mainly composed of monocrystalline quartz grains. Sedimentary rock fragments are commonly seen. The feldspar and volcanic rock fragments are highly depleted compared to typical Hill End Trough graywackes (see above). The graywackes are also significantly low in matrix content, which forms about 5% of the whole rock.

The graywackes belonging to the Chesleigh Formation show wide variation in mineralogical composition. They contain varied assemblages and proportions of quartz, feldspar, volcanic and sedimentary rock fragments. The graywackes of the western region (the Hill End section) contain abundant volcanic rock fragments and are similar to typical Hill End Trough graywackes, whereas graywackes of the eastern region (the Sofala section) are more quartzose and contain less volcanic and more sedimentary rock fragments.

3.3.3 Hodgkinson Formation

The graywackes of the Hodgkinson Formation contain abundant mono- and polycrystalline quartzose grains. The most distinctive feature of these rocks is the presence of abundant mica, K-feldspar and polycrystalline quartzose grains. K-feldspar constitutes about half of the total feldspar content. The abundant polycrystalline quartz grains indicate derivation from crystalline sources. Besides these, volcanic and sedimentary lithic grains are also present and on an average form about 8% of the whole rock. Heavy minerals such as zircon and tourmaline are common, garnet is somewhat rarer.

3.3.4 Bendigo Trough

The Bendigo Trough graywackes are quartz-rich and are characterised by a high abundance of monocrystalline quartz grains. Feldspar forms about 2% of the whole rock and is dominantly plagioclase.

The sedimentary-metasedimentary and polycrystalline quartzose grains show large variation in their abundance but generally form less than 5% of the whole rock. Detrital muscovite is abundant and there is a complete absence of volcanic rock fragments. Tourmaline, zircon and rutile grains are common. The average matrix content is ≅ 15% of the whole rock.

3.4 GRAYWACKE SUITES

3.4.1 Petrofacies and Suites

Abrupt lithological changes, structural complexities, the lenticular nature of arenite bodies and the lack of fossil control on stratigraphy, are common features of geosynclinal terrains. These features make it very difficult to adhere to classical schemes of lithostratigraphy. The stratigraphically controlled variations in detrital mineralogy offer a useful approach to divide such complex terrains into various petrofacies, each representing intervals of nearly constant or predictable petrographic composition (Dickinson and Rich, 1972; Ingersoll, 1978a; Mansfield, 1979; Zuffa et al. 1980).

In this section, the graywackes have been divided into various groups on the basis of detrital characteristics. However, the term "suite" has been adopted because of the widely differing geographic locations of the sedimentary basins studied. The term "suite" can be assigned to the "assemblage of sandstones (graywackes in the present case) which over given intervals of time were deposited within single geographical and geological entities defined according to constraints of plate tectonics" (Schwab, 1981).

3.4.2 Modal Comparison

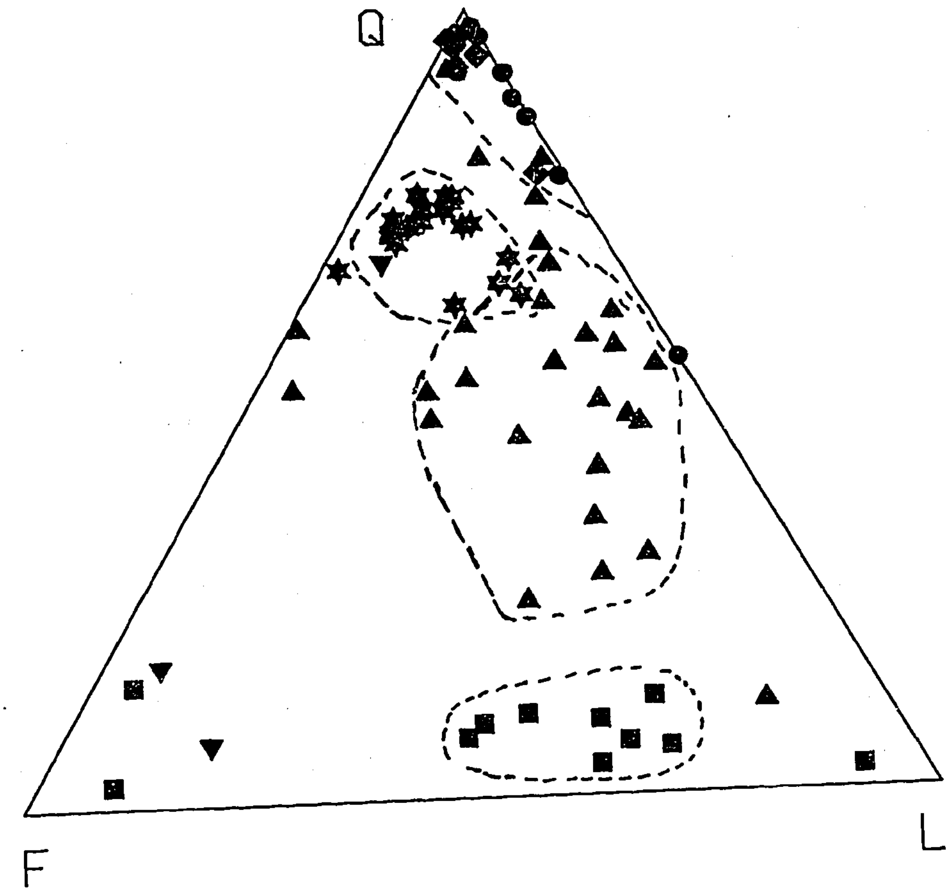
Various triangular plots, based on framework modes, were made. Two of the most discriminating plots are QFL and Qp Lv Ls (Figure 3.1). The following five main graywacke suites can be identified on these plots:

(1) Tamworth suite - mainly lithic graywackes (excluding the Crow Mountain Creek Beds)

(2) Hill End suite - mainly lithic but more quartzose compared to the Tamworth suite

Figure 3.1 QFL and QpLvLs plots showing the detrital characteristics of various graywacke suites. The dotted lines mark the typical field of various graywacke suites, but some samples in each suite plot outside the main field of the suite (also in Figure 3.2). Symbols are:

- ⊠ Tamworth suite
- ▽ Crow Mountain Creek Beds
- △ Hill End suite
- ✡ Hodgkinson suite
- ◈ Bendigo suite
- ⊛ Cookman suite


Q
F
L

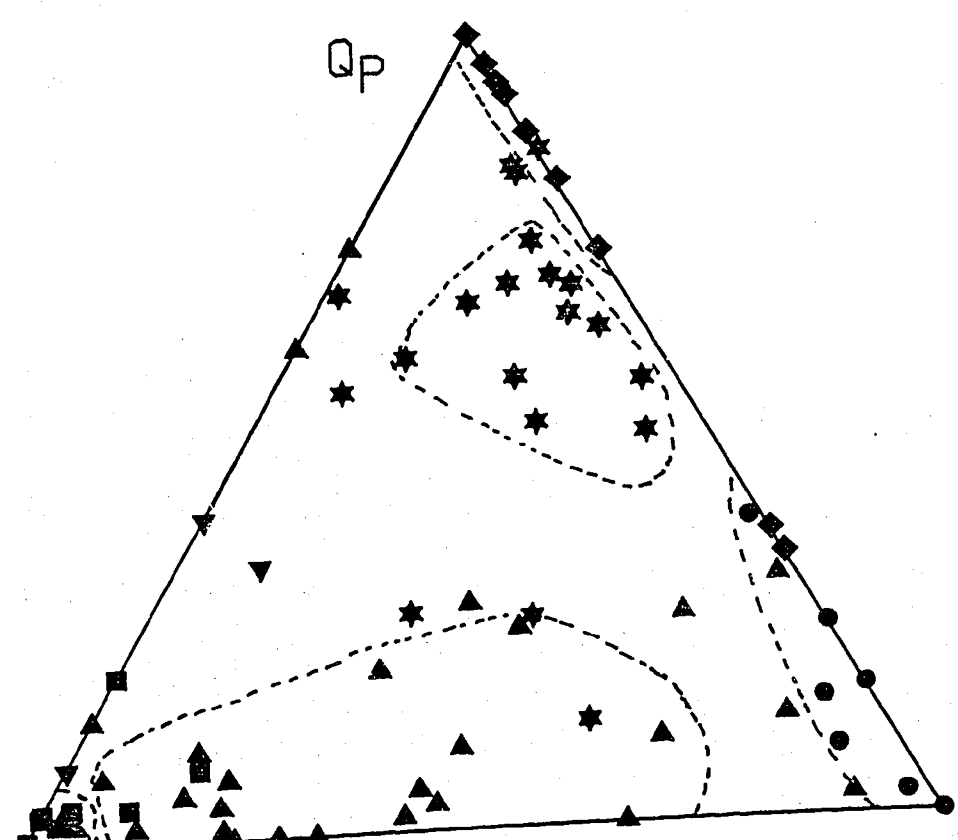

Qp
Lv
Ls

Table 3.3 Framework modes of graywacke suites

Suite		N	Q	F	L	Qm	F	Lt	Qp	Lv	Ls	Qm	P	K	P/F	Lv/L
Tamworth Suite	$\bar{X}$	11	7.8	40.5	51.8	6.2	40.5	53.0	4.8	92.4	2.7	14.3	81.3	4.4	0.94	0.97
	±L		2.5	14.9	15.6	2.3	14.9	15.7	3.6	5.1	3.0	4.9	7.2	4.1	0.05	0.03
Hill End Suite	$\bar{X}$	29	54.1	16.8	28.3	50.7	16.8	31.9	16.5	54.9	28.6	74.5	23.8	1.8	0.88	0.67
	±L		6.3	4.3	6.8	5.8	4.3	6.1	7.7	10.7	8.6	5.9	5.7	0.9	0.07	0.11
Hodgkinson Suite	$\bar{X}$	21	70.8	18.3	10.7	54.1	18.3	27.4	60.2	15.8	23.9	74.6	13.7	12.0	0.52	0.42
	±L		1.9	2.5	2.7	4.1	2.5	4.5	8.6	5.8	6.1	3.0	2.4	1.6	0.05	0.12
Bendigo Suite	$\bar{X}$	9	93.8	3.1	3.3	85.33	3.1	11.4	77.0	0	23.2	96.6	3.3	0	0.96	-
	±L		4.1	0.8	4.1	5.5	0.8	5.3	18.4	-	18.4	0.8	0.9	-	0.05	-
Cookman Suite	$\bar{X}$	8	86.5	0.9	12.6	83.9	0.9	15.3	19.5	1.9	78.8	99.1	0.9	0	1.00	.03
	±L		11.0	1.4	11.4	11.1	1.4	11.6	14.1	2.0	14.1	1.4	1.3	-	.01	-

Notes: N Number of samples
$\bar{X}$ Mean values
±L Uncertainities represent 95% confidence limits on the means

(3) Hodgkinson suite - sub-arkosic graywackes

(4) Bendigo suite - quartzose graywackes with common polycrystalline and feldspar grains

(5) Cookman suite - quartzose graywackes with common sedimentary rock fragments and negligible feldspar.

The framework modes characterising each suite are given in Table 3.3. The QFL effectively separates most samples of the volcanogenic Tamworth suite from both the more diverse and somewhat more quartzose Hill End suite and the more strongly quartzose rocks of the other three suites (Figure 3.1). There are not enough data but the three samples of the Crow Mountain Creek beds are more quartzose and show a large variation in mineralogy. They have a close affinity with the Hill End suite. Similarly, the Chesleigh Formation graywackes also show large variation in mineralogy, but because of the presence of common feldspar and volcanic rock fragments, they are included with those of the Hill End suite. The QpLvLs plot substantially separates the rocks of the Hodgkinson, Bendigo and Cookman suites, mainly on the basis of their different Qp:Ls ratios. The Bendigo and Cookman suite graywackes are highly quartzose and the differences between the two suites are not very large, though the Bendigo suite samples are generally enriched in Qp and the Cookman suite samples are rich in Ls. However, both suites have almost the same P/F ratio ≅ 1.

3.4.3 Maturity and Provenance Indices

The maturity of arenites has generally been defined by the relative proportions of stable (quartzose) and unstable (feldspar, volcanic rock fragments) grains. Thus, graywackes containing abundant feldspar and volcanic rock fragments are called immature or juvenile (e.g. Tamworth suite), and graywackes rich in quartzose grains are called mature (e.g. Bendigo and Cookman suites). Discrimination of the various graywacke suites can also be achieved by a plot of maturity index [MI = 100. Q/(Q+F+L)] against provenance index [PI = 100. F/(F+L)] (Figure 3.2). Zuffa et al. (1980) have used a similar plot to recognize various petrofacies in the Longobucco sequence of Italy. The Tamworth suite graywackes are distinguished from the Hill End suite graywackes by their low MI. The Bendigo and Cookman suite samples have the same MI. However, their PI differ somewhat - with the Cookman suite samples always having a PI < 20 and the Bendigo suite samples mainly having PI >

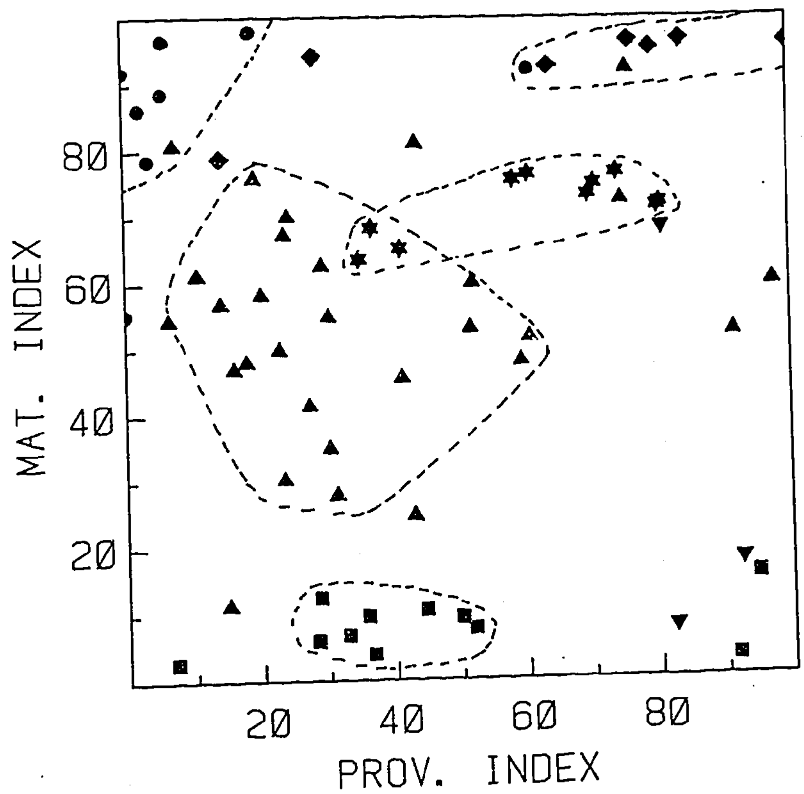


Figure 3.2 Plot of maturity index (MI) and provenance index for various graywacke suites. Only the Hodgkinson suite samples having the prefix MK are plotted, other samples also plot within the generalised field. Symbols as in Figure 3.1.

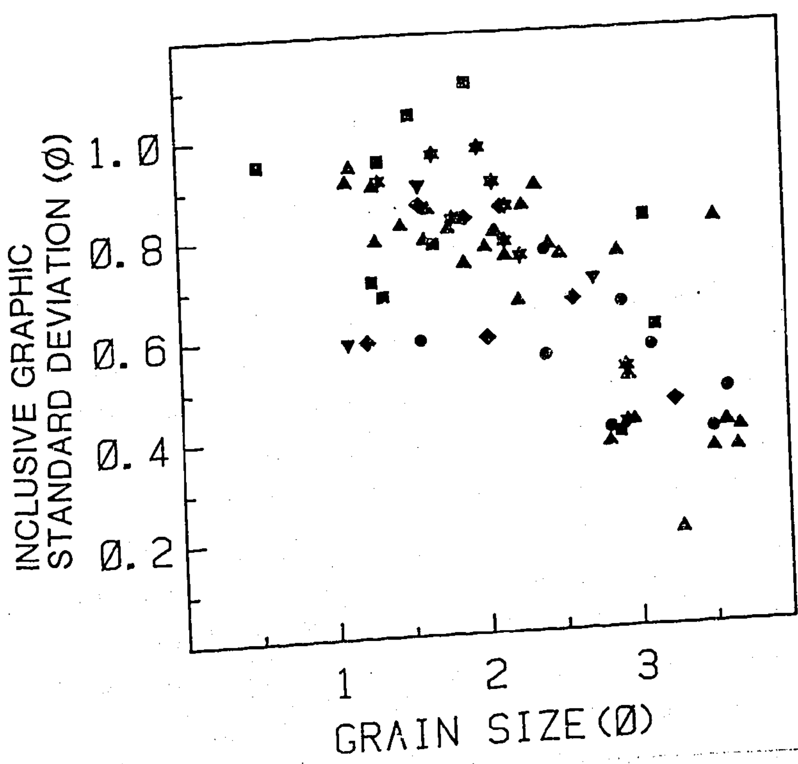


Figure 3.3 Plot of mean grain size versus inclusive graphic standard deviation for graywackes. Note that sorting improves with the decrease in grain size. Symbols as in Figure 3.1.

75. However, they can only be discriminated to a limited extent as two Bendigo suite samples plot near those of the Cookman suite.

Large variation is seen in the PI of almost all graywacke suites. There are not enough data but a detailed study may show that there are a number of petrofacies within each suite. For example, two petrofacies can be recognized within the Hill End suite : (a) comprising samples which are more feldspathic and show PI > 40 (mainly the Turondale Formation) (b) all other samples which are more lithic and have PI < 40. Similarly, there may be two petrofacies within the Hodgkinson suite as shown by the large variation in the PI of these samples. The limited data do not allow us to delineate various petrofacies within each suite.

3.5 PARAMETER ASSOCIATIONS

The correlation matrix has been computed in order to understand the relationship between the various framework parameters in different suites. The samples have been divided into three groups based on the suite: quartz-poor (Tamworth suite); quartz-intermediate (Hill End suite); and quartz-rich (Hodgkinson, Bendigo and Cookman suites). The three groups correspond to the three classes of graywackes of Crook (1974) and probably represent three "super-suites". The correlation matrix at the suite level would have been preferred but the small number of samples in some suites make inferences statistically insignificant.

The parameters selected are QFL% quartzose (Q), feldspar (F) and lithic grains (L); total mica (M); P/F and Lv/L ratios. Two textural parameters are also used for correlation purposes : mean grain size (Mz) and Inclusive Graphic Standard Deviation (S_I). One more parameter called the fan facies (FF) is also used for correlation matrix purposes (FF defined in Appendix A.7). The P/F and Lv/L ratios are preferred over the Q, F, L parameters because these ratios are not volumetrically complementary quantities. Consequently, correlation coefficients of ratios reflect better correlations of variables.

Correlation coefficients are calculated for each group independently and for the whole data set (Table 3.4). The 95% level of significance is accepted as the minimum value for identifying meaningful correlations, which are underlined in Table 3.4. High negative correlations between any of the two QFL parameters are not regarded as significant because of

Table 3.4 Correlation Matrix of Mineralogical and Textural Variables in Various Suites and in the Total Group (Significant correlations are underlined)

Quartz-poor Suite[1)]

	Q	F	L	M	P/F	Lv/L	Mz	S_I	FF
Q	1.00								
F	-0.13	1.00							
L	-0.47	-0.81	1.00						
M*	-	-	-	-					
P/F	-0.22	0.17	-0.28	-	1.00				
Lv/L	-0.38	-0.19	0.40	-	-0.12	1.00			
Mz	0.35	-0.04	-0.17	-	-0.11	-0.46	1.00		
S_I	-0.20	0.08	0.04	-	-0.11	0.24	-0.41	1.00	
FF	0.13	0.36	-0.40	-	0.10	-0.13	0.11	0.42	1.00

1) N = 11; r_{95} = 0.60; * No correlation because of absence of mica

Quartz-intermediate Suite[2)]

	Q	F	L	M	P/F	Lv/L	Mz	S_I	FF
Q	1.00								
F	-0.39	1.00							
L	-0.79	-0.25	1.00						
M	0.16	0.17	-0.28	1.00					
P/F	-0.14	0.16	0.04	0.05	1.00				
Lv/L	-0.15	0.42	-0.12	-0.36	-0.13	1.00			
Mz	0.02	-0.47	0.28	-0.13	-0.01	-0.16	1.00		
S_I	-0.10	0.42	-0.17	0.24	-0.04	0.18	-0.78	1.00	
FF	0.15	0.04	-0.17	-0.08	-0.28	0.13	0.04	-0.04	1.00

2) N = 29; r_{95} = 0.37

Quartz-rich Suites[3)]

	Q	F	L	M	P/F	Lv/L	Mz	S_I	FF
Q	1.00								
F	-0.58	1.00							
L	-0.78	-0.05	1.00						
M	0.39	-0.27	-0.26	1.00					
P/F	0.66	-0.43	-0.48	0.05	1.00				
Lv/L	-0.57	0.78	0.10	-0.22	-0.49	1.00			
Mz	-0.13	-0.30	0.39	0.18	-0.12	-0.13	1.00		
S_I	- .06	0.53	-0.33	-0.09	-0.16	0.39	-0.70	1.00	
FF	.03	-0.29	0.19	0.26	0.04	-0.11	0.17	-0.11	1.00

3) N = 24; r_{95} = 0.40

Total Group[4)]

	Q	F	L	M	PF	Lv/L	Mz	S_I	FF
Q	1.00								
F	-0.73	1.00							
L	-0.72	0.07	1.00						
M	0.51	-0.31	-0.45	1.00					
P/F	-0.29	0.25	0.17	-0.30	1.00				
Lv/L	-0.75	0.65	0.44	-0.55	0.26	1.00			
Mz	0.21	-0.31	0.02	0.08	-0.11	-0.21	1.00		
S_I	-0.18	0.28	-0.01	-0.04	-0.03	0.21	-0.70	1.00	
FF	-0.18	0.23	0.03	-0.02	0.06	0.21	-0.01	0.09	1.00

4) N = 64; r_{95} = 0.25

the volumetrically complimentary nature of these variables. The groupings of variables based on ratios can also be interpreted in more than one way, e.g., correlation between F and Lv/L could mean either F is positively correlated with Lv, or F is negatively correlated with L or both. The significance of correlation between P/F and Lv/L is even more difficult to interpret. Thus correlation coefficients determined in this study must be used cautiously and only as a first approximation of true associations.

The quartz-poor suite shows hardly any significant correlations. This could be due to the very small number of samples in this group. The quartz-intermediate and quartz-rich suites have some significant correlations which are also seen in the correlation matrix of the total group (Table 3.4). In the quartz-intermediate suite, grain size and standard deviation have a negative and positive correlation with the feldspar content, respectively. Similarly, in the quartz-rich suites, feldspar and lithic grains are related to standard deviation and mean size respectively. In general, there is a lack of significant correlation between fan facies and petrological parameters. As there is very small variation in FF (most samples are mainly from B, C and D facies), this relationship should be interpreted very cautiously. Ingersoll (1978a) has also found a general lack of significant correlation between "depositional facies" and petrological parameters in the Late Cretaceous sequence of California.

The parameter associations deciphered on the basis of correlation matrices are presented in Table 3.5. The quartz-poor suite shows only one doubtful association of LsMz. The quartz-intermediate suite has one volcanic (F Lv), one sedimentary-metasedimentary (M Ls) and one textural (FS_I) parameter association. The quartz-rich suites exhibit the maximum number of associations. There are two plutonic and metamorphic-sedimentary (QMP, K Ls); one volcanic (P Lv) and two textural (L Mz, F S_I) associations. In the total group, there is one plutonic and metamorphic (Q MK Ls), one volcanic (F Lv) and two textural (Lv Mz, F S_I) parameter associations. The volcanic association is prominent in the quartz-intermediate suite (and is probably also present in the quartz-poor suite but can not be deciphered due to the small number of samples), whereas plutonic, metamorphic-sedimentary and textural associations are more prominent in the quartz-rich suites.

Table 3.5 Parameter Associations in Various Graywacke Suites and Total Group

Quartz-poor suite

Ls Mz (?)

Quartz-intermediate suite

F Lv, Ls M, F S_I

Quartz-rich suites

QMP, K Ls, P Lv (?), L Mz, F S_I

Total Group

QMK Ls, P Lv, L Mz (?), F S_I

3.6 GRAIN SIZE AND MODAL COMPOSITION

Many recent investigations have shown that detrital composition is a function of the mean grain size of the rock (e.g. Okada, 1966; Odom et al. 1976). In a detailed study, Basu (1976) found that climatic differences in the source region produce size dependent trends in the principal constituents of the arenites. He observed that quartz and rock fragments generally decrease and feldspar increases in abundance with decreasing grain size in the Holocene fluvial sands. On the other hand, Misko and Hendry (1979) observed that quartz increases and rock fragments decrease in abundance with decreasing grain size in the Cretaceous and Paleocene sandstones of southern Saskatchewan. The difference between these two investigations suggests that may be there is no simple law governing the variation of detrital abundance with grain size in arenites.

The Inclusive Graphic Standard Deviation is a measure of the sorting of grains (Folk 1974). As is expected, sorting improves with the decrease in the mean grain size (Figure 3.3). The various suites overlap on this plot, but the linear relationship between the mean grain size and standard deviation is very clear in the total group ($r = -0.70$, Table 3.4).

The following observations, on the variation of modal abundance with grain size, are worth noting:

(a) Quartz decreases in the Hodgkinson and Bendigo suites, whereas it increases in the Hill End suite and probably also in the Cookman suite (Figure 3.5). However, the statistical valadity of these trends is not established.

(b) Feldspar decreases with decreasing grain size in most suites (Figure 3.5). This is further supported by a significant negative correlation ($r = -0.31$) between F and Mz in the total group (Table 3.4) and by parameter association (Table 3.5). However, this observation is in conflict with the contention of Basu (1976) and Odom et al. (1976) who have suggested that feldspar is enriched in the finer fractions. The apparent difference between the present observation and those of other authors is probably related to differences in the nature of material studied. The sediments examined in the present work are of geosynclinal type and were deposited with very little

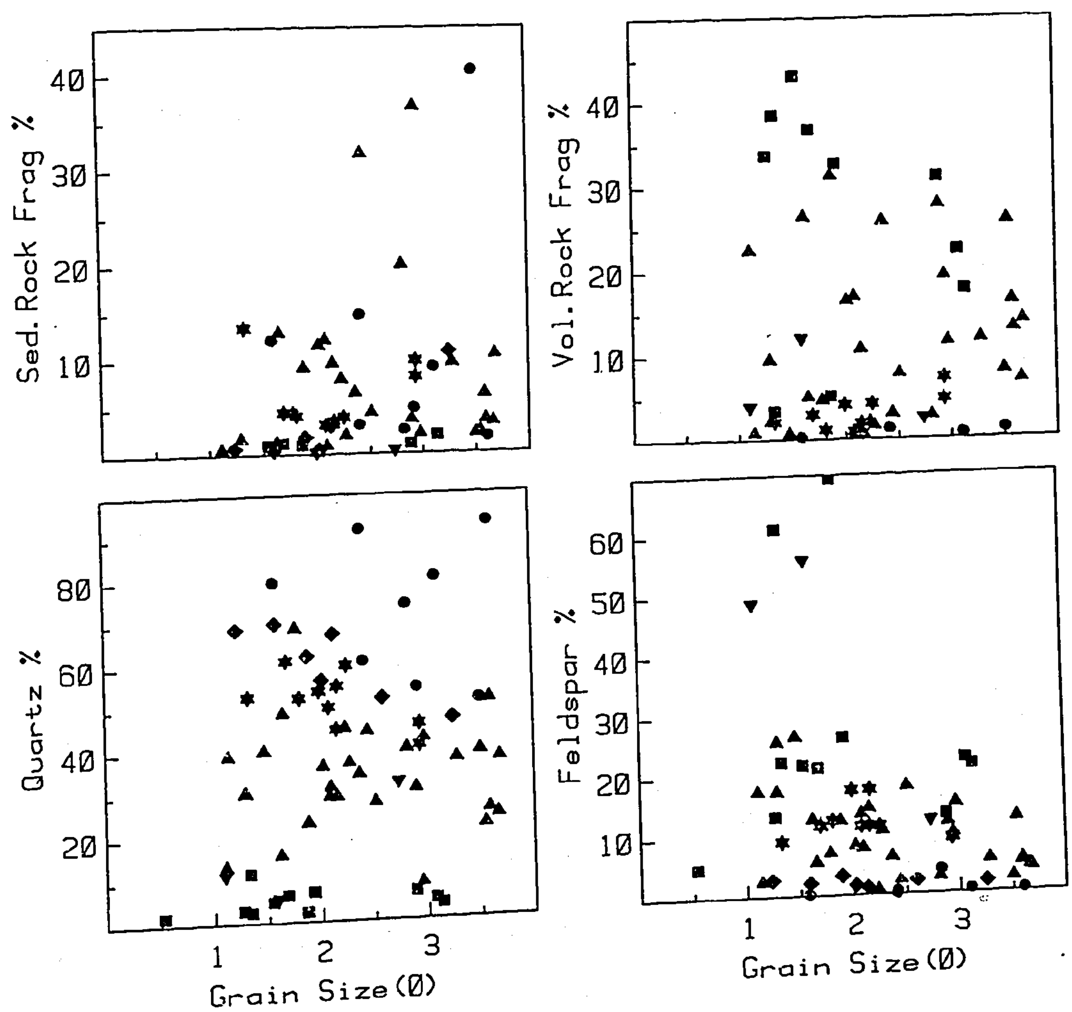


Figure 3.4 Plot of mean grain size versus sedimentary rock fragment, volcanic rock fragment, quartz, and feldspar percentage in graywackes. Symbols as in Figure 3.1.

chemical weathering, whereas those studied by Basu (1976) and Odom et al. (1976) were of continental type involving large scale chemical weathering. Thus, whereas in the flysch sequences, feldspar grains are enriched in the coarser fraction, in continental deposits feldspar grains are enriched in the finer fraction due to the significant weathering and decomposition of the larger grains.

(c) The data are not clear, but probably sedimentary rock fragments decrease in abundance with decreasing grain size (Figure 3.5). This is also supported by the weak negative correlation between Lv/L and Mz (Table 3.4). The true relationship between sedimentary rock fragments and grain size is difficult to determine because some of these fragments could be intra-basinal in character.

(d) In general, the volcanic rock fragments decrease with decreasing grain size in the Tamworth suite (Figure 3.5). The data are not enough to see this clearly but probably a similar trend exists in the Hill End suite and there is an opposite trend in the Hodgkinson suite. This is supported by a weak correlation of Lv/L with Mz in the total group (Table 3.4). The relationship of sedimentary and volcanic grains with grain size shows that these two detrital parameters compliment each other.

Thus on the basis of the above observations, it can be concluded that no simple grain size-detrital composition relation is valid for all the suites, though in most flysch sequences feldspar decreases with decrease in grain size. Probably opposite relationships of quartz abundance and grain size are noticed in the Hodgkinson and Hill End suites.

3.7 DIAGENESIS OF THE TAMWORTH TROUGH GRAYWACKES

3.7.1 Diagenetic Features

The Tamworth Trough graywackes show pronounced diagenetic changes due to burial metamorphism (Packham and Crook, 1960; Chappell, 1968). Three broad categories of diagenetic features occur : (a) authigenic cement (b) compaction features and (c) replacement features.

3.7.1a Authigenic Cement

A large variety of minerals such as calcite, phyllosilicates and iron-oxide now acting as cement were formed during diagenesis. No zeolite pore-fill cement was observed in the graywackes examined but such minerals are abundant in the upper part of the Parry and Kuttung Group graywackes (Packham and Crook, 1960). Phyllosilicate cement consists of pale green chlorite and occurs as well-crystallised flakes oriented perpendicular to the detrital minerals, unoriented microcrystalline aggregates or as clay coats. Calcite pore-fill cement is also common, particularly in the Tamworth Group graywackes. However, calcite pore-filling is probably related to the depositional environment, and is facies controlled rather than depth controlled (Galloway, 1974, 1979). Iron-oxide cement is minor and generally associated with clay coats.

3.7.1b Compaction Features

Crushing and mechanical compaction of the softer rock fragments is commonly observed. Argillaceous and volcanic rock fragments have been subjected to squashing, squeezing and crushing of various degrees to form "pseudo-matrix".

3.7.1c Replacement Features

Complex replacement and alteration of detrital grains is commonly seen in the graywackes. Chlorite, epidote, calcite, prehnite and pumpellyite are the major minerals seen replacing quartz, feldspar and volcanic rock fragments. Ca-plagioclase grains are completely to partly albitised. Devitrification of the volcanic material is common. Chlorite also impinges on and distorts the detrital grain boundaries.

3.7.2 Diagenetic Sequence

The diagenetic features observed in the Tamworth Trough graywackes are very commonly noted in volcaniclastics. The development of these features is related to the following diagenetic sequence (after Galloway, 1974, 1979; Burn and Ethridge, 1979):

Calcite pore-filling (Stage 1) → authigenic clay rims (Stage 2) → phyllosilicate pore-filling and zeolite cementation (Stage 3) → siliceous overgrowth and complex replacement (Stage 4).

The characteristic features of early stages also occur as relict features in the more diagenetically altered rocks.

The following three types of diagenetic reactions are known to form new minerals in volcanic graywackes (after Surdam and Boles, 1979) :

hydration, carbonatisation and dehydration. These reactions can be related to the diagenetic sequence envisaged by Galloway (1974) and given above. Early diagenesis is attributed to hydration and carbonatisation reactions whereas late diagenesis is attributed to dehydration reactions, though considerable overlap between hydration and dehydration reactions can occur. A descriptive framework of the diagenesis of volcanic graywackes (after Surdam and Boles, 1979), as related to the stratigraphic sequence of the Tamworth Trough is given in Figure 3.5 and the depth dependent variation of various features is presented in Figure 3.6.

3.7.3 Albitisation of Ca-plagioclase

The albitisation of Ca-plagioclase is a well known phenomenon in volcaniclastics and is dependent on the grain size of the rock and the amount of matrix or calcite cement present. Abundant amounts of matrix and calcite cement and the fine grained nature of the rock tend to inhibit albitisation of Ca-plagioclase (Coombs, 1954; Dickinson, 1962; Boles and Coombs, 1977). Fine grained samples are known to have low initial permeabilities and much of their original water and permeability may have been lost by compaction and/or cementation by the time albitisation occurred in medium and coarse grained rocks.

The process of the addition of sodium to detrital minerals has been discussed by many authors. According to Coombs (1961), sodium could be added to the system either by the formation of zeolites from volcanic glass at an early stage of diagenesis, or by the reaction of unusually saline water with phyllosilicates. Following Otalora (1964), Chappell (1968) suggested that the albitisation of Ca-plagioclase took place through the formation of analcime due to the reaction of connate water with clay minerals, rather than through the formation of zeolites in the Tamworth Trough graywackes. Experimental evidences are not sufficient to discount either of the mechanisms of albitisation. However where individual grains of rocks or large volumes of rock are albitised (as in the Tamworth Trough), Na^+ ions must be introduced from solution and excess Ca^{++} ions are released into solution in this manner (Boles and Coombs, 1977):

$$NaAlSi_3O_8 \cdot CaAl_2Si_2O_8 + 3SiO_2 + 2H_2O + Na^+$$
$$= 2NaAlSi_3O_8 + 0.5\ CaAl_2Si_4O_{12} \cdot 4H_2O + 0.5\ Ca^{++}.$$

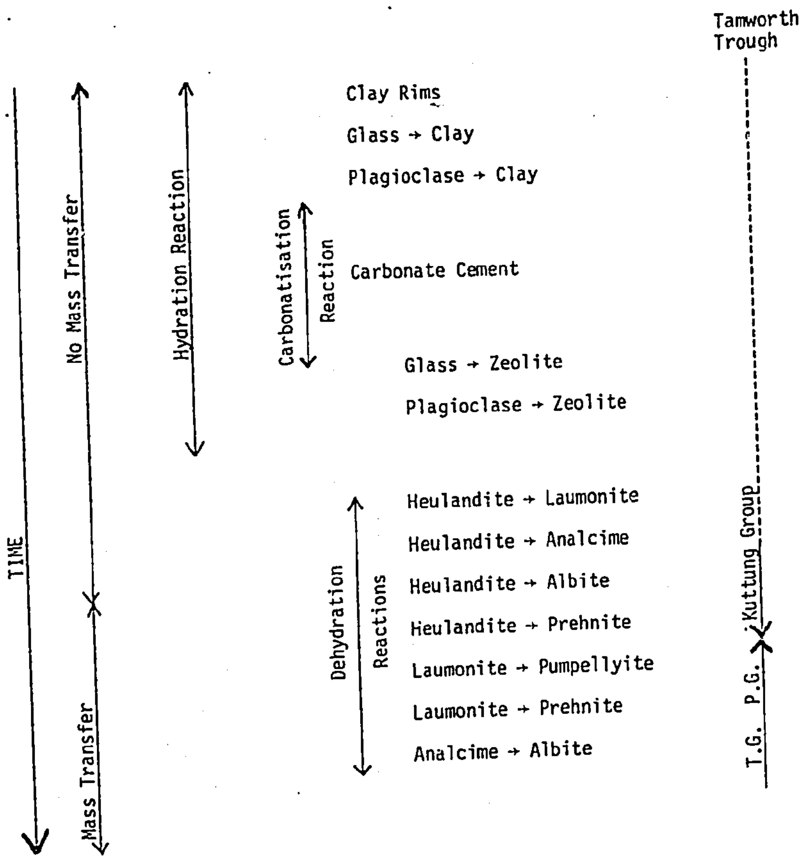


Figure 3.5 Descriptive framework for the diagenesis of volcanogenic graywackes (after Surdam and Boles, 1979) as observed in the Tamworth Trough stratigraphic sequence. (T.G. - Tamworth Group; P.G. - Parry Group)

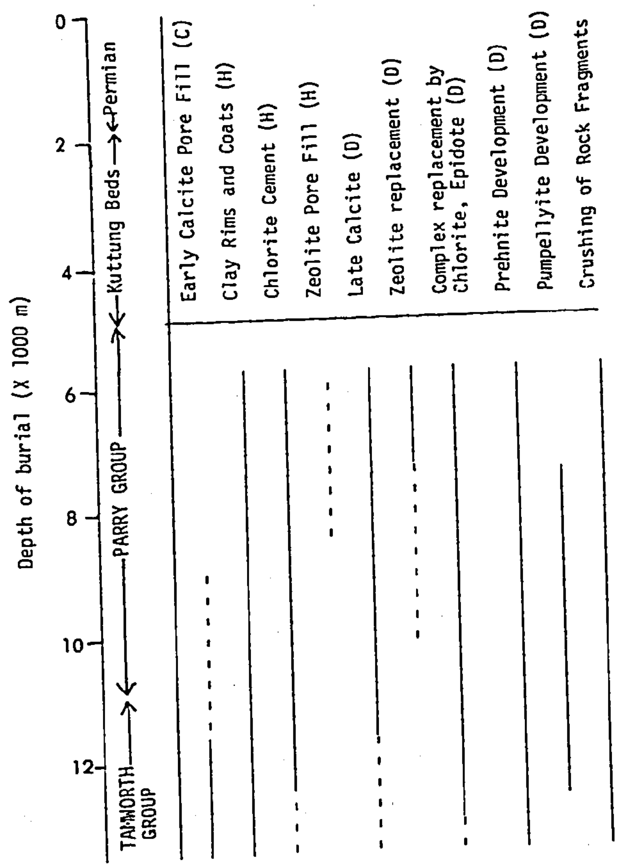


Figure 3.6 Burial Diagenetic History of the Tamworth Trough. The nature of diagenetic reaction denoted by symbols. C = Carbonatisation, H = Hydration D = Dehydration.

In this reaction SiO_2 can be provided by the local replacement of quartz. Boles and Coombs (1977) have pointed out that a considerable amount of sodium will be required for the above reaction. If connate sea water is the sole source of sodium, it has to be concentrated more than twice in sea water to accomplish the reaction. Boles and Coombs (1975) have found evidence that stratal fluids were mobile and that some sodium can also be released during the alteration of volcanic glass to chlorite and calcic heulandite. Thus an adequate quantity and concentration of sodium will be available for the albitisation of plagioclase in volcaniclastic graywackes.

The behaviour of sodium in sedimentary rocks is discussed in more detail in Chapter 6.

3.7.4 Burial Metamorphic Facies in the Tamworth Trough

Since the introduction of the term "burial metamorphism" by Coombs (1961), extensive work has been done on the diagenesis of volcaniclastics. Increased temperature (unrelated to igneous intrusions) and pressure associated with burial metamorphism was believed to lead to widespread mineral changes without the development of schistosity. In the original definition of burial metamorphism, heulandite and analcime were considered to be diagnostic of the diagenetic realm whereas laumonite was supposed to be indicative of metamorphism. Recently, Boles and Coombs (1977) have shown that this approach is unrealistic because a large number of variables control mineralogy.

Packham and Crook (1960) have observed that burial metamorphism produces sequentially, heulandite-analcime, laumonite, prehnite-pumpellyite and albite-epidote facies in the Tamworth Trough. On the basis of depth dependent changes in diagenetic features and minerals (Figures 3.5 and 3.6), the Kuttung Beds can be assigned to the heulandite-analcime diagenetic facies. Laumonite facies characterized by the presence of laumonite, albitised detrital plagioclase and chlorite can be recognized in the upper parts of the Parry Group rocks. Laumonite is completely absent in the graywackes examined in the present work. They lie below 5000 metres of burial depth and exhibit the development of prehnite, pumpellyite, albite and epidote minerals. This assemblage is indicative of high-temperature and high pressure prehnite-pumpellyite facies. The major part of the Tamworth Trough sequence examined belongs to the prehnite-pumpellyite diagenetic facies. Graywackes in the lower parts of the Tamworth Trough (i.e. belonging to the Tamworth Group) show albitisation and the development of epidote but there is a complete absence of prehnite and pumpellyite. Packham and Crook (1960) have named this facies as the 'albite-epidote' facies. The absence of complex replacement and alteration in these graywackes could be due to the abundance of calcite cement which inhibits the formation of prehnite and pumpellyite. If true, then albite-epidote will be a part of the prehnite-pumpellyite facies. However evidences are not sufficient to be unequivocal. Even in the 'zeolite facies', more than 25% of the arenites and most of the siltstone beds contain no zeolites and are non-diagnostic of this mineral facies in the Southland Syncline of New Zealand (Boles and Coombs, 1977).

Prehnite was once thought to be indicative of metamorphism. However, it has been suggested that it can form at temperatures as low as 90° to 130°C and is virtually present throughout the classical section of zeolite facies of the Southland Syncline, New Zealand (Boles and Coombs, 1977) as well as throughout the Tamworth Trough sequence. The presence of pumpellyite represents the advanced burial metamorphic conditions in zeolite facies. The estimated lower temperature limit for the formation of pumpellyite is 190-200°C. Thus prehnite-pumpellyite facies indicates a temperature of more than 200-250°C and 2 to 2.5 Kb of corresponding pressure (Coombs, 1971). A similar estimate of the temperature and pressure of diagenesis for the Tamworth Trough has been made by Chappell (1968) following a somewhat different approach.

3.8 DIAGENESIS OF THE HILL END TROUGH GRAYWACKES

3.8.1 Diagenetic Features

The Hill End Trough and adjacent region has been subjected to pronounced diagenesis (Smith, 1969). The sedimentary sequence of the eastern region (Sofala section) has undergone chlorite grade whereas the western region (Hill End section) has undergone the biotite grade of regional metamorphism.

The diagenetic features observed depend on the mineralogy of the graywackes. Two broad suites of graywackes have been recognized in the Hill End sequence : Hill End and Cookman suites. Diagenetic features observed in each suite and in each zone are tabulated in Table 3.6.

Table 3.6 Diagenetic Features in the Graywackes of the Hill End Trough Region

Diagenetic Features	Hill End Suite		Cookman Suite	
	Chlorite Zone	Biotite Zone	Chlorite Zone	Biotite Zone
<u>Authigeneic Cement</u>				
1. Formation of clay rims and clay coats	Common	Altered to biotite	Common	Altered to biotite
2. Unoriented microcrystalline aggregate of chlorite	Present	Altered to biotite	Absent	-
<u>Compaction Features</u>				
3. Detrital grain boundaries	Distorted and corroded	Irregular and diffuse	Slight distortion and corrision	Irregular and diffuse
4. Squashing of rock fragments	Moderate	Extensive	Moderate	Extensive
5. Parallel orientation of mica-flakes	Moderate	Extensive	Moderate	Extensive
6. Pore-linning and bending of phyllosilicates below quartz grains	Common	Difficult to discern	Common	Difficult to discern
7. Degree of pressure-solution	Low to moderate	High	Low to moderate	High
<u>Replacement Features</u>				
8. Devitrification of volcanic glass	Common	Difficult to discern	Absent	Absent
9. Albitisation of Ca-plagioclase	Common	Common	Absent (?)	Absent (?)
10. Formation and replacement by	Epidote, Calcite, Chlorite, Sericite	Biotite, Epidote	Chlorite Sericite	Biotite

The Hill End suite graywackes exhibit common authigenic and replacement features due to the presence of abundant labile grains whereas those of the Cookman suite mainly show compaction features because of their highly quartzose nature. The formation of clay rims and clay coats, the unoriented microcrystalline aggregate of chlorite and the replacement of detrital grains by chlorite, epidote, calcite and sericite are commonly observed in the Hill End suite graywackes of the chlorite zone. Such features are completely distorted in graywackes of the biotite zone due to high compaction and the formation of biotite. The Cookman suite graywackes mainly exhibit compaction features in the chlorite zone which become very pronounced in the biotite zone.

3.8.2 Regional Metamorphism of the Hill End Trough Sequence

Smith (1969) has demarcated zones of progressive regional and burial metamorphism in the Hill End Trough region. The graywackes are characterized by the presence of diagenetic chlorite and metamorphic biotite associated with complex alteration and replacement by epidote, calcite, chlorite and sericite. These features represent the "advanced burial metamorphic and tectonic phase" in the Galloway's (1974) scheme of diagenesis.

Rocks of the chlorite zone are characterized by the albite-epidote-chlorite-calcite assemblage and are probably equivalent to the 'albite-epidote facies' of Packham and Crook (1960). Smith has called it the 'actinolite zone' on the basis of study of the volcanic rocks of the region. With the progressive increase in metamorphism there is the development of abundant biotite. The transitional boundary between the chlorite and biotite zones can be deciphered near the Maitland Camp on the Sofala - Hill End road. Diagenetic features indicate that the Hill End Trough must have attained a temperature of 350-400°C and a pressure of 2-3 Kb during burial.

3.9 DIAGENESIS OF THE BENDIGO TROUGH GRAYWACKES

The quartzose nature and the abundance of matrix inhibits abundant diagenetic alteration of graywackes. The main diagenetic features are compaction type, authigenic and replacement features being minor only. Authigenic clay coats associated with iron-oxide are seen surrounding the detrital grains. The recrystallised phyllosilicate matrix also impinges on the detrital grains.

The parallel arrangement of mica flakes is common. Phyllosilicates and mica flakes are commonly bent and deformed below the quartz grains. Minor squashing and squeezing of argillaceous rock fragments is also observed. The Bendigo Trough graywackes represent the 'locomorphic stage' of diagenesis, according to the terminology of Dapples (1979), which is typical of lithification of clastic sediments.

3.10 DIAGENESIS OF THE HODGKINSON FORMATION GRAYWACKES

3.10.1 Diagenetic Features

The graywackes of the Hodgkinson Formation exhibit the following common authigenic, replacement and mechanical features:

3.10.1a Authigenic Cement and Replacement Features

The authigenetic formation of cement material is indicated by the common occurrence of clay coats along detrital grain boundaries. Brown tinted biotite is also formed due to the increased recrystallisation of phyllosilicates at places. Corrosion of grain boundaries by the recrystallised material is common.

3.10.1b Compaction Features

Common compaction features are the squashing and squeezing of rock fragments and their degradation to form pseudo-matrix, and the bending and deformation of phyllosilicates and mica flakes below the competent quartzose grains. Mica flakes are arranged along the foliation probably due to mechanical stress.

3.10.2 Diagenesis and Metamorphic Facies in the Hodgkinson Basin

On the basis of the diagenetic features enumerated above, the graywackes can be assigned to the "phyllomorphic stage" of diagenesis, following the terminology of Dapples (1979). This is the most advanced stage of diagenesis in the progression towards metamorphism. The Barron River metamorphics, lying in the west show a biotite grade of metamorphism. The elevated grade may perhaps be partly due to the presence of granitoid bodies at shallow depths. In the eastern part, prehnite and pumpellyite minerals are recognized in the basic volcanic rocks (Arnold and Fawckner, 1980). Thus a gradation from prehnite-pumpellyite through the chlorite grade (Hodgkinson Formation) to the biotite grade (Barron River metamorphics) can be inferred in the Hodgkinson Basin.

CHAPTER 4
GRAYWACKE SUITES AND THEIR PETROGENESIS

4.1 INTRODUCTION

In the previous chapter, graywacke suites were separated on the basis of framework grains. Various multivariate statistical tests were performed on the mineralogical and textural data in order to differentiate and characterize each suite, the results are presented in this chapter. Principal component analysis generates factors which help in understanding the parameter associations. Discriminant analysis discriminates between pre-defined groups and cluster analysis establishes the groups of cases. The nature of the source rocks and the provenance are inferred for each graywacke suite on the basis of their mineralogical characteristics.

4.2 PRINCIPAL COMPONENT ANALYSIS

The principal component analysis extracted six significant factors which account for 75% of the total variance in the original data. The varimax factor matrix, depicting the loading of each variable on six factors, and related statistics are given in Table 4.1. The six factors are

I (Lv., Cal, Op) versus (Q, M)
II (F, Chl, Py) versus (Ls, Q)
III (F, S_I) versus (Mz)
IV (F, Mat) versus (Q, M)
V (HM) versus (Py, Op, Ls)
VI (Op) versus (Ep)

The relative size of the eigenvalues shows that Factors I, II and III are much more important than the rest of the factors and together explain about 52% of the total variation in the data.

All factors are double barrelled. Factor I is characterized by the negative loading of quartzose and mica grains and the positive loading of volcanic rock fragments, calcite and opaque minerals. This could be called a "maturity factor" and shows the opposite natures of Q and Lv. Factor II is characterised by the positive loading of feldspar, chlorite and pyroxene and the negative loading of quartzose and sedimentary rock fragments. This factor can be called a "provenance factor".

Table 4.1 Factor Loadings for the First six Factors, after Varimax Rotation

VARIABLE	FACTORS I	II	III	IV	V	VI	COMMUNALITY
Q	-.634	-.393	-.146	-.520	.036	.115	.864
F	.112	.403	.462	.418	.110	-.224	.626
Lv	.871	.049	.162	.156	-.081	.031	.820
Ls	-.142	-.653	-.204	.105	-.318	.182	.634
M	-.352	.215	-.145	-.678	.234	.277	.782
Ep	.066	.224	-.044	.036	.196	-.808	.749
Py	.235	.685	-.055	.216	-.354	.096	.709
HM	.007	-.059	.072	.033	.823	.200	.728
Chl	-.107	.801	.190	.079	-.129	-.141	.732
Cal	.806	-.044	-.094	-.132	.161	-.171	.733
Op	.617	.221	.103	.091	-.423	.402	.790
Mat	-.122	.209	-.267	.762	.120	.189	.761
Mz	-.037	-.169	-.886	.035	.022	-.068	.822
S_I	.063	.058	.880	-.053	.080	.013	.792
Eigenvalue (Principal Component)	3.681	2.00	1.646	1.177	1.024	1.015	
% of variance explained	26.3	14.3	11.8	8.4	7.3	7.2	
Cumulative % of variance	26.3	40.6	52.4	60.8	68.1	75.3	

Factor III indicates that the feldspar content is related to the physical processes and increases with increase in grain size. This factor can be called a "textural factor" and accounts for ≅ 12% of the variation in the original data.

Factor IV is a complex factor having a positive loading of feldspar and matrix and a negative loading of quartzose and mica content. This factor probably represents some "recycling process", and is characterised by an increase in quartzose grains and a decrease in feldspar and matrix content in graywackes. Factor V reflects the effects of source rocks on the minor constituents of graywackes and can be called an "accessory mineral factor". This factor has a positive loading of heavy minerals (mainly zircon, tourmaline and rutile) and a negative loading of pyroxene and opaque minerals. The minor loading of sedimentary rock fragments with pyroxene on this factor is surprising and unexplained. Factor VI probably represents the diagenetic processes affecting the mineral composition of graywackes and explains about 7% of the variation in the data. This factor has a negative loading of epidote and a positive loading of opaque minerals. Both these minerals are diagenetic in origin.

The factor score measures the influence of coherently behaving variables of the factor on the individual sample. Thus a bilinear plot of factor scores would represent the variation in graywacke composition. Such a plot of Factor I versus II, for individual graywacke samples representing the various suites, is given in Figure 4.1. The positive scores along Factors I indicate a "juvenile" nature and substantial contribution from volcanic sources whereas the negative loadings along this factor indicate a substantial contribution from plutonic, metamorphic or sedimentary sources and a "matured" nature.

The Tamworth suite graywackes are heavily weighed by Lv, Cal, Op and slightly weighed by F, along Factors I and II respectively indicating their volcanogenic nature. The Hill End suite graywackes occupy a broad field indicating their varied nature but the majority of samples have a significant positive loading of Lv etc along the Factor I axis and of Ls and Q along the Factor II axis, thus confirming their sub-quartzose nature and the substantial contribution of volcanic sources. The Hodgkinson suite graywackes occupy almost a distinct field and are influenced by the negative loadings of Q and M along Factor I and Ls and

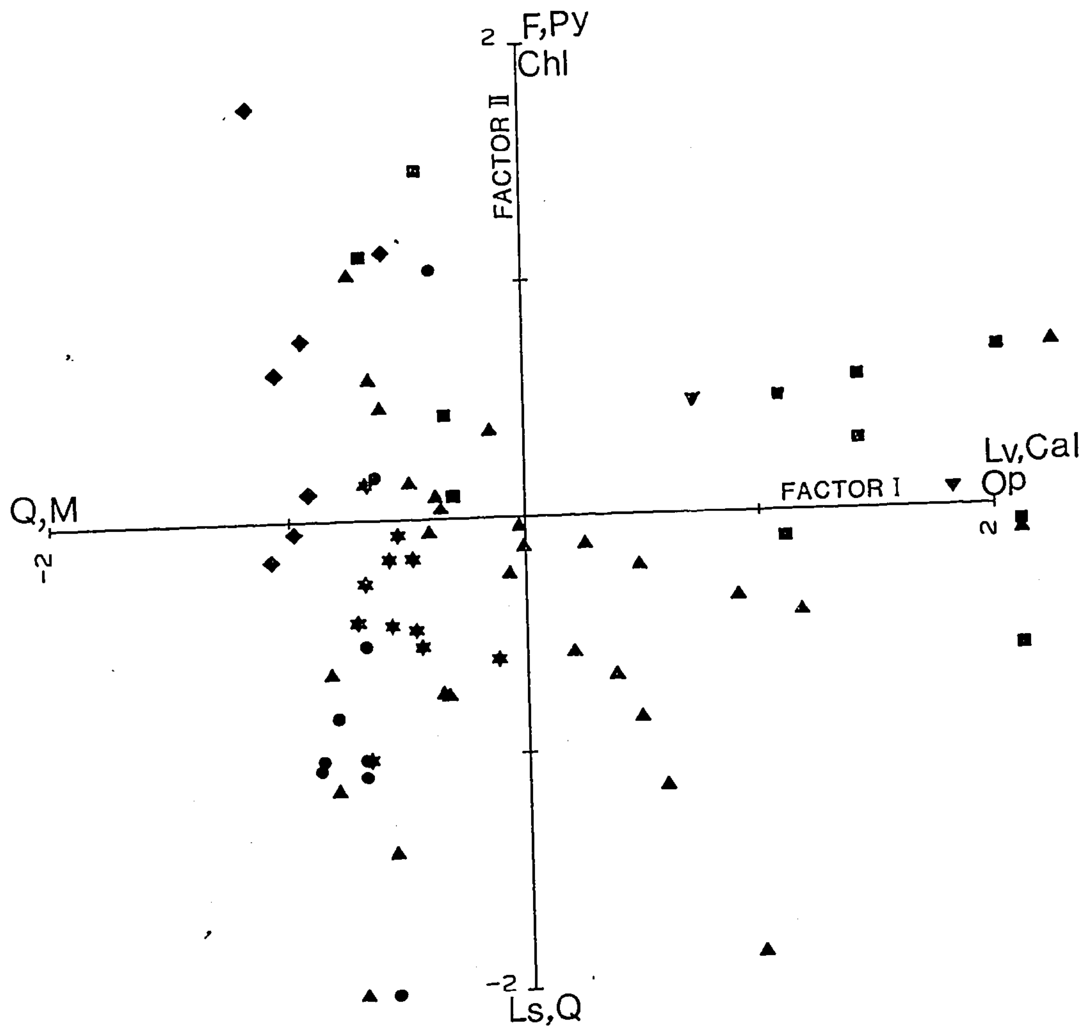
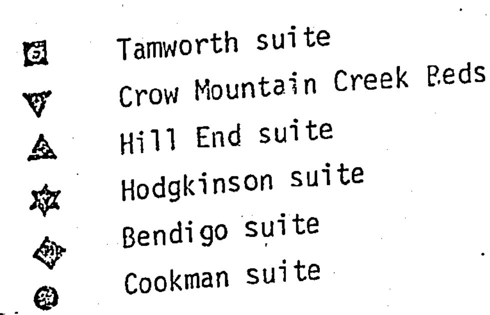


Figure 4.1 Plot of factor scores for graywackes, along Factor I versus Factor II.



Q along Factor II. The matured nature of the Bendigo and Cookman suite samples is indicated by the negative loading of Q and M along Factor I. However, along the Factor II axis, the Bendigo suite samples in general, have a positive loading indicating the presence of some feldspar whereas the Cookman suite samples have a high negative loading indicating the presence of sedimentary rock fragments. These observations are in agreement with the petrographic features discussed in Chapter 3.

The loading of mineralogical and textural variables on the factors confirm the framework parameter associations (Section 3.4). Factors I and II represent the relative contribution of plutonic and metamorphic-sedimentary versus volcanic sources and are equal to the QMKLs and LvF associations. Factor III shows the effect of grain size on the feldspar content and is equivalent to the F S_I association. Factor IV shows the association of feldspar with matrix and represents a textural as well as a mineralogical association (matrix is not considered in Section 3.4). Factor IV represents the source rock influence on accessory minerals. The factor scores show to some extent, the separation of various suites, but more importantly illustrate the relative effect of variables behaving coherently on various graywacke suites.

4.3 DISCRIMINANT FUNCTION ANALYSIS

The discriminant function analysis helps in establishing the differences between the various suites and also in classifying samples into pre-defined groups. Samples were assigned to five groups, corresponding to the five graywacke suites. The variables are slightly different to those used in the principal component analysis. Calcite and opaque minerals were ignored because of their high Wilks' lambda, suggesting their low significance in discrimination. Mica was divided into muscovite and biotite content. The discrimination result remained unchanged when textural parameters (Mz and S_I) were included in the run. This shows that although the abundances of certain grain types (e.g. feldspar) may be related to grain size, this does not affect the overall pattern of discrimination between the various suites and sedimentary provinces.

Standardized and unstandardized discriminant function coefficients and related statistics are presented in Tables 4.2 and 4.3. The high

Table 4.2 Standardised Discriminant Function Coefficients of the Mineralogical Variables and Related Statistics

	Discriminant Functions			
	I	II	III	IV
Q	-.971	-.280	.656	.090
F	.050	-.396	.670	-.057
Lv	-.211	.087	.443	.567
Ls	-.366	-.466	.161	.253
Mus	-.745	.712	-.139	.258
Bio	-.223	-.211	.466	.371
HM	.005	.052	.133	-.764
Ep	-.069	-.291	-.451	-.077
Py	-.191	.466	.838	-.053
Chl	-.045	-.249	-.161	.527
Mat	-.127	.019	-.169	-.064
Eigenvalue	9.683	2.716	0.882	0.369
% Variation explained	70.94	19.90	6.46	2.70
Cumulative % of variation	70.94	90.84	97.30	100.00
Canonical correlation	0.952	0.855	0.685	0.519
Wilks' Lambda	0.0097	0.1044	.3882	0.7307*

* Not significant.

Table 4.3 Unstandardised Canonical Discriminant Function Coefficients

Variable	Discriminant Function I	II	III
Q	-.090	-.026	.061
F	.005	.038	.064
Lv	-.020	.008	.042
Ls	-.051	-.064	.022
Mus	-.344	.329	-.064
Bio	-.049	-.047	.103
HM	.005	.053	.138
EP	-.013	-.056	-.086
Py	.118	.288	.518
Chl	-.020	-.111	-.072
Mat	-.012	.002	-.016
Constant	4.809	.012	-3.447

Table 4.4 Comparison of the Actual and Predicted Number of Samples on the Basis of Discriminant Functions in Each Graywacke Suite

Suite	Group	No. of Samples	Predicted Group Membership A	B	C	D	E	% Correctly Classified
Tamworth	A	11	11	-	-	-	-	100%
Hill End	B	29	28	-	-	-	1	97%
Hodgkinson	C	10	-	-	10	-	-	100%
Bendigo	D	7	-	-	1	6	-	85%
Cookman	E	8	-	-	-	-	8	100%

Total % cases correctly classified = 97%

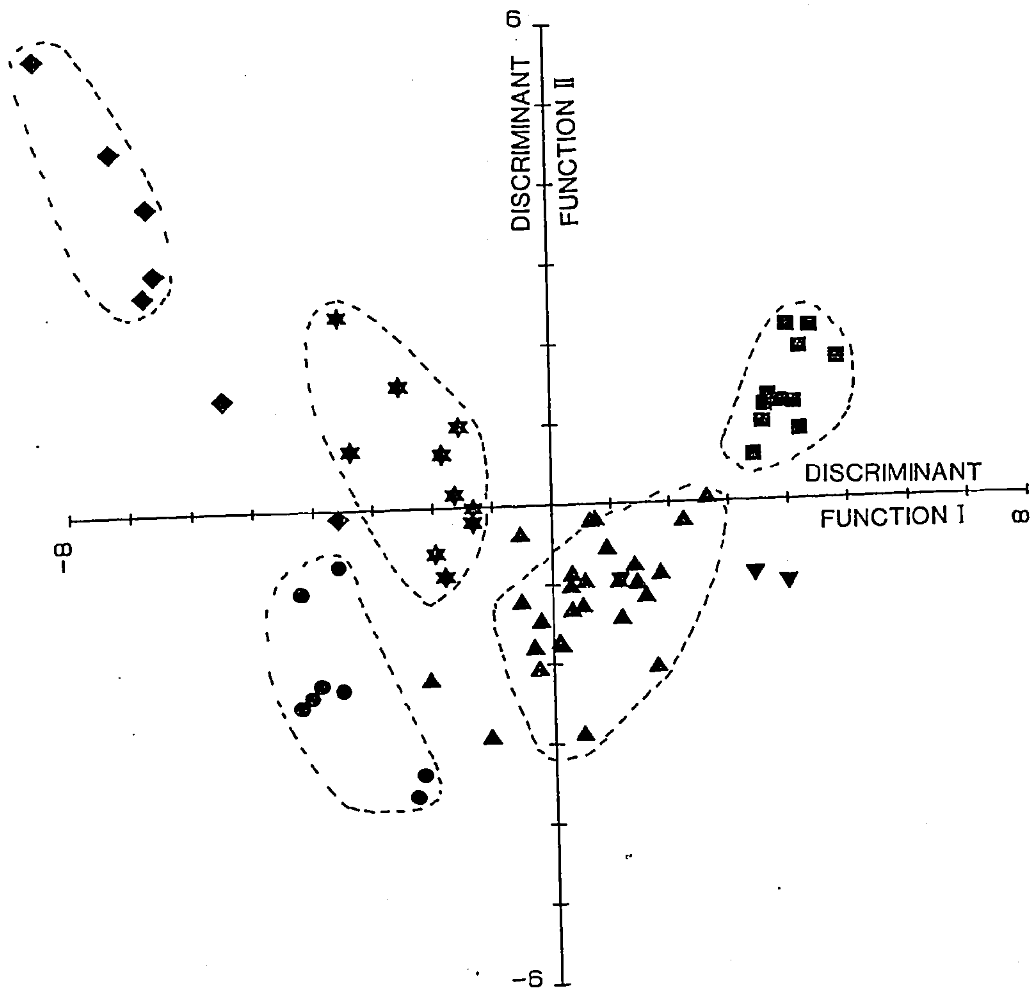


Figure 4.2 Plot of discriminant scores along Discriminant Function I versus II. Note the excellent discrimination of various graywacke suites.

- Tamworth suite
- Crow Mountain Creek Beds
- Hill End suite
- Hodgkinson suite
- Bendigo suite
- Cookman suite

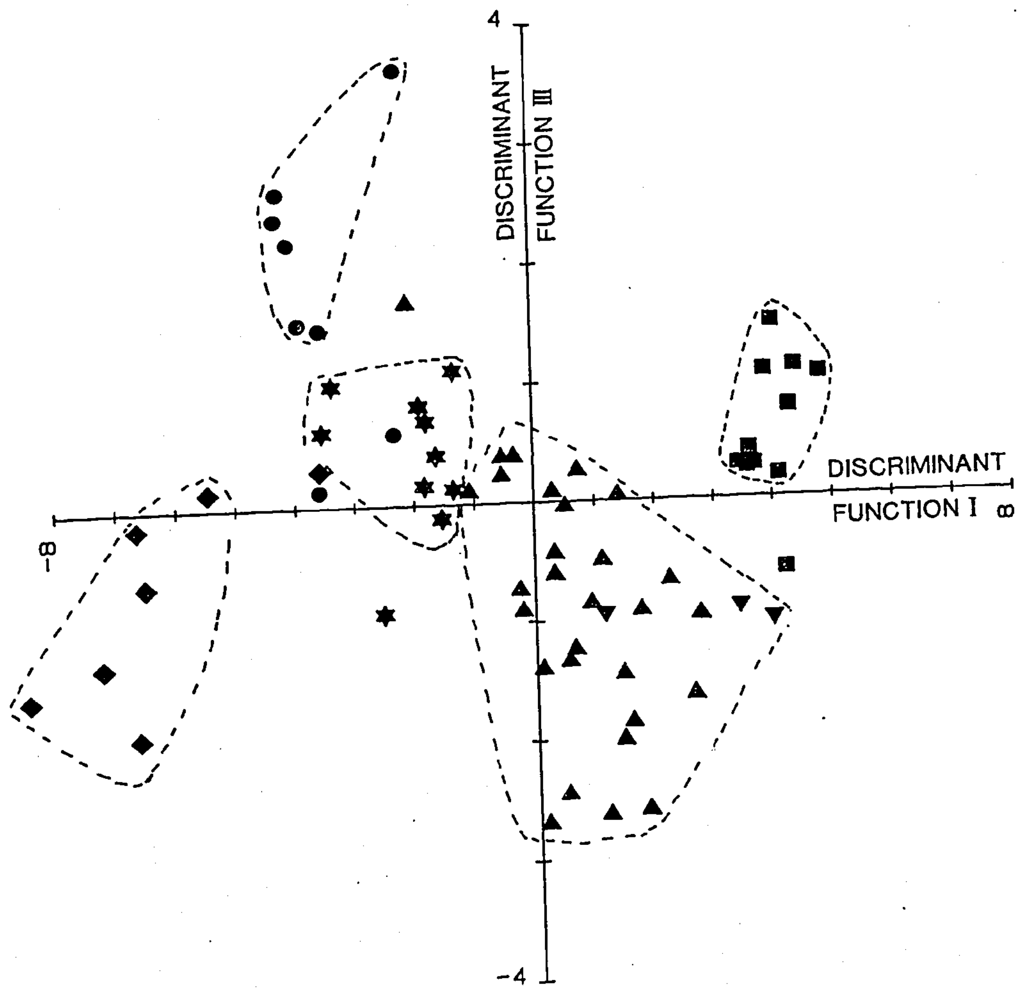


Figure-4.3 Plot of discriminant scores along Discriminant Function I versus III. Various graywacke suites occupy distinct fields.

- Tamworth suite
- Crow Mountain Creek Beds
- Hill End suite
- Hodgkinson suite
- Bendigo suite
- Cookman suite

eigenvalues and high correlation coefficients for Functions I and II indicate that these two functions are important, together explain about 90% of the variation in the original data and have high discriminatory strength. Function III explains only 7% of the variation in the data, with a comparitively low discriminating strength. Function IV explains only 3% of the variation in the data and its low canonical correlation value indicates its insignificant discriminating strength.

The bilinear plots of discriminant scores graphically illustrate the classification of individual samples into suites. In the plot of discriminant scores along Function I versus II, the graywackes of the five suites occupy distinct and unique fields with very little overlapping (Figure 4.2). The greater the distance between the fields of two suites, the higher the discrimination. Discriminant Function I discriminates the Tamworth and Hill End suites from the more quartzose Hodgkinson, Bendigo and Cookman suites. Discriminant Function II discriminates these three quartzose suites quite successfully. A comparison of the actual and predicted number of samples in each suite shows that, in all, 97% of the samples are correctly classified into their pre-defined suites, by discriminant Functions I and II (Table 4.4). An almost similar separation of the various suites is also achieved by plotting the scores along discriminant Functions I and III (Figure 4.3).

4.4 CLUSTER ANALYSIS

The cluster analysis was performed using the mineralogical variables given in Table 4.1. The cluster analysis establishes a set of groups of graywackes as shown by the simplified dendrogram (Figure 4.4). By selecting the arbitrary distance co-efficient ≅ 5, six major clusters are obtained. Four of these clusters correspond to the Hodgkinson, Bendigo, Cookman and Tamworth suites. The Hill End suite is split into two clusters.

In each cluster, the total number of samples and the number of samples of the corresponding suite (underlined) are shown in Figure 4.4. Cluster I contains only one misclassified sample which belongs to the Bendigo suite (sample MK 95), all the rest (9 samples) belong to the Hodgkinson suite. Cluster II contains all 6 samples belonging to the Bendigo suite. Cluster III shows the highest number of misclassified samples. Out of 12 samples in this cluster, 7 belong to the Cookman

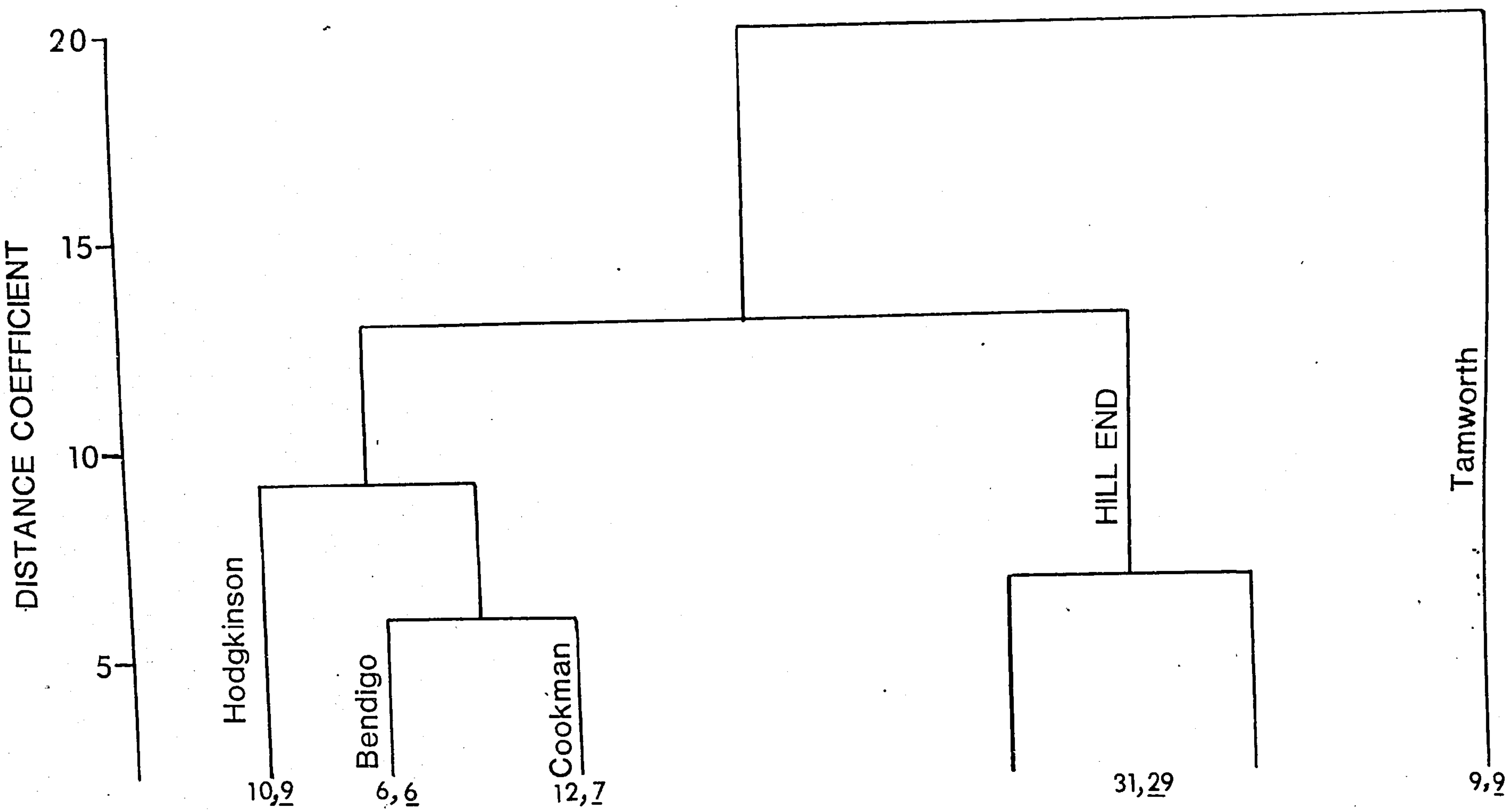


Figure 4.4 Simplified dendrogram showing various clusters of graywacke suites. The total number of samples in each cluster (like 10), and the number of samples of the most dominant suite (like 9) are given for each group.

suite, 4 to the Hill End suite (3 quartzose samples of the Chesleigh Formation and one Waterbeach sample) and one to the Hodgkinson suite. The grouping of these odd samples with the Cookman suite indicate their high quartzose content compared to the typically less quartzose nature of their suite. Clusters IV and V contain 31 samples, 25 of which belong to the Hill End suite. The three Crow Mountain Creek samples are also classified with these clusters. Out of the remaining 3 misclassified samples in these clusters, 2 belong to the Tamworth suite (MK 14, MK 15) and one to the Cookman suite (MK 54), probably due to the high abundance of lithic grains in them. Cluster VI contains 9 samples all belonging to the Tamworth suite.

The clusters obtained, correspond broadly to graywacke suites established on the basis of modal composition and discriminant analysis, but the Hill End suite samples are divided into two clusters, probably representing two petrofacies within this suite. However, these two clusters link together at a low distance coefficient of around 7 which indicates their close mineralogical similarity. At a distance coefficient of around 10, three broad groups are obtained, corresponding to quartz-rich (Clusters I, II & III); quartz-intermediate (Clusters IV & V); and quartz-poor (Cluster VI) graywackes, confirming observations based on modal compositions (Chapter 3).

4.5 PETROGENESIS : SOURCE ROCKS AND PROVENANCE

The mineral composition of arenites is a function of source rocks, tectonism, climate, environment of deposition and lithification. In all, there are 13 processes which control these attributes (Suttner, 1974). In this section, the relative influence of various attributes on the composition of graywackes is discussed, and the source rocks and provenance types are deciphered on the basis of the mineral characteristics of the graywacke suites.

4.5.1 Tamworth Suite

The dominance of microlitic volcanic rock fragments, the abundance of plagioclase, the common occurence of pyroxene and the paucity of quartzose grains clearly demonstrate a volcanic source made up of andesitic rocks for the Tamworth suite graywackes. The volcanic rocks which formed the provenance are largely buried under the Gunnedah and

Sydney Basins. However, the Devonian lavas, ignimbrites and sills occurring in the western margin of the Tamworth Trough may constitute a part of the provenance (Crook and Powell, 1976).

The abundance of fresh feldspar, pyroxene and volcanic rock fragments clearly suggests that large-scale climatic modifications were minimal and that the sediments were derived through the simple disintegration of the "active" source. The overall abundance of plagioclase grains in some of the beds is probably due to minor sorting of feldspars in the proximity of source terrain. The common occurrence of now devitrified volcanic glass, the similarity in the nature of feldspar grains and phenocrysts of the volcanic lithic grains, and the huge thickness of the sedimentary sequence indicate a penecontemporaneous volcanic source. All these evidences suggest that active tectonism and probably volcanism maintained a high relief and a continuous supply of detritus without much chemical reworking during the Devonian-Carboniferous deposition and thus exerted a strong influence on the composition of the Tamworth suite graywackes.

The Crow Mountain Creek beds are more quartzose than the Tamworth suite rocks and indicate a change to felsic sources in the Upper Carboniferous-Lower Permian.

4.5.2 Hill End Suite

The graywackes of the Chesleigh Formation (here grouped within the Hill End suite) were derived from a variety of sources as seen by the variation in the mineralogical characters within this formation. The graywackes of the western region contain common feldspar and volcanic rock fragments and thus were mainly derived from volcanic sources. On the other hand, the graywackes of the eastern region are mainly quartzose and had more contribution from sedimentary rocks. The obvious choice for the sedimentary source is the Ordovician rocks of southeastern Australia. Though the 'Sofala Volcanics' might have contributed a small proportion of the detritus, most of the volcanic material was derived from penecontemporaneous volcanic vents which became prominent in the later stages of the development of the Hill End Trough.

All other graywackes constituting the Hill End suite are of the quartz-intermediate type. Much of the detritus was derived from a felsic volcanic source which contributed bipyramidal volcanic quartz, and felsitic volcanic rock fragments containing phenocrysts of quartz and feldspar in a glassy groundmass. Part of the detritus, consisting of polycrystalline quartz and sedimentary rock fragments, is recycled. Some sedimentary rock fragments are of the argillaceous type and are intraclastic in nature.

The common occurrence of volcanic shards and the angular nature of the feldspar grains suggest that the dominant part of the detritus was derived from active penecontemparaneous volcanic vents. Older sedimentary as well as intraclastic material was eroded during periods of quiescene to constitute the framework grains. The volcanic vents are now completely missing and their only trace is in the form of felsic material in the graywackes.

During the deposition of the Hill End suite graywackes, modifications due to climate were very minor as suggested by the presence of angular feldspar grains and devitrified glass shards. Thus the disintegration was mainly of the mechanical type. Active tectonism resulted in high relief, supply of volcanic detritus and minimal chemical weathering. The only effect of sorting processes is the minor enrichment of feldspar grains in the coarser fraction.

4.5.3 Hodgkinson Suite

The common occurrence of large gneissic clasts in the conglomerates of the Hodgkinson Formation suggests gneissic rocks in the source terrain. Basu et al. (1975) have shown that the proportion of different quartz varieties can be successfully used in provenance determination. Polycrystalline quartzose grains are dominantly composed of more than 3 crystals per grain and have sutured boundaries, indicating their metamorphic provenance (Young, 1976). In each thin section, about 50-75 quartzose grains having grain sizes between 1 to 2 Ø, were point counted for various quartz types (after Basu et al. 1975) and their plot suggests low to high rank metamorphic source terrains for the Hodgkinson suite graywackes (Figure 4.5). This method though useful has some inherent problems because the varying mechanical and chemical stabilities of quartz types, as well as the strain crystallization phenomenon, can modify the original quartz populations during weathering and transportation (Blatt and Christie, 1963).

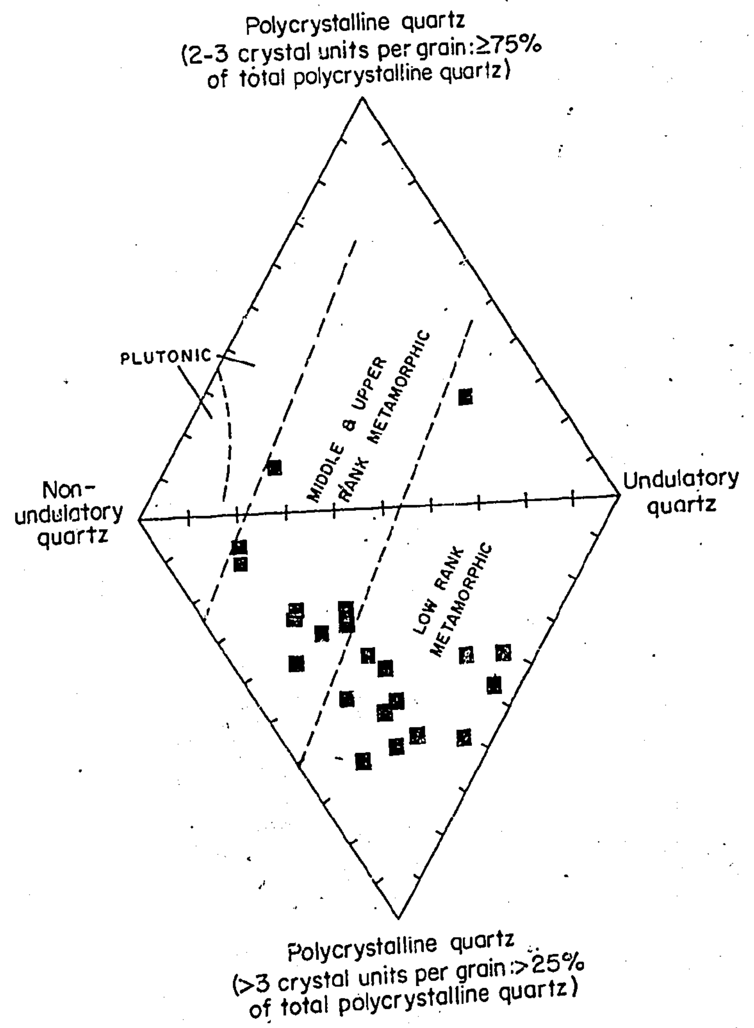


Figure 4.5 Plot of quartz varieties in the Hodgkinson suite graywackes, on the diagram proposed by Basu et al. (1975).

The volcanic lithic grains are of intermediate-mafic types and constitute only ≅ 2% of the whole rock, suggesting only a minor contribution from volcanic sources. However, their preferential decomposition during sedimentary processes can not be discounted. The feldspar grains are both of volcanic and crystalline types. Volcanic plagioclase grains are minor angular and contain abundant inclusions of glassy material which is now altered to chlorite. The dominant feldspar grains are derived from crystalline sources and are rounded, fresh and sometimes occur as quartzo-feldspathic lithic grains. The argillacious fragments are probably all intraclastic, derived by erosion beneath the turbidity currents within the basin. The presence of heavy minerals like zircon, tourmaline, rutile, pyroxene and epidote in decreasing order suggests a mixed provenance dominated by crystalline rocks. It is suggested that the rocks now making the Georgetown massif constituted the provenance for the Hodgkinson Basin. Paleocurrent data confirm the derivation of detritus from these rocks (de Keyser and Lucas, 1968).

The role of tectonism on the modal composition of graywackes is evident. Due to active tectonism, the deep seated crystalline basement must have been uplifted to provide detritus to the Hodgkinson Basin. The preservation of abundant feldspar (particularly plagioclase), polycrystalline quartzose grains, and relatively unstable mafic minerals like pyroxene, indicate a high relief and mild weathering in the source region and only minor modification of detritus due to climate. The intense weathering of igneous and metamorphic source rocks in an area of low relief can cause substantial destruction of feldspar and other labile grains and can produce quartz-rich sands (Mann and Cavaroc, 1973). The minor enrichment of feldspar in the coarser fraction is attributed to sorting processes.

4.5.4 Bendigo Suite

The Bendigo suite graywackes form a part of the extensively developed Ordovician quartz-rich graywackes of southeastern Australia. The source rocks and the paleogeographic setting of these rocks is debatable. Unfortunately, inspite of their extensive nature, very little data on the regional variation of composition and paleocurrents are available in literature.

The abundance of quartzose grains, the small fraction of feldspar and a complete absence of volcanic rock fragments suggest an overall mineralogical maturity of the graywackes. The presence of a small amount of polycrystalline quartzose grains, abundant mica, and heavy minerals (zircon and tourmaline) belonging to the ultrastable group, provides additional evidence of their high mineralogical maturity.

The origin of Bendigo suite type quartz-rich arenites, has been discussed by many authors in recent years. Are these quartz-rich sediments first-cycled and derived from igneous rocks or multicycled and derived from older sedimentary rocks? Commonly, such sediments have been thought to be recycled, but according to Potter (1978) first cycled quartz-arenite type sediments can be formed from quartz-rich igneous rocks in the following three ways:

(1) as fluvial sands in low relief and tropical watersheds
(2) weathering on tropical coastal plains where sand input is small rather than overwhelming and
(3) along high energy coastlines in tropical climates where the sand supply is largely derived locally from small rivers.

The deep water turbidite origin and the huge thickness of the Bendigo Trough sequence negate that these rocks were formed by any of the processes suggested by Potter (1978).

Mack (1978) has suggested criteria to decipher whether maturity has been caused by weathering, a shallow-marine environment or recycling. These criteria are based on the use of undulose and non undulose extinction of quartz grains and the percentage of perthite grains present in the rock. The application of these criteria is not justified in the present case as post-depositional deformation may have changed the original nature of extinction, and feldspathic grains constitute a very small fraction of the detritus. Moreoever, the differences between the effects of weathering and a shallow-marine environment on sandstone composition are difficult to distinguish. However, it has been noted that polycrystalline quartz grains are released under semi-arid soil forming conditions whereas such grains are generally destroyed under shallow-marine conditions (Mack, 1978). The Bendigo suite graywackes contain only a few polycrystalline quartz grains and hence the weathering conditions, in which polycrystalline grains are released, can be ruled out. There is no evidence of a tropical or humid climate or of the action of rivers or the coastline during the Ordovician in the region, thus probably negating fluvial or shallow-marine reworking of the original detritus to yield Ordovician quartz-rich graywackes.

On the other hand, the high mineralogical maturity characterized by the high abundance of monocrystalline quartz, the low abundance of feldspar grains, and almost negligible unstable lithic fragments, is evidence of a multicycled nature and sedimentary source rocks. Polycrystalline quartzose grains are of metamorphic type (Young, 1976). Some "tectonite type" mica grains are also present. These features point towards a lowgrade metamorphic source terrain.

Nathan (1977) and Wyborn (1977) suggested, mainly on the basis of geochemical evidences, that Ordovician sedimentary rocks of Australia and New Zealand are derived from the quartz-rich sedimentary rocks of the Robertson Bay Group of Antarctica and the Kanmantoo Group of South Australia. Broken, rounded, and abraded overgrown quartz grains are completely absent in Ordovician graywackes. Although "quartzite" type pre-Ordovician rocks are present in South Australia, Tasmania and Antarctica, the complete absence of such recycled grains means that quartzitic rocks were not abundant in the source terrain. However, the source terrain could be of a graywacke-argillite type or its metamorphic derivative.

Data on the Robertson Bay Group and Kanmantoo Group of sedimentary rocks are very scarce. The author had the opportunity to examine thin sections of graywackes of the Robertson Bay Group, Victoria Land, Antarctica collected by D. Wyborn of the BMR, Canberra. The graywackes are of the quartz- intermediate type and contain quartz, feldspar, igneous, metamorphic and sedimentary lithic grains. The polycrystalline quartzose grains form about 10% of the whole rock and are of igneous and metamorphic parentage (cf. Blatt, 1967; Young, 1976). Feldspar is almost all plagioclase. Some thin sections contain dominant to common volcanic lithic grains and devitrified glass shards whereas such grains may be rare in others. Thus the Robertson Bay Group may have some stratigraphic or facies controlled mineralogical variation not yet known. The absence of such information is the biggest lacuna in understanding the provenance history of Ordovician graywackes.

Volcanic rock fragments are completely absent and metamorphic rock fragments are few in the Ordovician graywackes, whereas such lithi; grains are common to abundant in the Robertson Bay Group graywackes. If the Robertson Bay Group formed the provenance for the Ordovician, the absence of such grains can be explained by their selective abrasion. Metamorphic rock fragments are mechanically unstable and are destroyed by physical abrasion within a few kilometers of transport (Cameron and Blatt, 1971; Cleary and Conolly, 1971). Negligible abrasion of felsic volcanic rock fragments in the 160 km fluvial transport was observed by Cameron and Blatt (1971) but the preferential decomposition of mafic volcanic grains can certainly take place during transportation. Ordovician graywackes are characterized by the common presence of a fine grained matrix. Though a small part of it may have formed diagenetically, most of it is primary and may have been derived either from the older mudrock rich sequence or by the breakdown of volcanic and metamorphic lithic material. The feldspar of the Ordovician graywackes is almost all plagioclase and there is a general absence of K-feldspar grains. This feature is also observed in the Robertson Bay Group graywackes and supports the contention that these rocks constituted the provenance for the Ordovician sediments. Had the Ordovician sediments been derived from the crystalline complex of the craton, they should be rich in K-feldspar and depleted in plagioclase, as plagioclase is found to alter faster than K-feldspar during transportation (Basu, 1981).

There is a complete absence of course-grained material (conglomerates) in the whole of the Ordovician sequence of southeastern Australia. This suggests that tectonism played a subdued role in sedimentation and that the climate at the source region may have been responsible for the destruction of plagioclase and other labile grains. Sorting during sedimentation resulted in the enrichment of phyllosilicates in the finer fraction and quartzose grains in the coarser fraction.

4.5.5 Cookman Suite

The detrital assemblage of the Cookman suite is dominated by quartz grains. Volcanic rock fragments constitute a negligible proportion of the framework grains. The occurrence of abundant monocrystalline quartz, common chert and sedimentary rock fragments, and the low feldspar and matrix content suggest the multicyclic nature of the detritus and sedimentary provenance. The obvious choice of the source terrain lies in the Ordovician sedimentary sequence of the Lachlan Fold Belt, occurring towards the western margin of the Hill End Trough.

Compared to the Ordovician graywackes (e.g. the Bendigo suite), the Cookman suite graywackes are enriched in monocrystalline quartz and sedimentary rock fragments and depleted in feldspar, polycrystalline quartzose grains and matrix content. This can be attributed to the disintegration of labile grains due to recycling. The abundance of sedimentary rock fragments in some of the beds indicates that the relief may have been uneven. However, subdued tectonism resulted in the extensive weathering and sorting of quartz in the coarser fraction and clay material in the finer fraction.

CHAPTER 5
PETROLOGY AND CLASSIFICATION OF MUDROCKS

5.1 INTRODUCTION

The study of fine grained clastic sedimentary rocks has remained comparitively neglected as opposed to extensive work on arenites. However, like most natural objects, mudrocks also have a limitless number of attributes (Potter et al. 1980) and their importance depends on the type of investigation pursued.

In this chapter the textural and mineralogical characteristics of mudrocks have been described and an attempt has been made to differentiate mudrocks into suites. Corresponding to graywackes, the following five major suites are expected : Tamworth, Hill End, Hodgkinson, Bendigo and Cookman.

Mudrocks constitute between half to two-thirds of the stratigraphic sequences in the basins studied. Various structures like parallel lamination, cross lamination, parting lineation, mud balls, and flute and tool marks are commonly seen in these rocks. Mudrocks occur as "d" or "e" units of the modified "Bouma sequence" (Cas, 1978) or form part of the basin floor sequence.

5.2 MINERALOGY OF MUDROCKS

The identification and estimation of minerals in mudrocks has been done by thin sections for the framework silicates, iron-oxide and carbonates, and by X-ray diffraction for phyllosilicates (Table 5.1). Various techniques used are given in Appendix A.

5.2.1 Framework Silicates, Iron Oxide and Carbonates

Quartz: Quartz is present as the common detrital component in most mudrocks, except those of the Tamworth Trough where it occurs as radiolarian tests. In thin sections, detrial quartz grains are 0.1 to 0.04 mm in size but occassional larger grains of up to 0.2 mm are also seen. Quartz is also recognized by the prominent peak at 3.3 Å and the supplementary peak at 4.26 Å on X-ray diffractrograms.

Feldspar: Feldspar shows a large variation in its abundance (Table 5.1) and is almost all plagioclase. In the Tamworth and Hill End suites, the grains are 0.06 to 2 mm in size and exhibit a turbid appearance. In most other suites, feldspar grains are very small in size, however

Table 5.1 Estimates of the Mineral Composition of Mudrocks Suites*

Mudrock Suite	FRAMEWORK SILICATES			PHYLLOSILICATES (in clay fraction)				IRON OXIDES	CARBONATES
	Quartz	Feldspar	Misc.	Illite	Chlorite	Kaolinite	Mixed-layed		
TAMWORTH	XXX	XXX	XX	X	X	-	XX	XX	XX
HILL END	XX	XX	-	XX	XX	X	X	XX	XX
HODGKINSON	XX	XX	-	XX	XX	-	-	X	X
BENDIGO	XX	X	-	XXX	XXX	-	-	-	X
COOKMAN	X	-	-	XXX	-	XXX	-	-	-

* Estimated abundance index:

X: very small; XX: common; XXX: abundant; - :negligible or absent.

occassional larger grains show polysynthetic twinning. The presence of feldspar is also confirmed by the 3.2 Å and subsequent characteristic peaks on the X-ray diffractrogram.

Iron Oxide and Hydroxide: Coatings of iron oxide (mainly hematite) and some hydroxide are commonly seen in mudrocks. Pyrite is also present in some thin sections.

Carbonates: Carbonate is all calcite and is more commonly seen in the Tamworth suite and less commonly in the Hill End and Hodgkinson suite mudrocks, and is almost completely absent in the Bendigo and Cookman suite mudrocks (Table 5.1). Its presence is confirmed by the 3 Å peak on the X-ray diffractrogram.

Miscellaneous: Minor detrital pyroxene and diagenetic epidote are recognized in the Tamworth suite mudrocks. Diagenetic biotite is also seen in the Crow Mountain Creek mudrocks. Rare tourmaline grains were also recognized in the Bendigo suite mudrocks.

5.2.2 Phyllosilicates

The following phyllosilicates were identified in the clay size fraction of mudrocks.

Illite: Illite is present in almost all mudrocks and is identified by 10 Å and 5 Å characteristic peaks, which remain unchanged after ethylene glycol solvation.

Chlorite: Chlorite is a common phyllosilicate mineral and is identified by the 14 Å and 7 Å peaks on X-ray diffractrograms, which remain unchanged after ethylene glycol solvation.

Kaolinite: Kaolinite is a rare mineral and was detected in only two samples : one of the Hill End suite (MK58) and the other of the Cookman suite (MK55). It is identified by the presence of 7.17 Å and 3.57 Å peaks, which lose their crystalline character on heating to 600°C.

Mixed-layer Mineral: The mixed layered phyllosilicate minerals are present only in the Tamworth suite mudrocks and are probably of the smectite-chlorite type. They are identified by a strong 14 Å peak, which shifts on glycol solvation and heating.

5.3 MUDROCK SUITES

5.3.1 Semi-Quantitative Mineralogy

Many mineralogical investigations concentrate only on the clay size fraction of mudrocks. This procedure excludes important information on the total amount of tectosilicates and phyllosilicates present in the whole

Table 5.2 Semi-quantitative Mineralogy, Maturity Index, Estimated Grain Size and Sorting Index of Mudrocks

	Illite	Chlorite	Quartz	Feldspar	Calcite	Kaolinite	Quartz# (IR)	Mean Size (ϕ)	Sorting Index (ϕ)	MMI##	Mudrock Nomenclature
Tamworth											
MK18	3	30	39	17	11	-	29	6	0.10	37	Phyllo-tectic siltstone
MK34	11	17	43	29	-	-	40	8	0.10	28	Tectic mudstone
MK35	14	-	35	52	-	-	29	9	0.01	14	Tectic mudstone
MK36	12	9	41	37	3	-	56	9	0.01	22	Tectic mudstone
MK38	7	17	32	41	3		47	8	0.03	25	Tectic siltstone
MK41	7	-	51	37	5		33	8	0.05	7	Tectic mudstone
MK43	6	4	63	26	-	-	47	7	0.06	10	Tectic siltstone
MK44	9	8	60	24	-	-	49	8	.05	17	Tectic mudstone
MK45	8	15	47	29	-	-	51	8	0.06	23	Tectic mudstone
MK19*	3	3	18	73	3		75	5	0.20	-	Biotite-bearing mudrock
MK39*	7	19	31	41	2	-	48	7	0.03	-	Biotite-bearing mudrock
MK40*	6	11	22	60	-	-	53	5	0.20	-	Biotite-bearing mudrock
MK37**	9	19	8	36	30		13	4	0.40	-	Calcareous mudrock
MK42**	-	23	15	62	-	-	29	5	0.10	-	Recrystallised cherty mudrock
X̄	9	11	46	32	-		42			20	
σ	3	9	10	10	-		10			9	
Hill End											
MK32	16	20	33	24	7	-	31	6	0.10	38	Phyllo-tectic siltstone
MK33	18	22	47	13	-	-	35	8	0.10	40	Phyllo-tectic siltstone
MK48	-	9	36	57	-	-	37	5	0.08	9	Tectic siltstone
MK51	16	6	43	26	9	-	56	9	0.05	24	Tectic mudstone
MK52	22	17	38	23	-	-	56	4	0.10	39	Phyllo-tectic siltstone
MK56	19	-	38	38	-	5	37	7	0.18	20	Tectic siltstone
MK62	7	9	23	49	12	-	28	8	0.08	18	Tectic mudstone
MK66	18	15	29	38	-	-	25	7	0.10	33	Phyllo-tectic siltstone
MK73	21	21	31	25	-	-	38	10	0.01	42	Phyllo-tectic claystone
X̄	15	13	35	33	-	-	38			30	
σ	7	7	7	14	-	-	11			11	
Hodgkinson											
MK92	28	24	26	22	-	-	28	8	0.06	52	Phyllo-tectic mudstone
MK94	16	18	25	34	6	-	40	8	0.05	36	Phyllo-tectic mudstone
X̄	22	21	26	28	3		34			44	
Bendigo											
MK100+	19	9	78	4	-	-	50	8	0.05	-	"Black Shale"
MK101	21	53	17	9	-	-	29	8	0.07	74	Phyllic mudstone
MK102	36	35	19	10	-	-	20	9	0.05	71	Phyllic mudstone
X̄	29	44	18	9			25			73	
Cookman											
MK55	48	-	14	5	-	33	37	8	0.02	81	Phyllic mudstone

\# Quartz by Infra-red
* Crow Mountain Creek Beds - not included in the mean
** Not included in the mean
+ Black shale - not included in the mean
\#\# MMI - Mudrock Maturity Index
X̄ ± σ : Mean and Standard Deviation

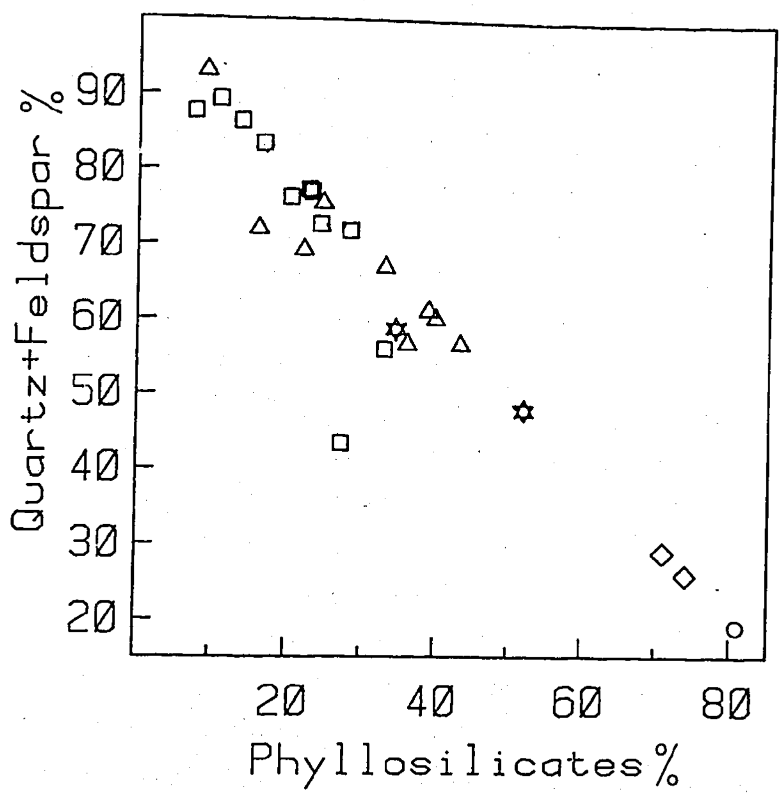


Figure 5.1 Plot of Phyllosilicate versus Quartz + Feldspar content in mudrocks.

□ Tamworth suite
△ Hill End suite
✡ Hodgkinson suite
◇ Bendigo suite
○ Cookman suite

rock, and thus results in an erroneous estimation of the quantitative mineralogy of the rock (Towe, 1974). In the present investigation, mineral determinations were done on whole rock samples. The constituents recorded are illite, chlorite, quartz, feldspar, kaolinite and calcite. The mixed-layer minerals, noted in the clay size fraction of the Tamworth suite mudrocks, were not recorded by this technique because of their low abundance. The determinations are only a semi-quantitative estimate of the minerals present and are useful in comparing the relative abundances of the constituents in the mudrocks. The technique employed is given in Appendix A and the accuracy of the results are probably within $\pm$ 15% as can be inferred by comparing the quartz content determined by X-ray diffraction and Infra-red techniques (Table 5.2). Because of the presence of diagenetic biotite which was not recorded in the present work, the Crow Mountain Creek mudrocks are not included in this generalisation.

In general, mudrocks of various suites have almost similar mineral constituents. The occurrence of kaolinite in the Cookman suite may be due to recent weathering. However, the relative amounts of phyllosilicates and other constituents help in characterising mudrock suites. A plot of total phyllosilicate (illite+chlorite+kaolinite) versus quartz + feldspar shows that, in general, there is a gradation from Tamworth to Hill End-Hodgkinson to Bendigo-Cookman suite mudrocks, characterised by a decrease in feldspar and quartz content and an increase in phyllosilicates (Figure 5.1). The Tamworth suite mudrocks are characterised by a high feldspar and low phyllosilicate content. The high quartz content in these rocks is due to the presence of radiolarian quartz and volcanic glass. The Hill End suite mudrocks show large mineralogical variation, some plot in the Tamworth suite field, but in general, they have a high phyllosilicate and a low feldspar content. The Hodgkinson suite mudrocks can not be distinguished on the basis of mineral abundance from the Hill End suite samples. The Bendigo and Cookman suite samples are characterised by a high phyllosilicate content and a low feldspar and quartz content. Thus on the basis of semi-quantitative mineralogy, the discrimination between each suite is not perfect but the suites can be grouped into the following three classes : (a) Tamworth suite (b) Hill End and Hodgkinson suites and (c) Bendigo and Cookman suites.

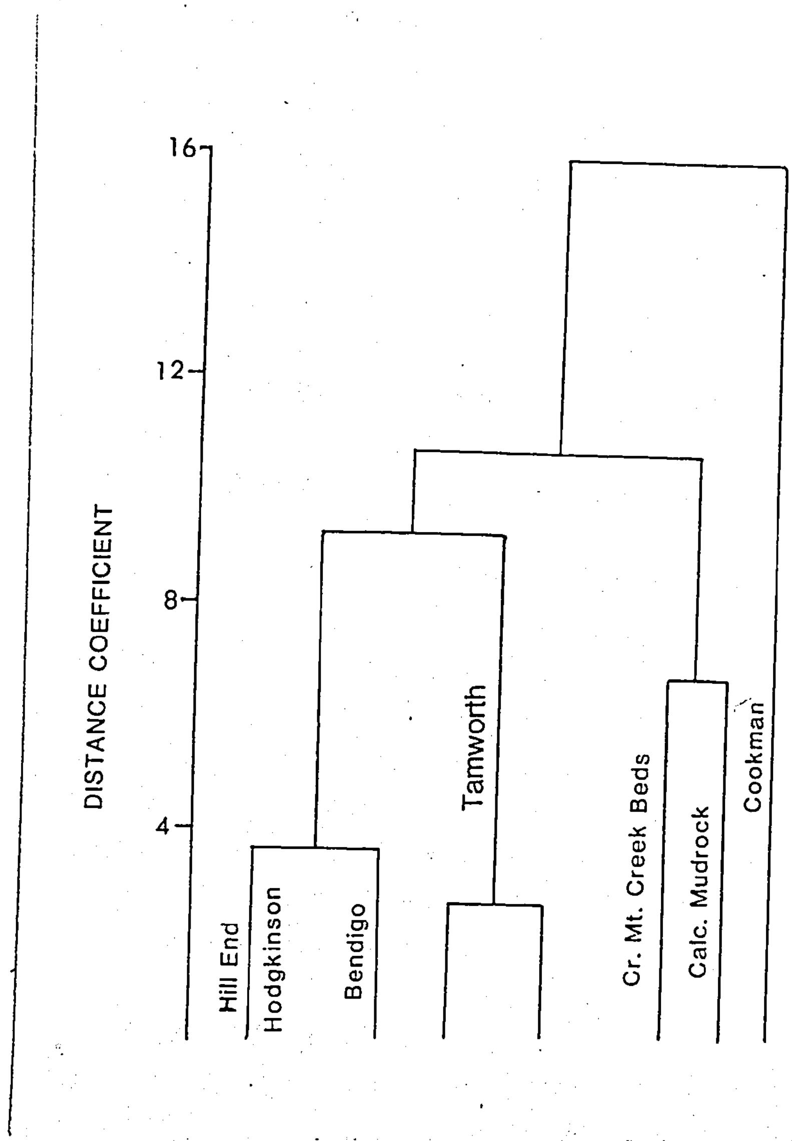


Figure 5.2 Simplified dendrogram showing various clusters of mudrocks.

5.3.2 Cluster Analysis

Discriminant function analysis may not be very meaningful in characterising mudrock suites because of very small data set in the Hodgkinson, Bendigo and Cookman suites. The cluster analysis was performed on all samples (including those of the Crow Mountain Creek Beds), using mineralogical variables to understand the grouping of cases, and the result is presented in a simplified dendrogram (Figure 5.2). At a distance coefficient of around 3, the cluster analysis establishes four major groups. Cluster I is constituted by 2 samples of the Hodgkinson suite and 7 samples of the Hill End suite. Cluster II contains only two samples, both belong to the Bendigo suite. Cluster III is the biggest group and contains 11 samples in all, 9 belong to the Tamworth suite and 2 to the Hill End suite. At a low similarity coefficient, this group can be divided into two sub-groups. The highly diagenetic altered Crow Mountain Creek Bed mudrocks are separated from all the others to form Cluster IV. Sample MK37 of the Crow Mountain Creek Beds makes a separate entity because of the presence of abundant calcite, and the only sample of the Cookman suite also forms a separate cluster characterised by the presence of abundant kaolinite. These results suggest that mudrock suites can be characterized on the basis of their mineralogy, though the Hill End and Hodgkinson suites can not be discriminated; and the Tamworth and Hill End suites overlap.

5.4 MUDROCK TEXTURE

Texture is the least understood attribute of the mudrock composition (see also discussion in Section 5.6.1). The true mean size and sorting of mudrocks are difficult to measure because of their fine grained nature and high compaction. The mean size and sorting index has been estimated for each mudrock sample (Table 5.2) (the method is given in Appendix A). The small number of samples studied in the present work does not allow us to make any unequivocal statements on the relationship between texture and composition. Most mudrock samples exhibit fair to good sorting. However, it can be seen that the sorting improves with decreasing grain size (Figure 5.3). Plots of grain size versus abundances of quartz + feldspar and phyllosilicates do not show any definite overall relationship between textural and mineralogical variables (Figure 5.3).

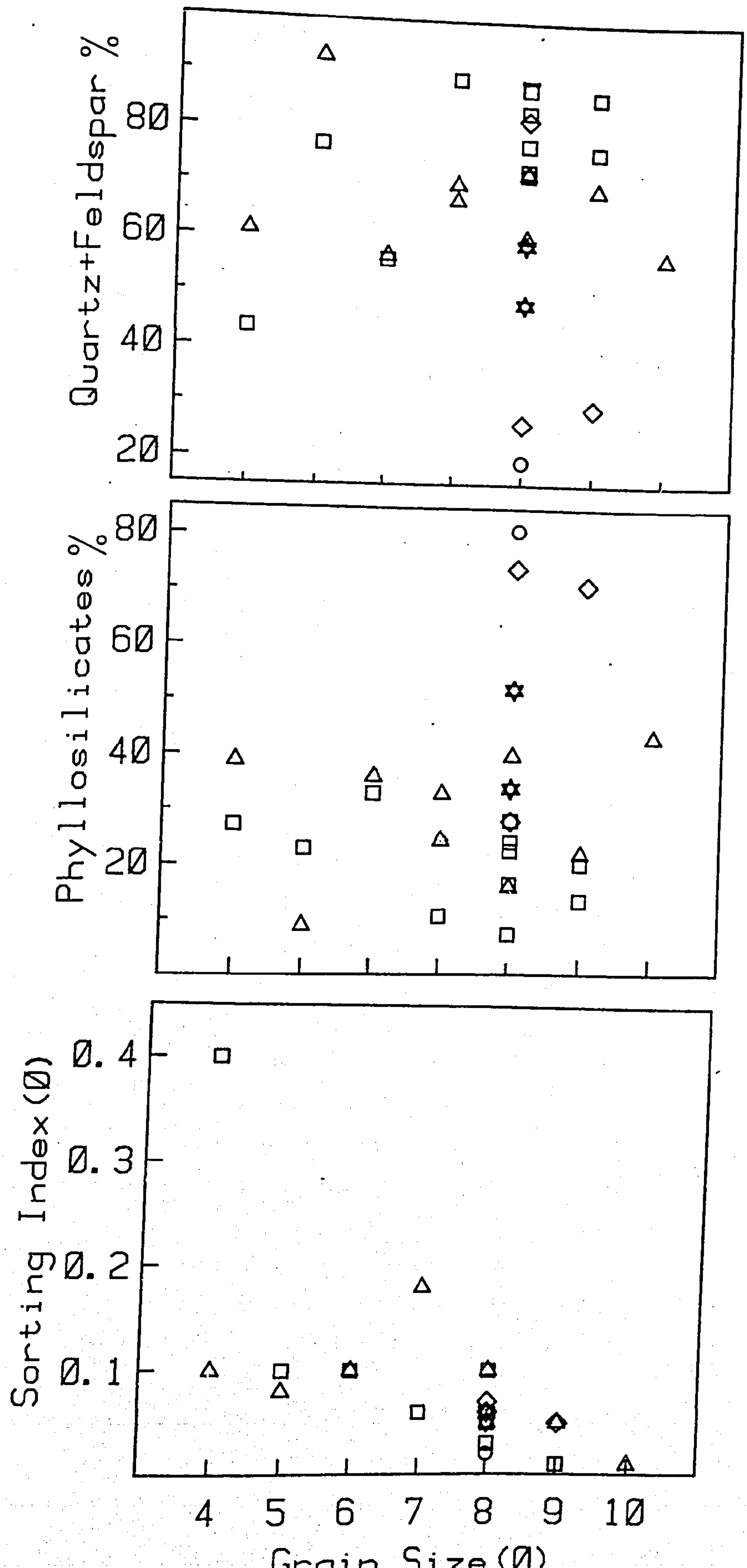


Figure 5.3 Plot of estimated mean grain size (ø) versus quartz + feldspar, phyllosilicate, and sorting index in mudrocks. (Symbols as in Figure 5.1).

5.5 PETROGENESIS OF MUDROCKS

Mudrocks are thought to be a homogeneous group of rocks with very little variation in their characters (Pettijohn, 1975). The present work has shown that mudrocks vary in their overall characteristics and can be classified to some extent into various groups (Section 5.3). In this section, an attempt is made to understand the factors which control this variation.

Many recent investigations of bore-hole samples have established that kaolinite and mixed-layer minerals dominate in shallow-depths and chlorite and illite content increases with increasing depth due to increasing diagenesis (e.g. Hower et al. 1976; Parry and Hower, 1970), involving the following reaction:

Smectite + K-feldspar + mica = Illite + chlorite + quartz

A large survey of the mudrocks of North America showed that illite and chlorite form the dominant component of the clay size fraction of Paleozoic mudrocks and that kaolinite and mixed-layer phyllosilicates are abundant in younger mudrocks (Weaver, 1967). Post-depositional modifications of the type suggested for the vertical profiles in well-logs were attributed to the alteration of mixed-layer minerals to illite and chlorite (Hower et al. 1976; Mackenzie, 1975). Experimental evidences have generally substantiated the depth-temperature-age relationship in mudrocks (Hiltabrand et al. 1973). However, Blatt et al. (1980) have cautioned that inferences on the basis of bore-hole data may not be conclusive and that vertical changes could also be due to other factors such as : changes in source rocks, weathering and climatic conditions.

The original mineralogy of mudrocks may have been modified by burial, however, the specific mineral changes in various types of mudrocks have not been extensively evaluated. Van Moort (1971) suggested that though burial metamorphism has modified the minerals, the differences in mineralogical characteristics between the Mesozoic shales of Papua New Guinea and the Tertiary shales of Louisiana, are due to differences in the nature of the source rocks and weathering conditions. Studies on recent sediments have shown that provenance controls the mineralogy of mud (e.g. Biscaye, 1965; Porrenga, 1975). Potter et al. (1980) have also suggested that provenance is the major factor and that illite is derived from the weathering of pre-existing muscovite or illite; chlorite from pre-existing chlorite; and smectite is commonly associated with volcanic source terrains.

The general failure to characterise mudrocks is due to the fact that most studies are based on the clay size fraction and because of the bias introduced, true estimation of the total mineralogy thus remains unrevealed. The present work shows that the original mineralogy may be modified to some extent, by burial metamorphism, however differences between various mudrock types can be deciphered on the basis of feldspar and phyllosilicate content. Thus the study of the mineralogy of the whole rock is essential in order to understand the petrogenesis of mudrocks.

As for arenites, the environment of deposition and the tectonism (in the form of source rocks and relief) control the composition of mudrocks (Weaver, 1978). According to Weaver (1978) the authigenic and diagenetic changes are minor in marine conditions and most illite and chlorite are of terrigenous origin in rapidly deposited geosynclinal basins. The Tamworth suite mudrocks are rich in feldspar and low in phyllosilicates. This indicates "active" tectonism which resulted in high relief and low weathering conditions, thus inhibiting the decomposition of feldspar. The presence of smectite indicates a volcanic source terrain which provided abundant feldspar grains and substantiates an andesitic source envisaged on the basis of graywacke mineralogy.

The Hill End suite mudrocks contain abundant feldspar indicating low weathering conditions and high relief. These mudrocks are characterised by the higher abundances of phyllosilicates and detrital quartz compared to Tamworth suite mudrocks and thus are compatible with a felsic volcanic source terrain. Smectite is identified in only two samples and is probably altered to chlorite due to diagenetic modifications. The Hodgkinson suite mudrocks are similar to Hill End suite mudrocks but probably contain more phyllosilicates. This, along with the common occurrence of feldspar in the Hodgkinson suite mudrocks, indicates a moderate relief and probably a crystalline source terrain.

The Bendigo suite mudrocks are characterised by the high abundance of chlorite, which may have been derived from older chlorite rich rocks or the conversion of volcanogenic smectite. The high phyllosilicate and low feldspar content indicates a dominantly sedimentary-metasedimentary source terrain with minor volcanic material and high weathering conditions. This is compatible with the contention that the Robertson Bay Group constituted the provenance, as envisaged on the basis of graywacke mineralogy.

Only one sample of the Cookman suite was studied. This is highly enriched in phyllosilicates (minly kaolinite) and depleted in feldspar, suggesting a multicycled nature and extensive weathering conditions. Kaolinite is present in deep-sea sediments and represents low-latitude continental detritus. Mudrocks of the Cookman Formation are commonly weathered and thus kaolinite may have formed due to the recent weathering of illite, involving the following reaction:

$$\underset{\text{Illite}}{2KAl_5Si_7O_{20}(OH)_4} + 2H^+ + 2HCO_3^- + 13H2O$$

$$\rightarrow 5\ \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 4H_2SiO_4 + 2K^+ + 2HCO_3^-$$

5.6 CLASSIFICATION OF MUDROCKS

5.6.1 Introduction

Current efforts to classify fine-grained clastic sedimentary rocks are very timely (Table 5.3). Six mudrock classifications were proposed in the 1970's. A renewed interest was witnessed in 1980 and four new mudrock classifications were proposed. Thus we may be entering into the "Mudrock Classification Era", somewhat similar to the "Sandstone Classification Era" of 1960's and 1970's.

There is a general lack of understanding of the fundamental characteristics of various mudrock types. The composition and texture of mudrocks in various regimes may vary because of differences in controlling factors. Thus, significant progress can be achieved if classification is attempted on the basis of the characteristics features of various mudrock suites.

5.6.2 Existing Classifications

The existing classifications of fine-grained clastic sedimentary rocks (Table 5.3) are of three type and based on

(1) grain size and physical character

(2) lithic grain type

(3) mineralogy and texture

In the classifications based solely on the grain size and the physical character (Pettijohn, 1975; Blatt et al. 1972, 1980; Lundegard and Samuels, 1980), the emphasis is to distinguish fine-grained claystones from siltstones. These classifications are only useful for field and

Table 5.3 Recent Classifications of Mudrocks

Author(s)	Description
Fuchtbauer & Muller (1970)	Textural and mineralogical classification. Presumes all quartz in the silt size and phyllosilicates in the clay size fraction.
Picard (1971)	Textural and compositional. Mainly based on the type of silt size grains.
Blatt, Middleton & Murray (1972)	Textural classification. Divide mudrocks into siltstone, mudstone and claystone based on the presence of the silt size fraction.
Pettijohn (1975)	A field classification based on grain size, lamination and fissility.
Larese & Heald (1977)	A broad classification of sedimentary rocks based on texture and composition. End members of the classification are Shale-Sandstone - Siltstone and Shale-Siltstone-Dolomite.
Lewan (1978)	A laboratory classification based on texture and mineralogy. Divide mudrocks into shale and mudstone depending upon the percentage of the < 5 μm fraction.
Spears (1980)	Divides mudrocks into five classes on the basis of quartz percentage and its supposed correlation with grain size.
Lundegard & Samuels (1980)	A field classification based on the silt size fraction and lamination.
Potter, Maynard & Pryor (1980)	A comprehensive classification based on texture, mineralogy and physical characters. Divides mudrocks into three broad categories based on clay-size constituents.
Weaver (1980)	Separates texture from mineralogy. Divides mudrocks into two textural classes : siltstone and claystone. Mineralogical modifiers "physil" and "physillic" are used for rocks having more than 50% and less than 50% phyllosilicates, respectively. Confusing terminology.

descriptive purposes. However, in geosynclinal terrains, it is difficult to measure the true grain size, and physical characters are subjected to modifications due to burial.

Besides the difficulty of measuring the grain size of fine grained rocks, even its significance is not completely understood because grain size increases with increased burial. It has generally been thought that textural and mineralogical terms for mudrocks are synonymous and that all material finer than 4 μm is phyllosilicate (e.g. Füchtbauer and Müller, 1970; Lundegard and Samuels, 1980). Weaver (1980) has pointed out that mineralogy has no fixed relationship with grain size and it is a mistake to assume that silt size material is largely quartz and that phyllosilicates are generally clay sized. In the Tamworth and Hill End suite mudrocks, the clay size fraction is more than 50% of the rock but the phyllosilicate content is generally less than 30%, meaning that a large part of the feldspar and quartz grains must constitute the clay size fraction. Thus, the assumption that all phyllosilicates are in less than 4 μm fraction and all quartz and feldspar are in the silt size fraction is erroneous. A large part of the silt fraction could contain phyllosilicates, (also Scotford, 1965) and significant quartz and feldspar can occur in the clay size fraction.

Picard (1971) proposed a classification of mudrocks, based on the nature of lithic grains, and adopting the terminology of sandstone classification. However, it is virtually impossible to identify the nature of rock fragments in mudrocks of geosynclinal terrains. Spears (1980) proposed a classification on the basis of correlation between quartz content and grain size. The general applicability of this criterion rests upon his belief that "relationship will hold from other systems, but for a given grain size of quartz the clay proportion may vary, probably related to maturity "(Spears, 1980, p. 126). This scheme may hold true for sediments derived from cratonic and recycled orogens where the size-abundance relationship is due to weathering, but not in many geosynclinal terrains where abundant first cycled material is present and composition is not related to grain size in a simple way.

Lewen (1978) proposed a classification based on textural and mineralogical studies. However, he has grouped tectosilicates and phyllosilicates together and as is shown in the next section, it is the ratio of these variables which is critical in understanding the nature of mudrocks. According to his classification, a mudrock containing 50% feldspar and 20% phyllosilicates will have the same value of silicate fraction as a mudrock containing 5% feldspar and 65% phyllosilicates, all others being same.

5.6.3 Proposed Classification of Flysch Mudrocks

The present classification is based on the whole rock mineralogy and textural characteristics of flysch mudrocks. The term "clay" has both a textural and mineralogical connotation. Weaver (1980) has proposed that it should be used strictly in a textural sense for particles finer than 1/256 mm in size and coined another term "physil" having a strictly mineralogical connotation for all phyllosilicate minerals. However, the term "physil" can be very easily confused with the term "fissile" so commonly used in the description of mudrocks (Potter et al. 1980; Blatt et al. 1980) and may generate more confusion than serving any good purpose. The term "phyllosilicate" is adequate enough to indicate a mineralogical meaning and "phyllic" can be used as an adjective for phyllosilicate-rich rocks.

A classification should be descriptive, easy to communicate and should be based on natural characteristics of the objects, so that the descriptive features could lead to genetic interpretation. The term "mudrock" is recommended for fine-grained clastic sedimentary rocks of the geosynclinal sequences. Flysch mudrocks can be divided into three broad clans as shown in the triangular plot of quartz-feldspar-phyllosilicates (Figure 5.4). The "tectic mudrocks" represented by the Tamworth suite are characterised by abundant feldspar and biogenic quartz or volcanic glass, and a low abundance of phyllosilicates, indicating a dominantly volcanic source terrain. The "phyllo-tectic mudrocks" constituted by the Hill End and Hodgkinson suite samples, are characterised by detrital quartz, feldspar and phyllosilicates suggesting quartzo-feldspathic source regions. The Bendigo and Cookman suites constitute the "phyllic mudrocks" and are characterised by the high abundance of phyllosilicates and a very small proportion of quartz and feldspar, indicating their recycled nature.

The data from eastern Australia show that with the increasing maturity of flysch mudrocks, there is an increase in phyllosilicates and a decrease in tectosilicates. Thus, a mudrock maturity index can be defined as :

Table 5.4 Proposed Classification of Flysch Mudrocks and their Modern Analogues (Fine Grained Deep Sea Sediments)

MINEROLOGY : Mudrock Maturity Index	TEXTURE : Percentage of Clay Size Constituents		
	0 - 33	34 - 67	68 - 100
< 33	TECTIC SILTSTONE Tectic Silts	TECTIC MUDSTONE Tectic Mud	TECTIC CLAYSTONE Tectic Clay
33 - 67	PHYLLO-TECTIC SILTSTONE Phyllo-tectic Silt	PHYLLO-TECTIC MUDSTONE Phyllo-tectic Mud	PHYLLO-TECTIC CLAYSTONE Phyllo-Clay
< 68	PHYLLIC SILTSTONE Phyllic Silt	PHYLLIC MUDSTONE Phyllic Mud	PHYLLIC CLAYSTONE Phyllic Clay

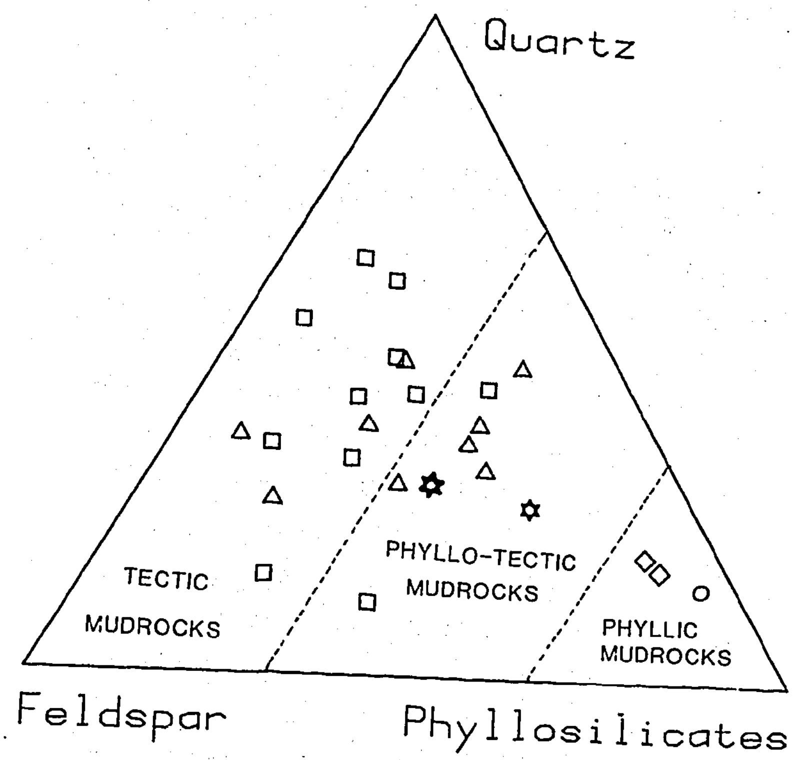


Figure 5.4 Mineralogical classification of mudrocks based on quartz-feldspar-phyllosilicate content. (Symbols as in Figure 5.1).

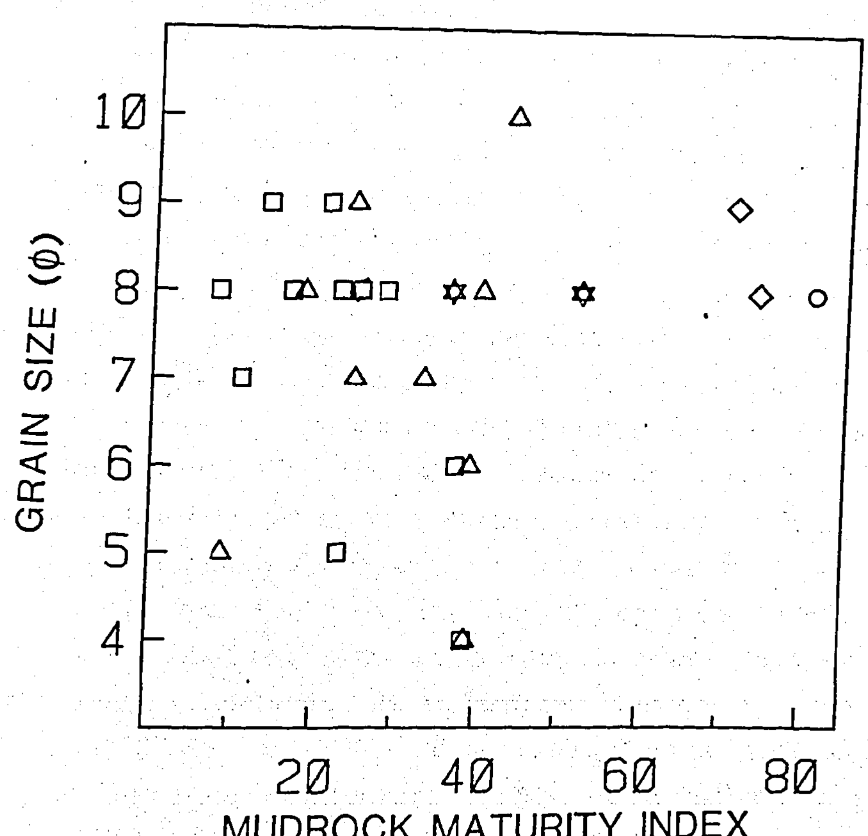


Figure 5.5 Plot of Mudrock Maturity Index versus estimated mean grain size (ϕ). Note maturity has no systematic relationship with grain size. (Symbols as in Figure 5.1).

$$\text{Mudrock Maturity Index} = \frac{\text{Phyllosilicates}}{\text{Phyllosilicates + Quartz + Feldspar}} \times 100$$

Quartz appears in various forms such as biogenic silica, volcanic glass and detrital grains. The decrease in quartz abundance in recycled mudrocks could be due to either

(1) weathering and loss in solution
(2) enrichment in arenits due to sorting
(3) the increase in phyllosilicates affecting the quartz content due to the closure problem.

The mudrocks are divided into siltstone, mudstone and claystone depending upon the clay size constituent present (Blatt et al. 1980). A two fold classification into siltstone and claystone is also equally useful (Weaver, 1980). The clay size constituent can be estimated from thin sections. An extended classification based on mineralogy and texture is presented in Table 5.4. The prefixes tectic, phyllo-tectic, and phyllic are a function of the mineralogy of mudrocks, and their boundaries can be broadly demarcated at the mudrock maturity index of 33 and 67. If distinction on the basis of the clay sized constituent is possible, the suffix siltstone, mudstone and claystone can be used. The suffix silt, mud and clay can be adopted for fine grained deep sea sediments, the modern analogue of flysch sequences. Grain size and diagenesis can be suspected to control the systematic change and the classification of mudrocks. Though the data is extremely meagre, a plot of mudrock maturity index and grain size fails to show that grain size is the first order factor controlling maturity (Figure 5.5). Similarly, no systematic relationship is observed between the degree of diagenesis and maturity. The Hill End suite mudrocks show a higher degree of diagenesis but a low phyllosilicate content compared to Bendigo suite mudrocks.

The present classification is essentially descriptive but can be related to the tectonic setting of the sedimentary basin (Chapter 7). It is mainly designated for flysch sequences and may not be applicable in the cratonic realms, where the quartz-phyllosilicate content forms a continuous gradation and the composition is related to the grain size due to its recyclic nature and widespread weathering (e.g. Blatt and Schults, 1976; Spears, 1980). The classification is based on a very small data set but the results are highly encouraging, considering the determinations are only semi-quantitative. An improved technique and more data will contribute substantially towards understanding the widespread fine-grained clastic sedimentary rocks.

CHAPTER 6
GEOCHEMISTRY OF FLYSCH SEDIMENTARY ROCKS

6.1 INTRODUCTION

Major and trace element geochemical data on well defined sedimentary suites are very meagre. The following aspects are covered in this chapter : variation in major and trace element geochemistry of the various suites; the relationship between petrological and geochemical variables; comparison of average sedimentary suite and provenance compositions; and element redistribution during sedimentary cycles. The major and trace element data are given in Appendix E. Correlation matrices for geochemical variables in graywackes and mudrocks are given in Tables 6.1 and 6.2, respectively. The correlation coefficients between mineralogical maturity indices and the geochemical variables is also shown in these tables. Correlation coefficients of textural (Mean Size and Sorting Indices) and "fan facies" variables are not significant and hence excluded. The correlation coefficient should be interpreted cautiously. Only positive correlations are significant, as negative correlations can arise because of the "closure problem". Large correlations can also arise due to similar abundance trends rather than due to the similar crystochemical behaviour of the elements.

6.2 MAJOR ELEMENT GEOCHEMISTRY

Variations in the major element geochemistry of various graywacke suites are shown on Harker diagrams (Figure 6.1). In general, SiO_2 increases and TiO_2, Al_2O_3, FeO^t (total Fe as FeO), MnO, MgO, CaO and Na_2O decrease from the Tamworth through the Hill End, Hodgkinson, Bendigo to Cookman suite graywackes due to the increase in mineralogical maturity. K_2O first increases from the Tamworth through Hill End to the Hodgkinson suite, due to the increase in the K-feldspar and mica content, and then decreases towards the feldspar depleted Bendigo and Cookman suites.

The data set for the Hodgkinson, Bendigo and Cookman suite mudrocks is very small and the variations in major element geochemistry are less marked. However, in general there is an overlapping increase in Al_2O_3, FeO^t, K_2O and decrease in CaO, Na_2O and to some extent in SiO_2 from the Tamworth-Hill End towards the Hodgkinson-Bendigo-Cookman

Table 6.1 Correlation Matrix of Chemical Elements and Maturity Index in Graywackes (N = 68)*

	Si	Al	Ti	Fe	Mn	Mg	Ca	Na	K	P	S	Ba	Rb	Sr	Pb	Th	U	Zr	Nb	Y	La	Ce	Nd	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	MI#
Si	1.00																															
Al	-.77	1.00																														
Ti	-.69	.64	1.00																													
Fe	-.83	.75	.88	1.00																												
Mn	-.72		.28	.41	1.00																											
Mg	-.77	.74	.79	.94	.30	1.00																										
Ca	-.81	.31	.35	.47	.94	.39	1.00																									
Na	-.71	.81	.54	.67	.24	.65	.33	1.00																								
K				-.28	-.27	-.30	-.31		1.00																							
P	-.45	.41	.64	.54		.49	.24	.35		1.00																						
S	-.31	.26		.34		.37	.25				1.00																					
Ba									.73			1.00																				
Rb	.43	-.28	-.37	-.44	-.33	-.46	-.39	-.41	.86	-.28	-.25	.53	1.00																			
Sr	-.38	.47		.28		.27		.43		.43		.35	-.30	1.00																		
Pb	.45	-.29	-.43	-.52	-.30	-.56	-.35	-.36	.49	-.42	-.23	.28	.63	-.27	1.00																	
Th	.59	-.49	-.41	-.51	-.37	-.52	-.49	-.49	.41	-.29	-.24		.68	-.41	.63	1.00																
U	.43	-.31		-.34	-.31	-.39	-.39	-.33	.36				.51	-.30	.52	.86	1.00															
Zr	.49	-.48		-.33	-.28	-.35	-.38	-.46					.27	-.34	.25	.62	.55	1.00														
Nb	.39	-.28		-.25	-.30	-.32	-.37	-.38	.26		-.25		.61	-.37	.58	.74	.64	.64	1.00													
Y									.25				.39		.27	.55	.48	.43	.47	1.00												
La	.57	-.41	-.34	-.47	-.44	-.50	-.51	-.46	.42		-.26		.63	-.34	.57	.79	.71	.48	.64	.63	1.00											
Ce	.56	-.41	-.30	-.46	-.41	-.47	-.49	-.56	.43		-.25		.63	-.31	.52	.81	.74	.48	.62	.56	.89	1.00										
Nd	.51	-.36	-.28	-.43	-.39	-.47	-.46	-.42	.30				.47	-.28	.51	.68	.62	.42	.50	.66	.93	.86	1.00									
Sc	-.85	.66	.87	.89	.55	.78	.60	.55	-.25	.54	.26		-.44		-.47	-.58	-.39	-.32	-.26		-.49	-.48	-.42	1.00								
V	-.77	.65	.86	.95	.42	.89	.46	.60	-.34	.49	.35		-.47		-.49	-.52	-.37	-.27			-.48	-.47	-.43	.89	1.00							
Cr			.40	.37		.40									-.28									.41	.46	1.00						
Co	-.64	.58	.64	.71	.31	.70	.38	.57	-.24	.47	.36		-.34	.25	-.35	-.38		-.24			-.41	-.40	-.37	.63	.72		1.00					
Ni	-.30		.37	.41		.43																		.33	.41	.71	.52	1.00				
Cu	-.52	.37	.52	.54	.34	.51	.38	.32		.51			-.29		-.42	-.36			-.32					.55	.53	.29	.53	.45	1.00			
Zn	-.75	.76	.89	.90	.30	.82	.37	.62		.57			-.31	.31	-.35	-.41		-.24			-.35	-.31	-.31	.85	.85	.34	.73	.49	.50	1.00		
Ga	-.70	.86	.70	.78		.71	.27	.69		.42				.39		-.33		-.40			-.31	-.26	-.29	.63	.67		.59	.30	.34	.80	1.00	
MI#	.76	-.69	-.54	-.65	-.43	-.62	-.51	-.69		-.35	-.26		.45	-.50	.47	.67	.54	.48	.50	.25	.66	.64	.58	-.64	-.63		.51		-.41	-.57	-.58	1.00

* Correlation coefficients below 0.24 omitted.
$r_{95} = .24$ $r_{99} = .31$

\# Mineralogical Maturity Index

Table 6.2 Correlation Matrix for Chemical Elements and Maturity Index in Mudrocks (N = 29)*

	Si	Ti	Al	Fe	Mn	Mg	Ca	Na	K	P	S	Ba	Rb	Sr	Pb	Th	U	Zr	Nb	Y	La	Ce	Nd	Sc	V	Cr	Co	Ni	Cu	Zn	Ga	MMI#
Si	1.00																															
Ti	-.66	1.00																														
Al	-.69	.58	1.00																													
Fe	-.70	.52	.50	1.00																												
Mn	-.58		-.61		1.00																											
Mg	-.54	.54		.80		1.00																										
Ca							1.00																									
Na								1.00																								
K			.66		-.37			-.47	1.00																							
P							.54			1.00																						
S			-.68	-.37	.87				-.47		1.00																					
Ba					.69						.56	1.00																				
Rb			.46					-.59	.84				1.00																			
Sr							.55	.50	-.40				-.57	1.00																		
Pb		-.41							.38				.69	-.45	1.00																	
Th							-.45	-.42	.68				.91	-.61	.77	1.00																
U				-.42	.44						.62	.42	.44	-.40	.68	.52	1.00															
Zr									.41		-.35		.44		.43	.54		1.00														
Nb							-.45	-.49	.57				.85	-.63	.69	.94	.51	.45	1.00													
Y							.40			.87										1.00												
La										.82										.87	1.00											
Ce										.77										.83	.97	1.00										
Nd										.84										.87	.98	.95	1.00									
Sc	-.79	.84	.59	.68		.58									-.42		-.41							1.00								
V					.47						.68							-.53							1.00							
Cr			.37					-.58	.50				.72	-.48		.60										1.00						
Co	-.43	.49		.71		.74																		.41			1.00					
Ni				.42		.51		-.40					.49	-.41	.37	.42			.52							.71	.52	1.00				
Cu				.38												-.39		.64						.37	.61				1.00			
Zn	-.45		.38	.65		.42																		.39				.49	.58	1.00		
Ga		.66	.77	.41		.57		-.38	.58				.61			.47			.53					.59		.61		.51			1.00	
MMI#			.39					-.49	.51				.67	-.40		.65			.74							.61		.45				1.00

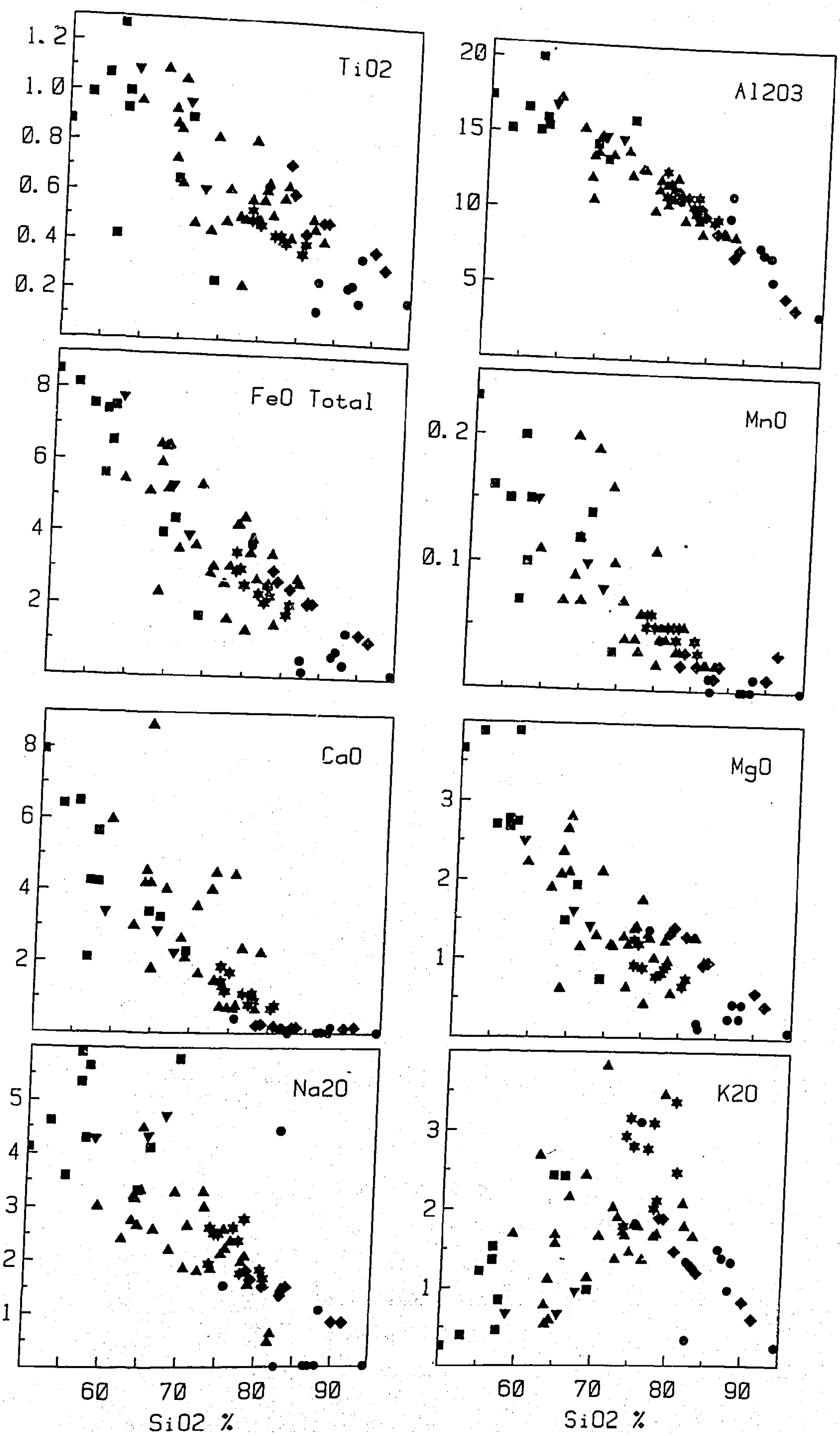
* Correlation Coefficients below 0.37 omitted

$r_{95} = .37$ $r_{99} = .47$

\# Mudrock Maturity I:dex

Figure 6.1 Harker variation diagrams of major elements in graywackes.

- Tamworth suite
- Crow Mountain Creek Beds
- Hill End suite
- Hodgkinson suite
- Bendigo suite
- Cookman suite


TiO2
Al2O3
FeO Total
MnO
CaO
MgO
Na2O
K2O
SiO2 %
SiO2 %

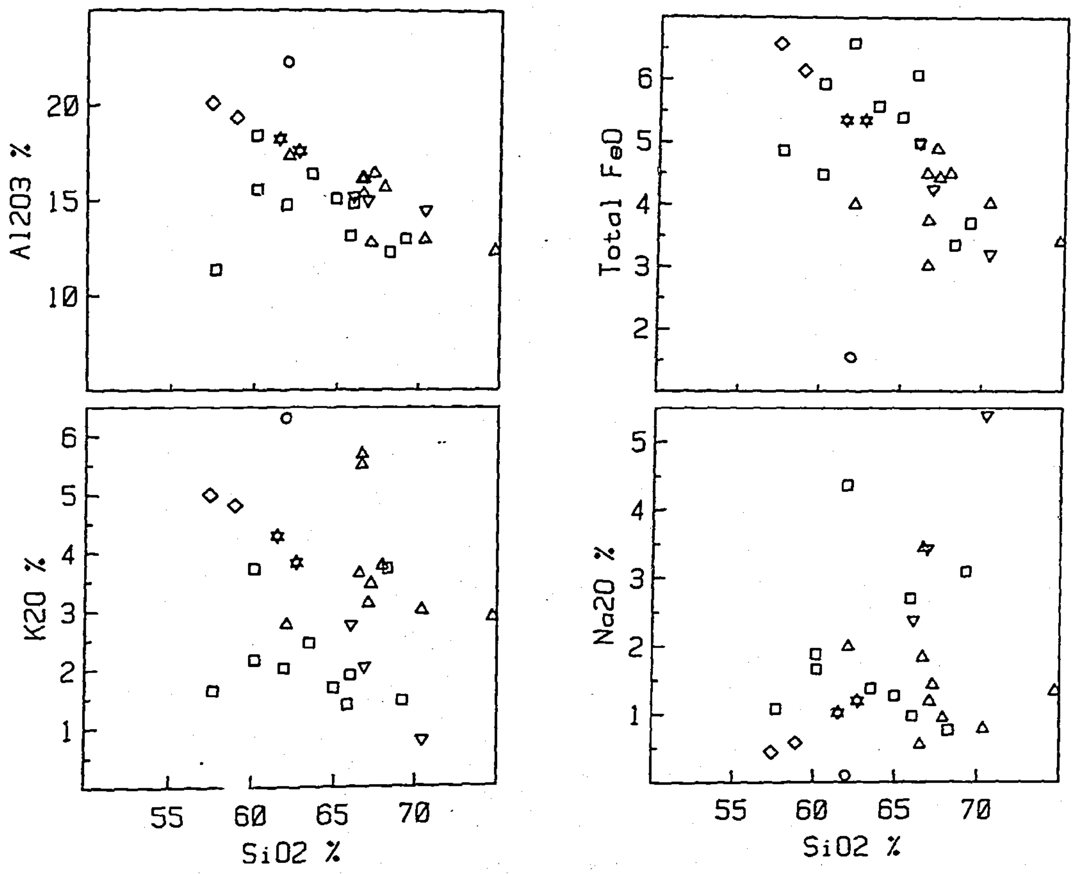


Figure 6.2 Plot of SiO_2 versus Al_2O_3, total FeO, K_2O, and Na_2O in mudrocks.

suite mudrocks (Figure 6.2). This trend is due to the increased abundance of phyllosilicates with the increase in maturity. The high SiO_2 content of the Tamworth suite mudrocks is due to the presence of common radiolarian and volcanic glass. No systematic variation was noted in the TiO_2, MgO and MnO abundances in mudrocks.

In general, the FeO^t, Al_2O_3 and to some extent SiO_2 decrease in mudrocks and increase in graywackes with increasing maturity. On the other hand, Na_2O and CaO decrease both in graywackes and mudrocks with increasing maturity.

6.3 TRACE ELEMENT GEOCHEMISTRY

6.3.1 Ba-Rb-Sr-Pb

Rubidium follows potassium in sedimentary rocks and is significantly enriched in mudrocks compared to the corresponding graywackes in each suite (Figure 6.3a). The highest Rb and K_2O contents in the graywackes, occur in the Hodgkinson suite and reflect the abundant presence of mica and K-feldspar. In mudrocks, most Rb is associated with phyllosilicates and increases from the Tamworth through the Hill End, Hodgkinson, Bendigo to Cookman suites. The K/Rb ratio is significantly high in the Tamworth suite and some of the Hill End suite sedimentary rocks, and decreases in the Hodgkinson, Bendigo and Cookman suites (Figure 6.3a), similar to the decrease of K/Rb from mafic to felsic igneous rocks (Heier and Adams, 1964). Thus a high K/Rb ratio indicates substantial contribution from volcanic sources.

The strontium content, in general, decreases from the Tamworth through the Hill End, Hodgkinson to Bendigo and Cookman graywackes and mudrocks (Figure 6.3c). A high correlation of Sr with Na indicates that most Sr in graywackes and mudrocks is held in feldspar (Table 6.1). The Rb/Sr ratio increases in sedimentary rocks from the Tamworth through the Hill End, Hodgkinson, Bendigo to Cookman suites, due to increased maturity resulting in the loss of Sr.

Barium shows a large variation in its abundance in sedimentary rocks (Figure 6.3; also Puchelt, 1972). The high correlation coefficient ($r = 0.73$) between Ba and K_2O in graywackes indicates that Ba is mainly held in K bearing phases, such as K-feldspar and mica. In mudrocks, Ba generally increases with the increase in Rb from the Tamworth through the Hill End, Hodgkinson to Bendigo-Cookman suites, probably

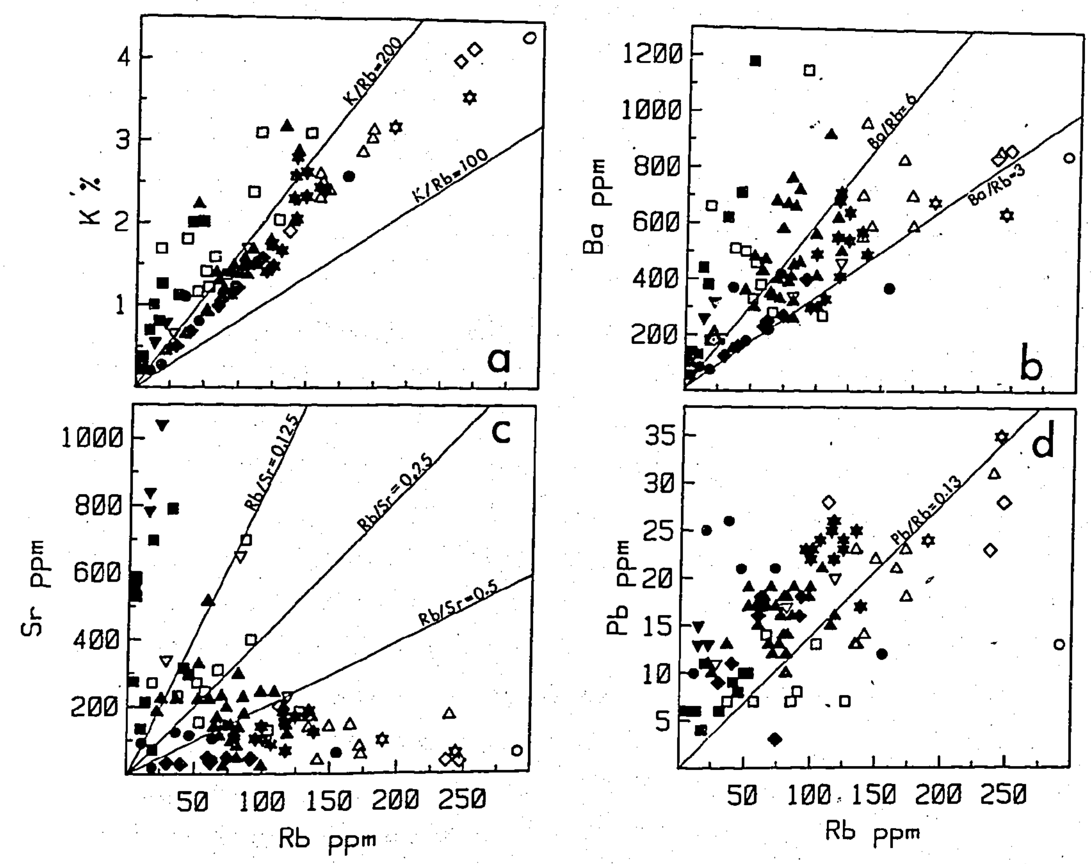


Figure 6.3 Variation in the Rb, Sr, Ba and Pb abundances in sedimentary rocks. Solid symbols are for graywackes (as in Figure 6.1), and open symbols are for mudrocks (as in Figure 6.2).

due to the increase in phyllosilicates (Figure 6.3b). A high correlation of Ba with Mn (r = 0.59) in mudrocks, may suggest that some Ba is held in the cementing material. The Ba/Rb ratio is generally significantly high (Ba/Rb > 6) in the Tamworth and Hill End suite graywackes and thus a high Ba/Rb ratio indicates substantial contribution from volcanic rocks.

Lead behaves coherently with Ba and Rb in most sedimentary rocks. The high abundance of Pb in the Hodgkinson suite graywackes indicates its association with K-bearing minerals (Figure 6.3d). Sediments dominantly derived from volcanic rocks (e.g. the Tamworth and Hill End suites) have a high Pb/Rb ratio. The Pb/Rb ratio may be related to grain size, as most mudrocks are characterised by Pb/Rb < 0.13, compared to the higher ratio observed in corresponding graywackes (Figure 6.3d).

6.3.2 Ferromagnesian Elements

The distribution of ferromagnesian elements is related to the iron and magnesium content in the sedimentary rock. The abundance of Sc, V, Co, Zn and to some extent Cu, decreases with the decrease in FeO^t from the Tamworth through the Hill End, Hodgkinson, Bendigo to Cookman suite graywackes (Figure 6.4). These elements are mainly enriched in rocks containing abundant pyroxene, amphibole, and volcanic material, thus their decrease in graywackes is indicative of increasing maturity. However, no systematic variation was observed in the abundances of these elements in mudrocks, probably due to their complex relation with phyllosilicates, though Cu and Zn are significantly enriched in mudrocks compared to graywackes.

Chromium and nickel show a complex behaviour in sedimentary rocks (Tardy, 1975a,b). No systematic variation was noted in Cr and Ni in graywackes but a significantly high abundance of these elements in the Hill End suite graywackes can be related to the weathering of volcanic detritus. In mudrocks, Cr and Ni generally increase from the Tamworth through the Hill End-Hodgkinson to Bendigo (includes some other Ordovician mudrocks of southeastern Australia - data from Wyborn, 1977) suites (Figure 6.5) and is probably due to the adsorption of these elements on phyllosilicates with increasing recycling (see further discussion in Section 6.9).

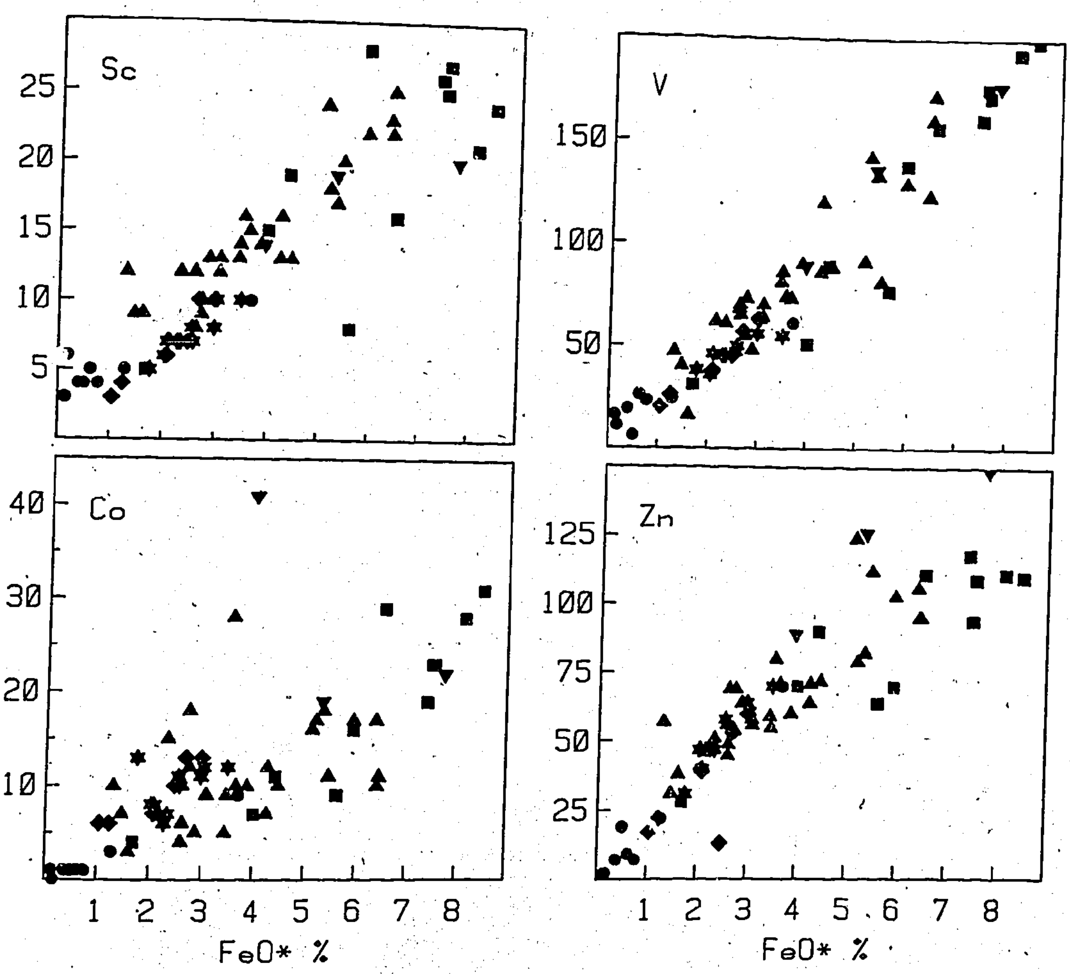


Figure 6.4 Plot of total Fe as FeO versus Sc, V, Co and Zn for graywackes. Symbols as in Figure 6.1 .

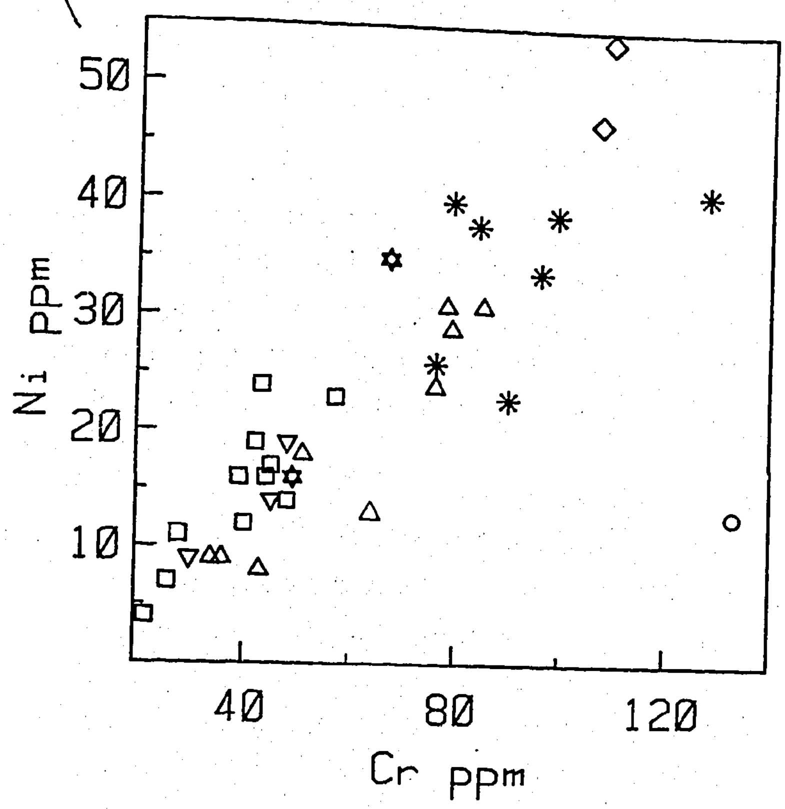


Figure 6.5 Cr versus Ni plot for mudrocks. Symbols as in Figure 6.2. * Ordovician mudrocks from the Snowy Mt. region, N.S.W. (data from Wyborn, 1977).

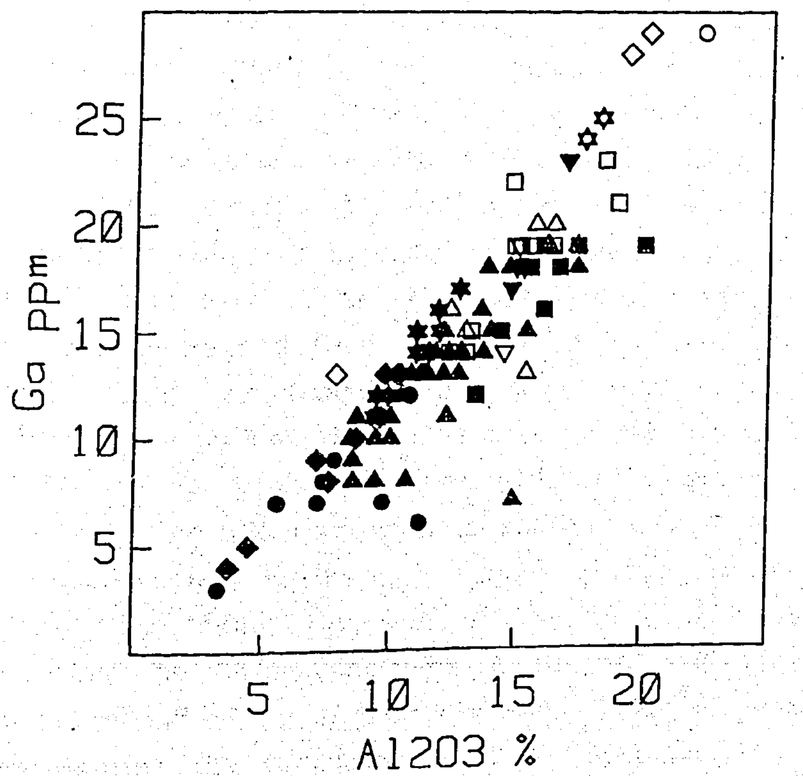


Figure 6.6 Plot of Al_2O_3 versus Ga in graywackes and mudrocks. Symbols as in Figures 6.1 and 6.2.

Gallium is exclusively concentrated in the detrital fraction consisting of alumino-silicates, and forms an isomorphous series with Al and Fe. Ga shows a near perfect linear increase with Al_2O_3 in sedimentary rocks (Figure 6.6) and in general decreases in abundance in graywackes and increases in mudrocks with increasing maturity.

6.3.3 Th-U-Zr-Nb

Elements Th, U, Zr and Nb, generally occur in accessary minerals or in the lattice sites of a variety of detrital grains. High correlation coefficients between these elements confirm their coherent behaviour in sedimentary processes (Tables 6.1 and 6.2). The exception is the lack of correlation between U and Zr in mudrocks. In general there is an increase in Th, U, Zr and Nb with the increasing maturity of graywackes (Figure 6.7). However, U can be significantly low in the highly recycled sediments, like those of the Cookman suite. Zr is significantly enriched in most Bendigo-Cookman suite samples compared to the less quartzose Hodgkinson suite graywackes. An enrichment of Th, U and Nb with increasing maturity is also observed in mudrocks, but the variation in Zr abundance is not well marked.

6.3.4 Rare Earth Elements

Elements La, Ce and Nd constitute a part of the rare earth elements (REE) and due to their large ionic radii they are called the light rare earth elements (LREE). Element Y behaves similar to Er-Ho and is thus considered to represent the heavy rare earth elements (HREE). The high correlation coefficients between La, Ce, Nd and Y confirm that these elements behave coherently in sedimentary processes (Table 6.1 and 6.2). Rare earth elements also show a high correlation with large highly charged cations (e.g. Th, U and Nb in Tables 6.2 and 6.3) indicating their occurrence with heavy accessory minerals such as zircon, monazite and apatite. The high correlation coefficients of REE with P_2O_5 and the weak correlation with CaO in mudrocks (Table 6.2) suggest that some REE may occur in apatite or organic material in fine-grained sedimentary rocks. The REE characteristics can be best understood by taking the sum of La, Ce and Nd abundances as representing the LREE concentration in the rock, and the ratio of chondrite normalised La to chondrite normalised Y [given by La_N/Y_N], as representing the enrichment of LREE over HREE. The chondrite values are adopted from Taylor and McLennan (1981a). (A full

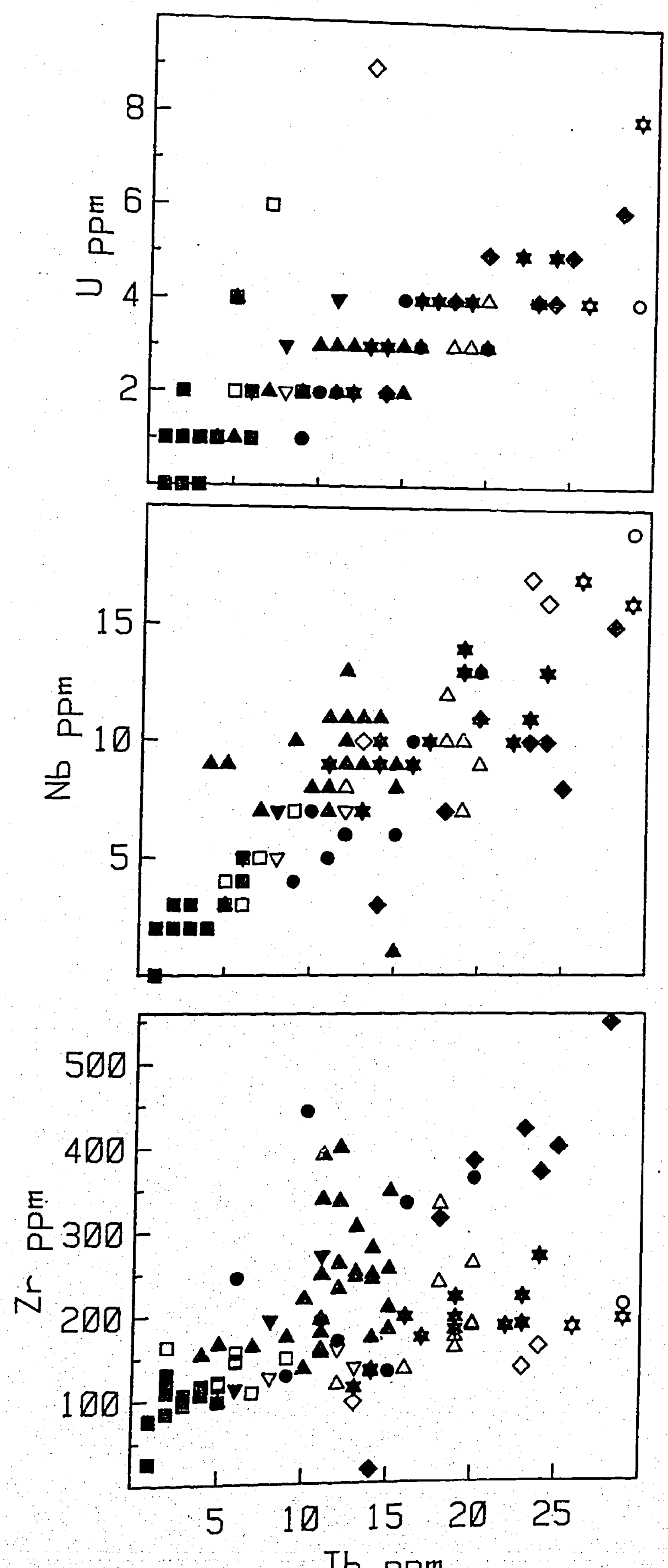


Figure 6.7 Plot of Th versus U, Nb and Zr for graywackes and mudrocks. Symbols as in Figures 6.1 and 6.2.

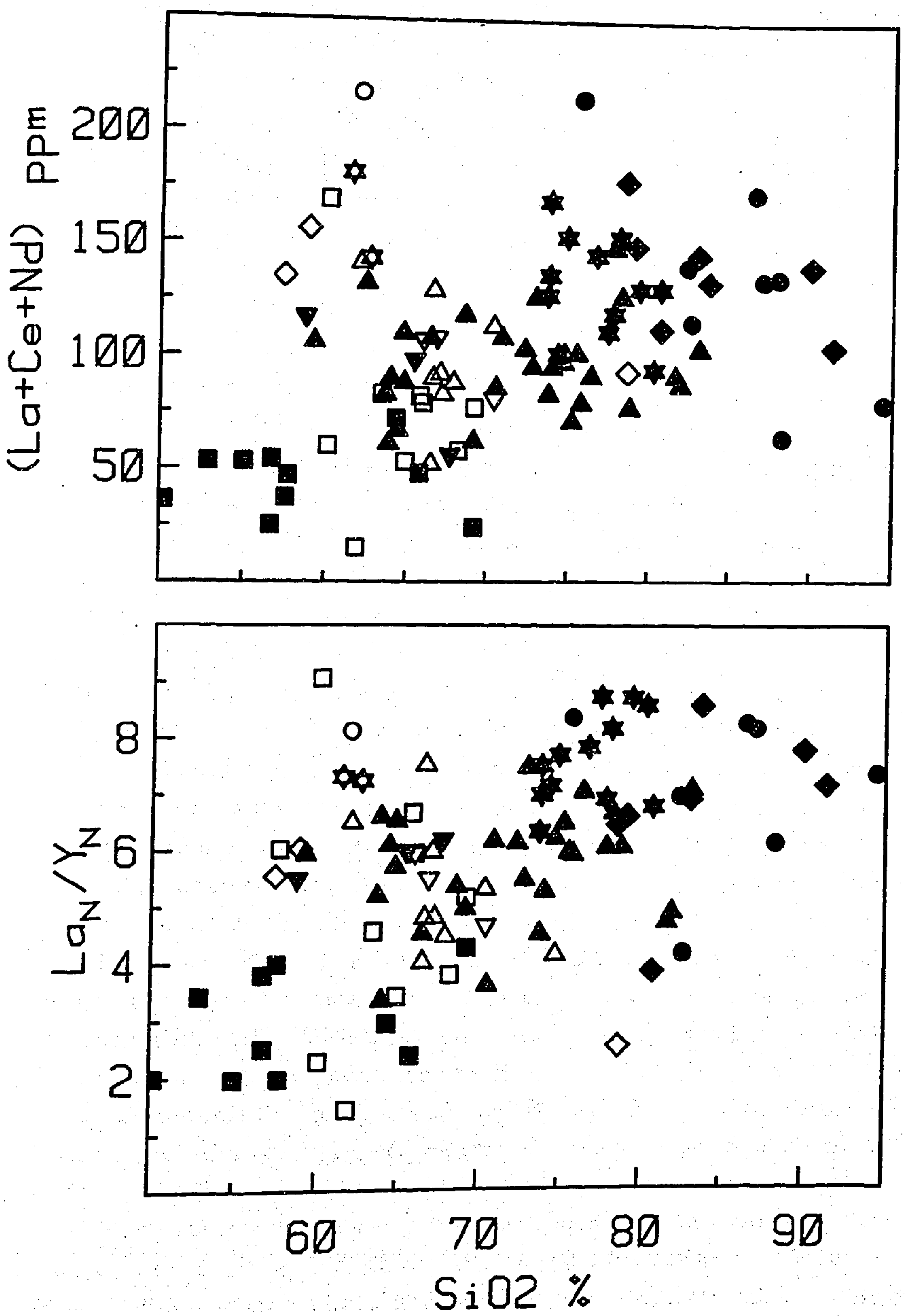


Figure 6.8 Variation in the rare earth element characteristics of graywackes and mudrocks. Plot of SiO_2 versus ΣLa+Ce+Nd, and the ratio of chondrite normalised La to chondrite normalized Y (La_N/Y_N). Symbols as in Figures 6.1 and 6.2.

discussion on the rare earth element geochemistry is given in Chapter 8). A plot of SiO_2 versus $\Sigma La + Ce + Nd$ shows a large variation of LREE in sedimentary rocks, but in general there is an overlapping increase in graywackes and mudrocks with increasing maturity (Figure 6.8). Similarly, an increase in the La_N/Y_N ratio with increasing maturity also suggests that there is a significant enrichment of LREE compared to HREE with increasing maturity in sedimentary rocks (Figure 6.8).

6.4 PETROCHEMISTRY

Mineralogy, texture and facies are attributes of the present composition of sedimentary rocks. The R-mode principal component analysis was performed to understand the relation between the geochemical, mineralogical, textural and facies variables. This approach is very useful when there are large number of variables but the results should be interpreted cautiously because, as pointed out earlier, the variable association within the factors could be due to a similar trend rather than their coherent behaviour.

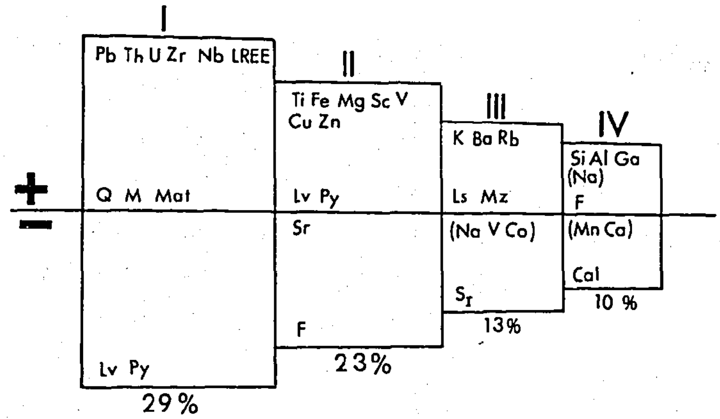
6.4.1 Graywackes

The variables used are major and trace element abundances, mineralogical (Q, F, Lv, Ls, M, Py, Cal, HM, Ep, Mat), textural (Mz, S_I) and facies (FF) parameters. The data were grouped into quartz-poor (Tamworth suite); quartz-intermediate (Hill End suite); and quartz-rich (Hodgkinson, Bendigo and Cookman suites) graywacke groups. The analysis was first performed on each graywacke group separately and then on all the samples together. The results are expressed on simplified diagrams (Figure 6.9), in which each block represents a factor of that group. Variables having positive loadings are written above the horizontal line and variables having negative loadings are written below the horizontal line.

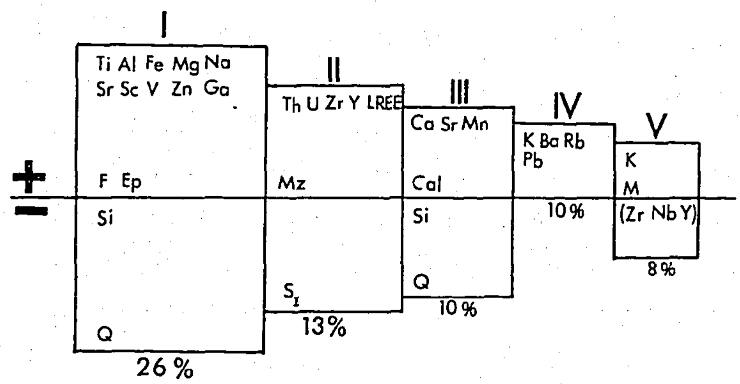
The factors of the total group explain satisfactorily the element associations and the mineralogical control of the chemical composition in all suites. The first six factors explain about 70% of the variation in the data. Factor I shows that most ferro-magnesian elements (Al, Fe, Ti, Mg, Sc, V, Co, Zn, Ga) and Na are associated with volcanic material in the form of lithic grains (Lv), pyroxene (Py) and epidote (Ep). This factor also shows that most of the silica (Si) is in the quartzose grains (Q). However quartz forms a very small component of the quartz-poor

Figure 6.9 Diagram showing the major loadings of geochemical, mineralogical and textural variables on each factor, in various graywacke suites and in the total group. Minor loadings are given in brackets. Numbers on top of each block refer to the Factor No. of the group, and numbers below the block refer to the percentage of variation explained by the factor. Variables having positive loadings are given above the horizontal line, and variables having negative loadings are given below the horizontal line.

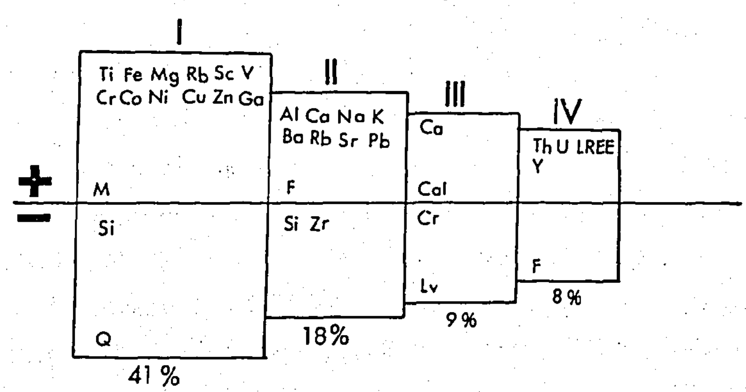
Quartz-poor Graywackes



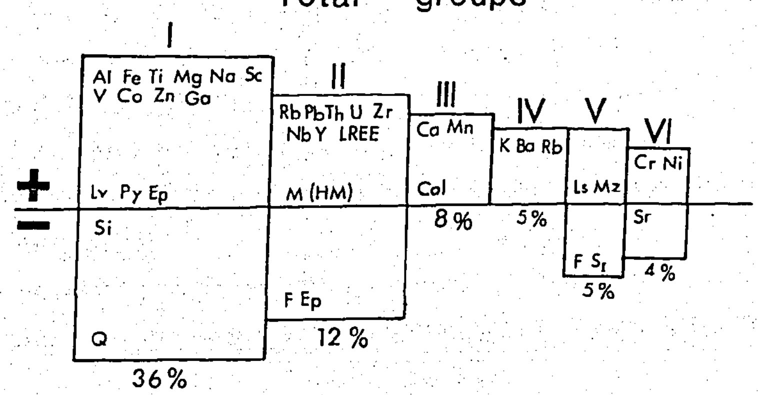
Quartz-Intermediate Graywackes



Quartz-rich Graywackes



Total groups



graywackes, and a large part of Si is in the feldspar grains, as shown by Factor IV of the quartz-poor graywackes (Figure 6.9). The group of elements and the mineralogical variables having positive and negative loadings in Factor I of the total group, represent two characteristics of graywacke composition and are mutually opposite to each other. This factor can be called a "Maturity Factor" and is equivalent to Factor II of the quartz-poor suite and Factor I of the quartz-intermediate and quartz-rich suites.

Factor II shows that the abundances of REE (La, Ce, Nd), large-ion highly charged cations (Th, U, Nb, Zr), Y, Rb and Pb are related to mica (M) and heavy minerals (HM) and are mutually opposite to the feldspar and pyroxene content of the rocks. A high feldspar (F) and pyroxene (Py) content indicates a volcanic source and the high abundance of mica (M) and heavy minerals (HM) is associated with the significant enrichment of LREE, Th, U, Zr and Nb etc., and suggests a granitic or recycled detritus. This factor can be called a "Provenance Factor" and is represented by Factor I in the quartz-poor suite, and Factors II and IV in the quartz-intermediate and quartz-rich suites, respectively.

Factor III shows the association of Ca and Mn with calcite. This association is inherited from Factor III of the quartz-intermediate and quartz-rich suites, and Factor IV of the quartz-poor suites.

Factor IV shows the coherent behaviour of large cations (K, Ba, Rb) which are mainly concentrated in K-feldspar (K-feldspar is not represented as a separate variable in this analysis). Factor V is a very small factor and explains only 5% of the variation in the data. It is termed as the "Textural Factor" and shows that the mean grain size (Mz) and the sorting index (S_I) control the feldspar and sedimentary rock fragments to some extent, but do not affect the geochemistry to any significant degree as revealed by the lack of association of the geochemical elements in this factor. Factor VI is also a very small factor, termed as a "Weathering Factor", it shows the mutually opposite behaviour of Cr and Ni versus Sr. The elements Cr and Ni are enriched due to adsorption, and Sr is depleted during weathering processes.

6.4.2 <u>Mudrocks</u>

The R-mode principal component analysis was performed to understand the relationship between geochemical, mineralogical, textural

Mudrocks

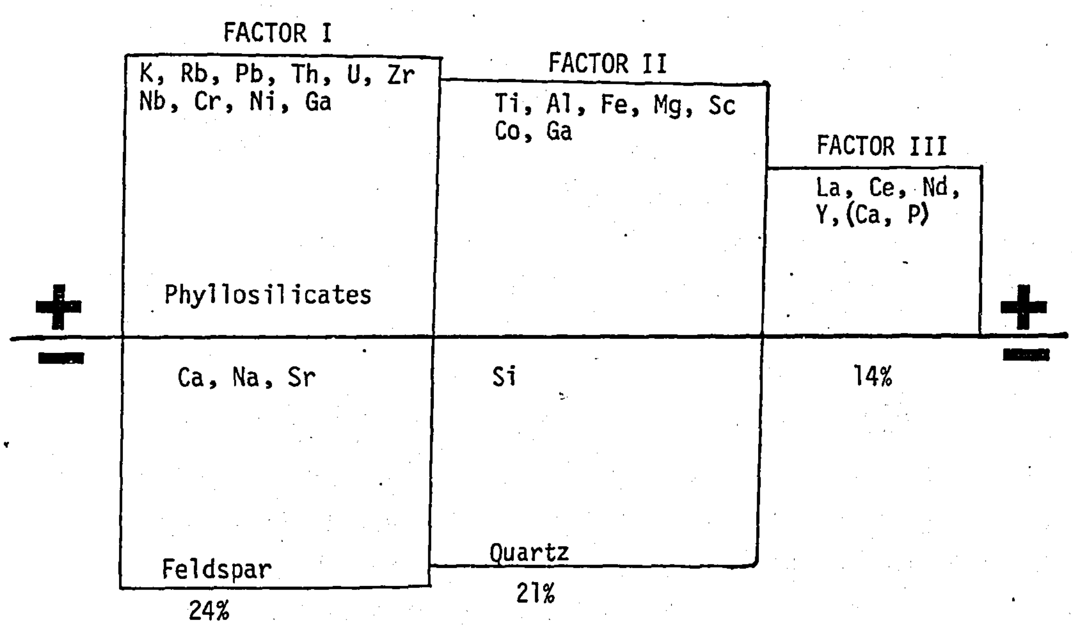


Figure 6.10 Diagram showing the major and minor (within brackets) loading of geochemical and mineralogical variables in various factors in total mudrock group. The % figure below each block represents the % variation in the data explained by the factor.

and facies variables in mudrocks. All the samples representing the various suites were run together. The assemblage is dominated by samples of the Tamworth and Hill End suites and hence the characteristics of these suites will be reflected most prominently in the total group. A large number of variables and a comparitively small number of samples render the interpretation partial. The first three factors explain only about 60% of the variation in the data (Figure 6.10).

Factor I shows the association of Rb, Pb, Th, U, Zr, Nb, Cr, Ni and Ga with phyllosilicates, and of Ca, Na and Sr with feldspars in mudrocks. The associations shown by this factor are mutually exclusive and opposite. With the increase in maturity there is an increase in phyllosilicates and an increase in large cations (K, Rb, Pb) and large highly charged cations (Th, U, Zr, Nb), Cr, Ni and Ga. The increase in maturity is accompanied by a decrease in feldspar and consequently a decrease in Ca, Na and Sr. Hence this factor can be called a "Mudrock Maturity Factor".

Factor II is equally important and has heavy loadings of most ferromagnesian elements (Ti, Fe, Al, Mg, Sc, Co, Ga) and strong negative loadings of quartz and Si. This factor is probably inherited from the Tamworth suite and suggests that some ferromagnesian elements may be associated with the unidentified volcanic component of the mudrocks. Factor III has strong positive loadings of LREE (La, Ce, Nd), Y and the minor loading of Ca and P, probably suggesting the presence of REE in the small apatite grains in mudrocks.

Many similarities are noted between the graywacke and mudrock factors. The association of Ca, Na and Sr with feldspar and Si with quartz are seen in both rock types. The abundance of large cations (K, Rb, Ba) is related to the K-feldspar and mica content in graywackes whereas in mudrocks these are associated with phyllosilicates. Rare earth elements are associated with accessory minerals in graywackes whereas in mudrocks these may be associated with small apatites which are difficult to identify. Ferromagnesian elements are associated with the volcanic component both in graywackes and mudrocks, though such material is difficult to identify in mudrocks. However, the Cr and Ni content depends on the amount of phyllosilicates present in the clastic sediments.

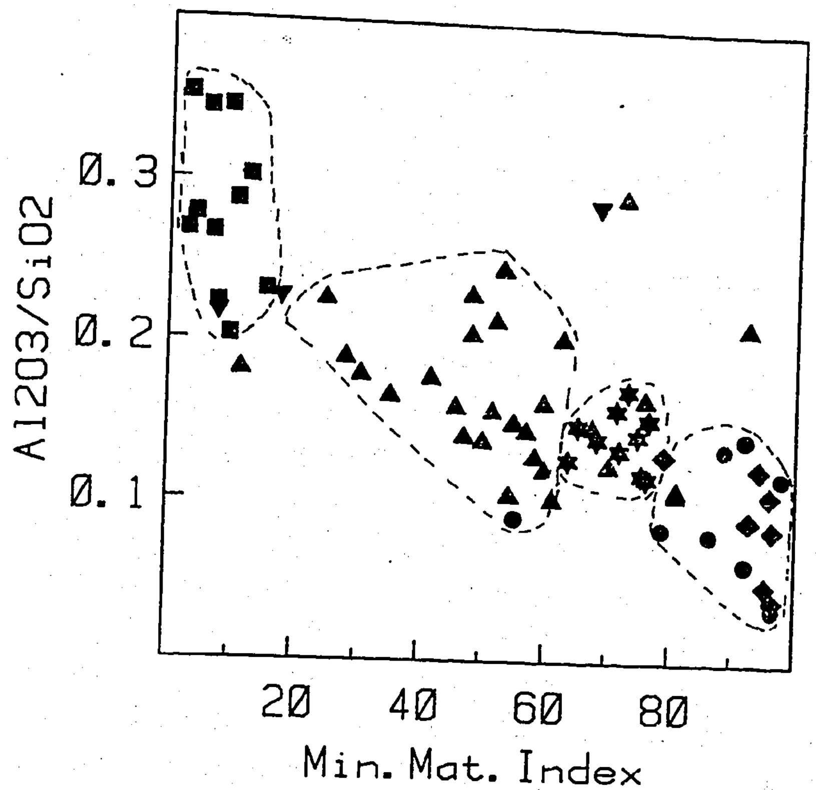


Figure 6.11a Plot of mineralogical maturity index versus Al_2O_3/SiO_2, showing the discrimination of various graywacke suites. Note the lack of discrimination between the Bendigo and Cookman suites on this plot. Symbols as in Figure 6.1.

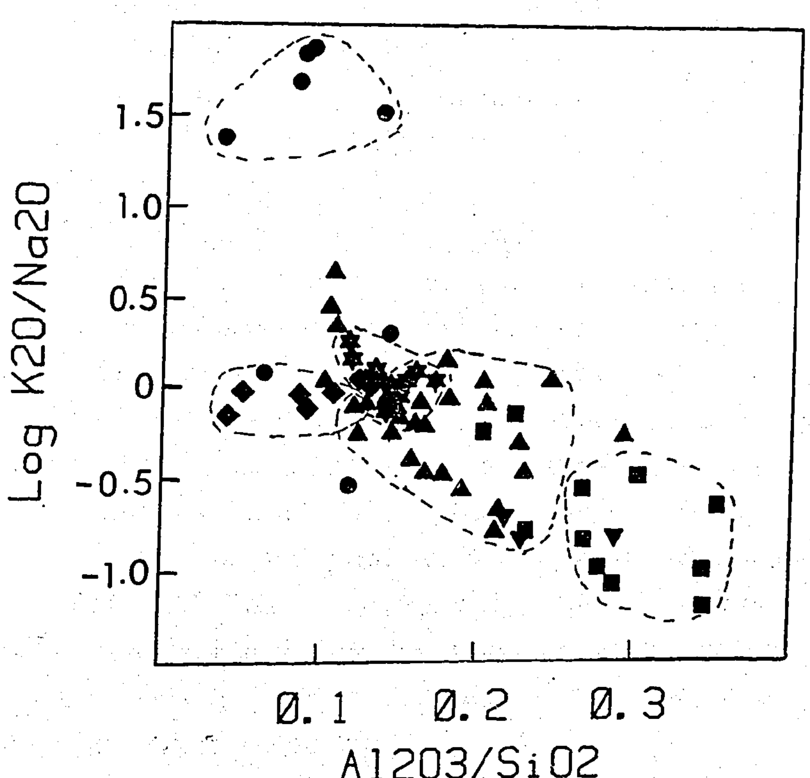


Figure 6.11b Plot as Al_2O_3 versus Log K_2O/Na_2O, showing the discrimination of various graywacke suites. Symbols as in Figure 6.1.

6.5 GEOCHEMICAL DIFFERENTIATION OF GRAYWACKE SUITES

6.5.1 Chemical Maturity Indices

Five graywacke suites have been recognised on the basis of detrital mineralogy (Chapters 3 & 4). The geochemical characteristics of the various suites are seen on the Harker variation diagrams (Figure 6.1). Particularly useful are plots of SiO_2 versus Al_2O_3, FeO^t, K_2O, Na_2O and K_2O. The Al_2O_3/SiO_2 and K_2O/Na_2O ratios are useful indicators of the maturity of sedimentary rocks. A plot of Al_2O_3/SiO_2 and the mineralogical maturity index of graywackes shows that with increasing mineralogical maturity there is a decrease in the Al_2O_3/SiO_2 ratio (Figure 6.11a). The Tamworth, Hill End, Hodgkinson and the Bendigo-Cookman suites occupy distinct fields. However the Bendigo and Cookman suites can not be discriminated from each other satisfactoraly on this plot. Similarly, a K_2O/Na_2O versus Al_2O_3/SiO_2 plot also discriminates various suites (Figure 6.11b). There is an increase in the K_2O/Na_2O ratio with the decrease in the Al_2O_3/SiO_2 ratio as the nature of the suites change from Tamworth, through Hill End, Hodgkinson to Bendigo-Cookman. The Cookman suite graywackes exhibit a large variation but in general have a higher K_2O/Na_2O ratio compared to the Bendigo suite graywackes. The geochemical distinction between the Bendigo and Cookman suite graywackes is not well marked, though the Cookman suite graywackes are slightly lower in CaO, Na_2O, MgO, FeO^t and TiO_2, indicating their more mature character.

6.5.2 Discriminant Function Analysis

The discriminant function analysis was performed using 11 major elements as variables and five graywacke suites as pre-defined groups. The standardised coefficients and related statistics for four functions are presented in Table 6.3. Discriminant Functions I and II together explain about 90% of the variation in the data and their high canonical correlation coefficients and low Wilks' lamba values signify their high discriminating power. Function I is mainly influenced by Na_2O and CaO and Function II by SiO_2, CaO and FeO. Functions III and IV explain only a small variation in the data and their low canonical correlation coefficients and high Wilks' lambda values signify their low and insignificant discriminating power, respectively.

Discriminant scores for each sample were calculated using the unstandardised discriminant coefficients for the first three functions

Table 6.3 Standardised Discriminant Function Coefficients and Related Statistics of Graywackes

	DISCRIMINANT FUNCTIONS			
	I	II	III	IV
SiO_2	-.309	-2.910	1.166	-3.610
TiO_2	-.198	.405	.337	.628
Al_2O_3	.0167	-1.171	-.502	-1.767
Fe_2O_3	-.119	-.248	-1.011	.076
FeO	.257	-1.991	-.379	-.266
MnO	-.397	.351	.419	-2.542
MgO	.089	.558	1.444	-.622
CaO	.621	-2.894	.812	-.822
Na_2O	.642	-.158	.607	-.524
K_2O	-.022	-1.271	.606	-.186
P_2O_5	.441	.425	.465	-.235
Eigenvalue	3.42	1.17	0.27	0.19
% of variation explained	67.5	23.1	5.4	3.9
Cumulative Variance	67.5	90.6	96.0	99.9
Canonical correlation	0.879	0.735	0.464	0.407
Wilks' Lambda	0.068	0.301	0.654	0.834

Table 6.4 Unstandardised Discriminant Function Coefficients used to Calculate Discriminant Scores for Graywackes

	Discriminant Functions		
	I	II	III
SiO_2	-.0447	-.421	.169
TiO_2	-.972	1.988	1.657
Al_2O_3	.008	-.526	-.226
Fe_2O_3	-.267	-.551	-2.248
FeO	.208	-1.610	-.306
MnO	-3.082	2.720	3.258
MgO	.140	.881	2.281
CaO	.195	-.907	.254
Na_2O	.719	-.177	.681
K_2O	-.032	-1.840	.878
P_2O_5	7.510	7.244	7.913
Constant	.303	43.57	-15.87

Table 6.5 Comparison Between Actual and Predicted Number of Samples in Each Graywacke Suite on the Basis of Discriminant Analysis

Group/Suite	No. of Samples	Predicted Group Membership					Percent Correctly Classified
		1	2	3	4	5	
1 Tamworth	11	11	0	0	0	0	100%
2 Hill End	29	20	2	3	1	3	69%
3 Hodgkinson	10	0	2	8	0	0	80%
4 Bendigo	7	0	0	0	7	0	100%
5 Cookman	8	0	2	0	0	6	75%

Total % of samples correctly classified = 81%

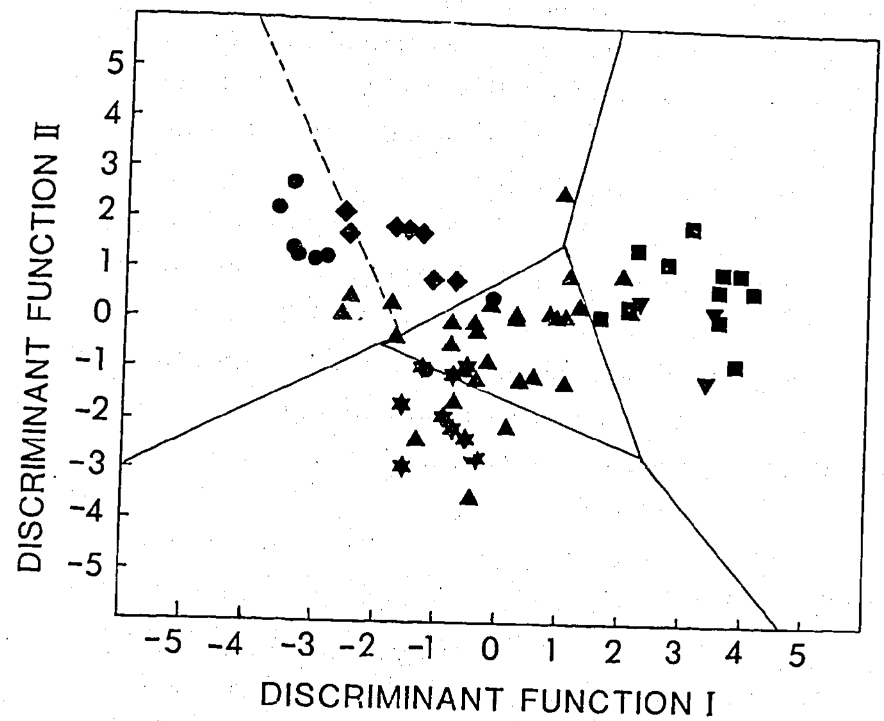


Figure 6.12 Plot of discriminant scores along Function I versus Function II, to discriminate the various graywacke suites.

- Tamworth suite
- Crow Mountain Creek Beds
- Hill End suite
- Hodgkinson suite
- Bendigo suite
- Cookman suite

(Table 6.4). A plot of scores along Function I versus Function II differentiates various graywacke suites (Figure 6.12). Function I discriminates between the Tamworth and Hill End suites and Function II discriminates between the Hodgkinson and Bendigo-Cookman suites. The close plotting of the Bendigo and Cookman suite samples indicates that the differences between these two suites are not very high and the probability of misclassification is very large. The Bendigo suite samples have only a slightly higher loading of CaO and Na_2O along Function I.

A comparison of the actual and predicted number of samples in each suite on the basis of Discriminant Functions I and II, shows that in all, 81% of the samples are correctly classified into their pre-defined groups (Table 6.5). The highest misclassification is seen in the Hill End suite, due to the mixing of volcanic and sedimentary detritus in various proportions.

6.6 GEOCHEMICAL DIFFERENTIATION OF MUDROCK SUITES

6.6.1 Geochemical Maturity Indices

The ratios K_2O/Na_2O and $Al_2O_3/(Na_2O+CaO)$ are found to be most useful in differentiating between the various mudrock suites. A plot of K_2O/Na_2O versus the mudrock maturity index (Figures 6.13) shows that there is an increase in the K_2O/Na_2O ratio with the increase in maturity and the following three groups can be identified. (1) the Tamworth suite; (2) the Hill End and Hodgkinson suites; (3) the Bendigo and Cookman suites. A similar inference can also be drawn from a triangular plot of CaO-Na_2O-K_2O, on which the Tamworth; Hill End-Hodgkinson; and Bendigo-Cookman groups can be related to the tectic, phyllo-tectic, and phyllic type mudrocks, respectively (Figure 6.14). The increase in K_2O (and also in Al_2O_3) is due to the enrichment of phyllosilicates, and the depletion of Na_2O and CaO is due to the loss of feldspar with increasing maturity in mudrocks.

6.6.2 Discriminant Function Analysis

The discriminant analysis was performed using the major elements as variables. However, P_2O_5 was left out in the analysis due to its extremely high Wilks' lamba and its low discriminating power. As there is only one sample of the Cookman suite, it was grouped with the Bendigo suite, thus in all, 4 groups of mudrocks were pre-defined. The standardised discriminant function coefficients along with related

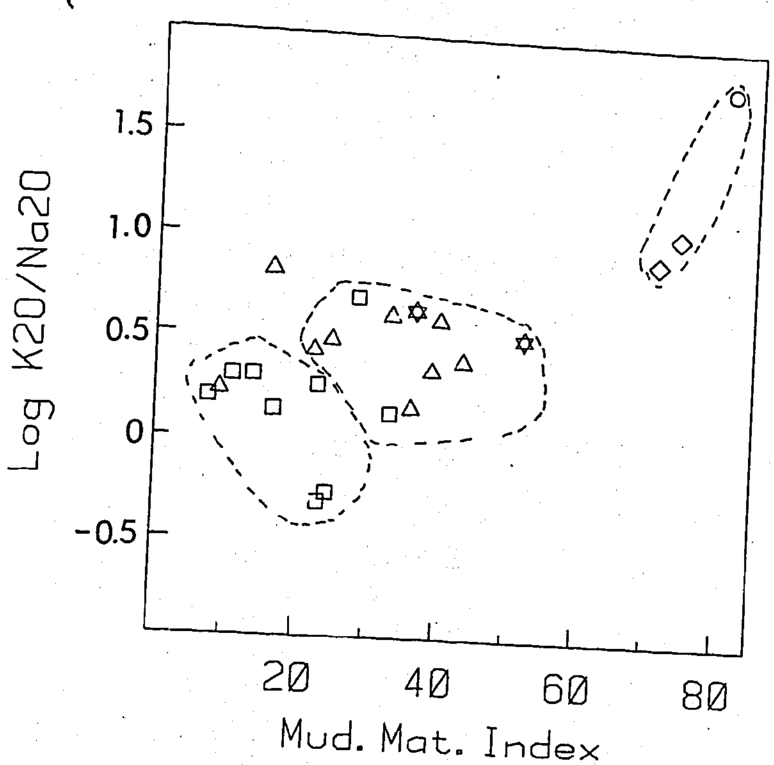


Figure 6.13 Plot of the mudrock maturity index versus Log K_2O/Na_2O, for the discrimination of various mudrock suites. Note that there are 3 major mudrock groups.

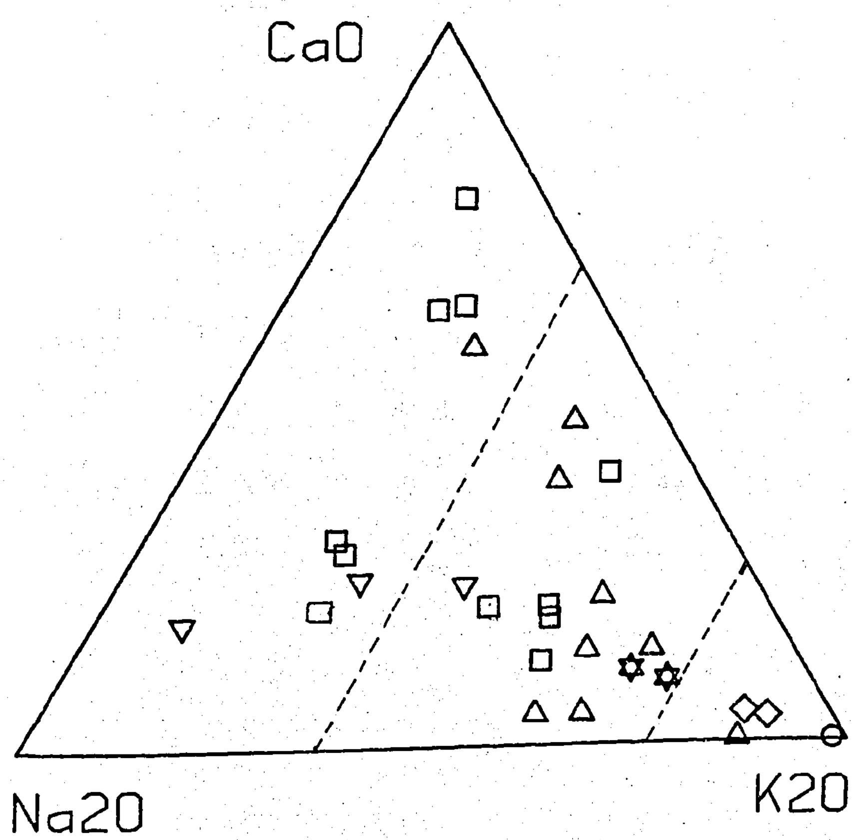


Figure 6.14 CaO-Na_2O-K_2O plot to discriminate the mudrock suites. Note the three broad mudrock groups. Symbols as in Figure 6.2.

Table 6.6 Standardised Discriminant Function Coefficients and Related Statistics for Mudrocks

	Discriminant Functions		
	I	II	III
SiO_2	-1.680	-4.234	-2.414
TiO_2	-1.203	0.582	-0.315
Al_2O_3	2.336	-2.533	-0.979
Fe_2O_3	-0.822	-2.343	0.343
FeO	-1.128	-2.006	2.033
MnO	1.820	-0.671	-0.732
MgO	1.589	0.224	-2.388
CaO	0.669	-2.498	-1.835
Na_2O	-1.241	-0.602	-0.497
K_2O	0.411	-0.760	-0.252
Eigenvalue	4.803	2.407	0.575
% of variation explained	61.7	30.9	7.4
Cumulative variation	61.7	92.6	100
Canonical Correlation	0.909	0.841	0.604
Wilks' Lambda	0.032	0.186	0.635

Table 6.7 Unstandardised Discriminant Function Coefficients Used to Calculate Discriminant Scores for Mudrocks

	Discriminant Functions	
	I	II
SiO_2	0.273	-0.687
TiO_2	-9.628	4.663
Al_2O_3	0.579	-0.628
Fe_2O_3	-0.567	-1.616
FeO	-0.664	-1.180
MnO	17.99	-6.628
MgO	1.985	0.280
CaO	0.285	-1.066
Na_2O	-1.074	-0.521
K_2O	0.323	-0.598
Constant	-22.01	62.61

Table 6.8 Comparison Between Actual and Predicted Number of Samples in Mudrock Suites, on the Basis of Discriminant Analysis

Group/Suite	No. of Samples	Predicted Group Membership				Percent Correctly Classified
		1	2	3	4	
1 Tamworth	9	7	-	2	-	78%
2 Hill End	9	-	7	2	-	78%
3 Hodgkinson	2	-	-	2	-	100%
4 Bendigo-Cookman	3	-	-	-	3	100%

Total % of samples correctly classified = 89%

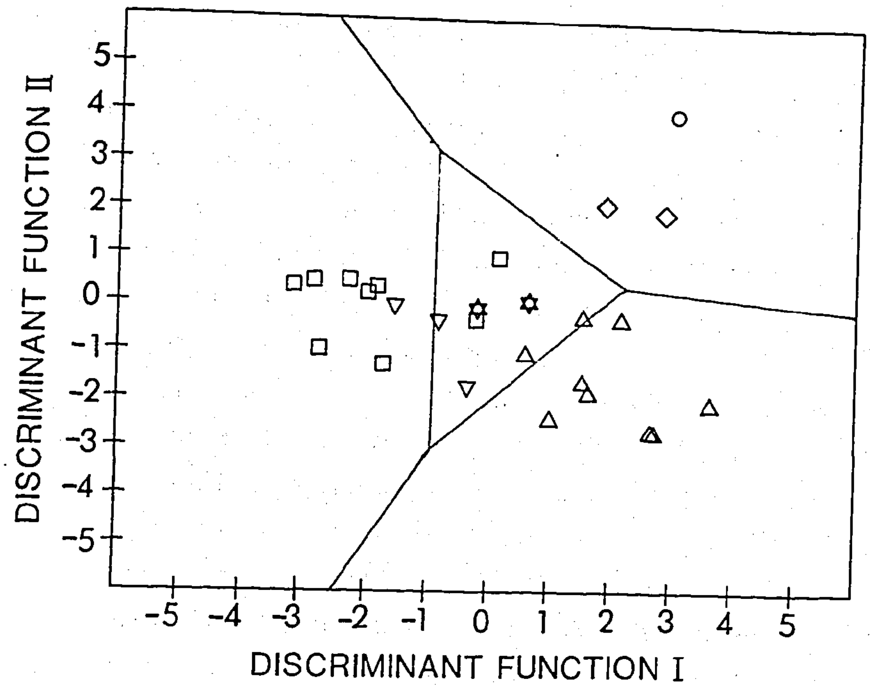


Figure 6.15 Plot of discriminant scores along Function I versus II, to discriminate the various mudrock suites.

□ Tamworth suite
▽ Crow Mountain Creek Beds
△ Hill End suite
✡ Hodgkinson suite
◇ Bendigo suite
○ Cookman suite

statistics are given in Table 6.6. Discriminant Functions I and II together explain about 93% of the variation in the data. The high canonical correlation coefficients and the low Wilks' lambda values signify their high discriminating power. Discriminant Function III explains only 7% of the variation in the data and has negligible discriminating power.

The discriminant scores were calculated using the unstandardised discriminant coefficients given in Table 6.7. The plot of discriminant scores along Function I versus Function II shows the grouping of the data (Figure 6.15). Function I discriminates the Tamworth and the Hill End-Hodgkinson suites. Function II discriminates the Bendigo-Cookman suite samples from the Hodgkinson-Hill End suites. The discriminant functions correctly classify 89% of the samples into pre-defined groups (Table 6.8). The discrimination between the Hill End and Hodgkinson suites, is not well established due to the extremely small data set. Thus on the basis of discriminant analysis, three broad groups of mudrock suites (i.e. Tamworth; Hill End-Hodgkinson; Bendigo-Cookman), can be established. This is in agreement with the discrimination of various mudrock suites on the basis of chemical and mineralogical maturity indices.

6.7 BULK COMPOSITIONS OF SEDIMENTARY AND COMMON IGNEOUS ROCKS

In this section, the major element compositions of graywackes and mudrocks are compared with the average compositions of common igneous rocks (andesite-dacite-granodiorite-granite). A plot of SiO_2 versus Fe_2O_3+FeO+MgO+CaO+Na_2O shows a larger variation in the composition of graywackes compared to the more restricted variation in the mudrock compositions (Figure 6.16). There is an increase in SiO_2 and a decrease in Fe_2O_3+FeO+MgO+CaO+Na_2O from the Tamworth through the Hill End, Hodgkinson, Bendigo to the Cookman suite graywackes. This variation is parallel to the trend from mafic to felsic seen from andesite through dacite, granodiorite to granite. A less restricted but an almost opposite trend is seen in the case of mudrocks from the Hill End through the Hodgkinson to Bendigo suites. The Tamworth suite mudrocks show wider variation in the major element geochemistry due to the presence of biogenic silica and volcanic glass. The composition of the Tamworth suite graywackes is close to the average andesite. The Hill End suite

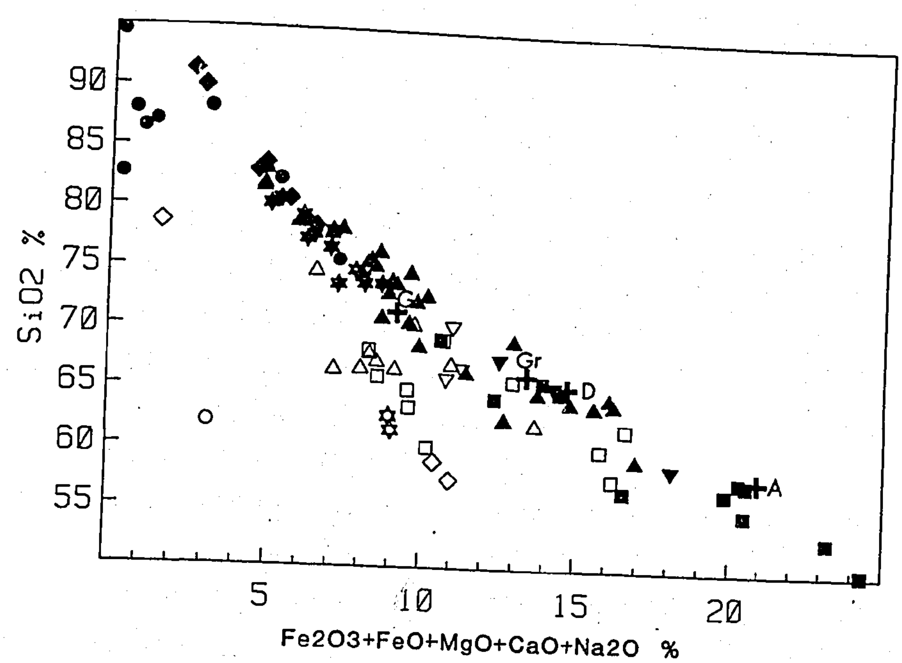


Figure 6.16 Plot of SiO_2 versus Fe_2O_3+FeO+MgO+CaO+Na_2O for graywackes and mudrocks. The averages of andesite (A), dacite (D), granodiorite (Gr), and granite (G) from Le Maitre (1976), are also plotted. Symbols as in Figures 6.1 and 6.2.

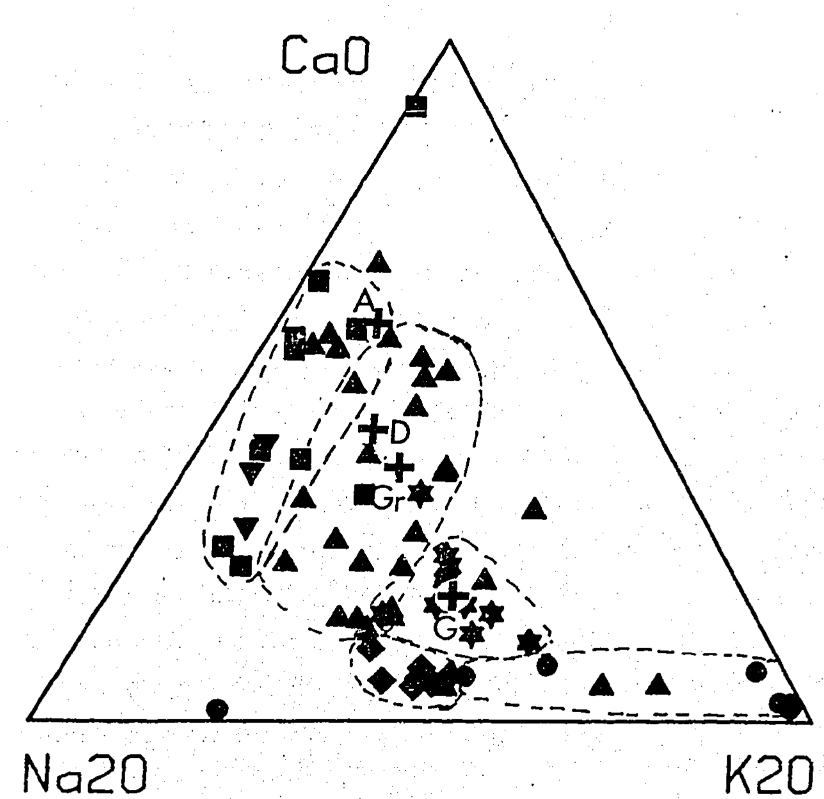


Figure 6.17 CaO-Na_2O-K_2O plot for graywackes. Also plotted are the averages of andesite (A), dacite (D), granodiorite (Gr), and granite (G) after Le Maitre (1976). Dotted lines mark the broad fields of various graywacke suites. Symbols as in Figure 6.1.

graywackes range in composition from average dacite to average granite. The Hodgkinson, Bendigo and Cookman suite graywackes are progressively enriched in SiO_2 and depleted in Fe_2O_3+FeO+MgO+CaO+Na_2O compared to the average granite, indicating their increasing maturity and geochemical fractionation.

A triangular plot of CaO-Na_2O-K_2O also shows the affinity of the compositions of graywackes and common igneous rocks (Figure 6.17). However, the mudrock compositions are far removed from common igneous rocks, as can be seen by a comparison of Figure 6.14 and 6.17. The Tamworth suite graywackes are slightly enriched in Na_2O compared to the average andesite. The Hill End suite samples plot around the average dacite and average granodiorite. The Hodgkinson suite samples plot around the average granite. The Bendigo suite samples also plot close to the average granite, but are slightly depleted in CaO and Na_2O. The Cookman suite graywackes are significantly enriched in K_2O and depleted in CaO and Na_2O compared to the average granite, confirming their matured nature.

6.8 GEOCHEMICAL COMPARISON OF AVERAGE SEDIMENTARY SUITE AND SOURCE ROCK COMPOSITIONS

The geochemical composition of sedimentary rocks is a function of source rocks and modifications of elements during weathering, transportation and diagenesis. Graywackes and mudrocks constitute the dominant lithologies of flysch sequences. It has been noted that the "average graywacke" composition is depleted by a factor of $\cong 0.8$ and the "average shale" is enriched by a factor of $\cong 1.2$ compared to the average magmatic rock (Wedepohl, 1968). A direct comparison of the average graywacke and the average mudrock compositions within each suite, and between the average sedimentary suite and source rock compositions, will help in understanding the behaviour of elements during sedimentary processes and the redistribution of elements in clastic sediments. However, uncertainty of the source terrain or inadequate data on source rock compositions can hinder such a comparison.

The average suite composition has been calculated by taking the average graywacke and mudrock compositions in a 1:1 proportion. This is the unweighted average composition of the suite and may not necessarily represent the average composition of the sedimentary basin (see Chapter 9). The average compositions are compared using log-log plots (Figures 6.18 to 6.22). An example is Figure 6.18a, on which the average graywacke composition is plotted along the X-axis and the average mudrock composition along the Y-axis. Thus, if an element has the same abundance it will fall on the diagonal line. Elements falling above the diagonal line are enriched in mudrock, whereas elements falling below the diagonal line are enriched in graywacke. A difference in composition by a factor of 1.2 is generally not considered significant in these comparisons.

6.8.1 Tamworth Suite

The Tamworth suite mudrocks contain common biogenic silica, this reflected in their high SiO_2 content. It is observed that in most suites, compared to the associated graywackes the mudrocks are depleted in SiO_2 and Na_2O. In order to obtain a more realistic average of the clastic fraction of mudrocks, the major element composition was recalculated by taking SiO_2 at 59.22% (graywacke value) and Na_2O at 2.78% (mudrock value) (Table 6.9).

A comparison of the average graywacke with the recalculated mudrock compositions reveals that graywackes are enriched in CaO, Na_2O, and Sr, and depleted in K_2O, Ba and Rb by a factor of 2 (Figure 6.18a,b). Al_2O_3, FeO^t, MgO, TiO_2, P_2O_5, Zn, Cr, Y, Ga and Sc occur in almost equal proportions in the two lithologies. The enrichment of Na_2O, CaO and Sr is due to the presence of more plagioclase in graywackes, whereas the significant enrichment of K, Rb, Ba, LREE (La, Ce, Nd) and large-highly charged cations (Th, U, Zr, Nb) is due to the enrichment of phyllosilicates during sedimentation.

The average Tamworth suite composition is similar to various estimates of the average andesite (Jakes and White, 1971; Le Maitre, 1976; Taylor, 1979; Table 6.9). A plot of the average Tamworth suite sample versus the average andesite of Taylor (1979) shows a tendency for most major elements to lie along the diagonal line indicating a strong similarity between the two (Figure 6.18c,d). K_2O and Ba are slightly enriched in the sedimentary rocks, probably due to the adsorption of these elements on phyllosilicates during weathering. Elements Th, La, Ce, Nd, Ni, Co, Cu and Co are slightly higher in the average andesite, however, the most significant difference between the two compositions is

Table 6.9 Compositions of Average Tamworth Suite Sedimentary Rocks and Average Andesites

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
SiO_2	55.79	62.40	63.98	67.76	59.22	59.22	59.22	58.52	58.78	58.0
TiO_2	0.81	0.73	0.89	0.58	0.87	0.97	0.92	0.88	0.84	0.8
Al_2O_3	15.37	15.23	15.53	14.91	16.37	20.13	18.27	17.19	15.58	18.0
Fe_2O_3	1.59	2.96	1.21	0.95	1.73	3.92	2.82	3.30	2.63	-
FeO	4.69	2.59	4.58	3.29	5.02	3.42	4.22	4.08	5.04	7.5*
MnO	0.22	0.08	0.11	0.06	0.26	0.10	0.18	0.14	0.11	-
MgO	2.57	2.06	1.84	1.56	2.74	2.71	2.73	3.36	4.57	3.5
CaO	6.65	2.59	2.85	1.49	7.62	3.46	5.54	6.86	8.02	7.5
Na_2O	4.49	2.16	4.46	3.74	4.78	2.78	3.78	3.51	3.39	3.5
K_2O	1.10	2.34	0.76	1.87	1.16	3.10	2.13	1.64	0.82	1.5
P_2O_5	0.18	0.13	0.24	0.13	0.18	0.17	0.18	0.21	0.22	-
S	0.36	0.14	0.09	0.04						
H_2O^+	2.55	3.52	2.06	2.52						
H_2O^-	0.42	1.24	0.39	0.24						
CO_2	2.88	1.78	0.52	0.74						
Ba	370	692	280	330			531		145	350
Rb	18	67	17	76			43		12	42
Sr	637	287	888	408			462		230	400
Pb	7	8.1	14	16			7.5		-	7
Th	2.27	5.5	8.33	11			3.89		0.8	4.8
U	1.10	2.4	3.0	2.3			1.75		0.4	1.25
Zr	96	130	194	141			113		80	100
Nb	2	3.7	7	6.3			2.8		-	11
Y	20	22	20	24			21		-	22
La	9	18	20	23			14		3.8	19
Ce	22	37	49	54			30		-	38
Nd	11	19	21	22			15		-	16
Sc	19	20	18	14			19		-	30
V	131	159	134	97			145		195	175
Cr	38	39	25	41			38		30	55
Co	18	15	27	13			17		-	25
Ni	11	15	12	14			13		22	20
Cu	23	44	13	27			34		-	60
Zn	89	104	121	93			97		-	-
Ga	17	19	19	17			18		-	18

* Total Fe as FeO

(1) Average Tamworth Suite graywacke (excluding Crow Mountain Creek Beds), (11 samples).
(2) Average Tamworth Suite mudrock (excluding Crow Mountain Creek Beds), (9 samples).
(3) Average Crow Mountain Creek bed graywacke (3 samples).
(4) Average Crow Mountain Creek bed mudrock (3 samples).
(5) Volatile free basis (1)
(6) Volatile free basis (2) recalculated at SiO_2 55.79% and Na_2O 2.16%.
(7) Average Tamworth suite composition (1:1 = Graywacke : Mudrock).
(8) Average andesite (Le Maitre, 1976).
(9) Developed Island Arc (Jakes and White, 1972).
(10) Average andesite (Taylor, 1979).

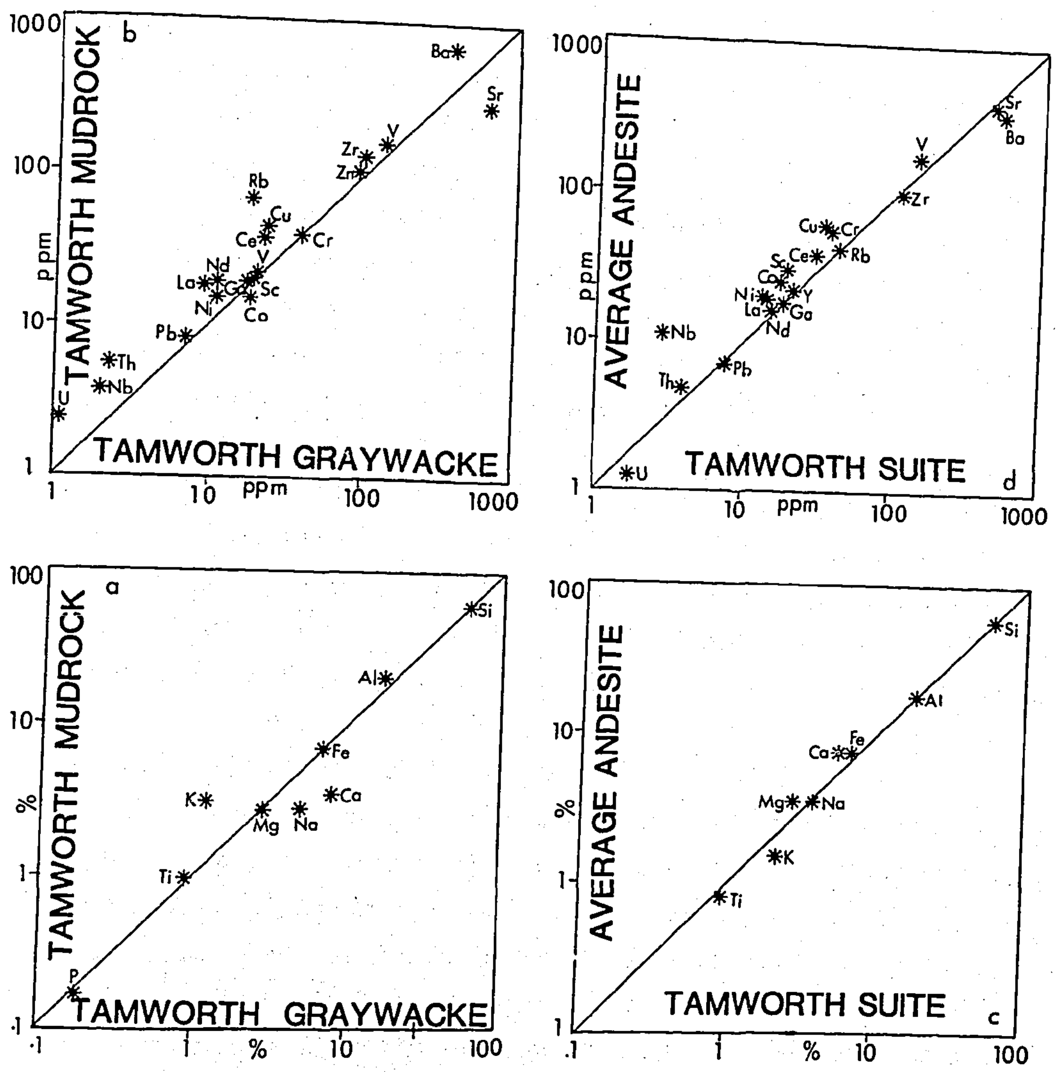


Figure 6.18 Comparison of the compositions of
(a,b): the average graywacke and mudrock of the Tamworth suite.
(c,d): the average Tamworth suite and the average andesite of Taylor (1979).

Note in Figures 6.18-6.22, major elements are plotted as oxides and total Fe as FeO.

seen for Nb. The average Nb content in the Tamworth suite is 2.8 ppm and is significantly low compared to 11 ppm Nb in the average andesite (Whitford, 1975; Taylor, 1979). Nb shows a large variation in its abundance in magmatic rocks (Johnson and Arculus, 1978), however, a low value of 4 ppm Nb has been reported in the andesites of the Bagana volcanics, Papua New Guinea (Bultitude et al. 1978). (This aspect is further discussed in Chapter 9).

The average Crow Mountain Creek beds are significantly high in SiO_2, Pb, Th, U, Zr, Nb and REE and low in TiO_2, Al_2O_3, FeO^t, MnO, MgO, CaO and Na_2O compared to the average Tamworth suite composition (Table 6.9). On the other hand, there is a close similarity in the Crow Mountain Creek bed and Hill End suite compositions, thus suggesting a substantial contribution from a felsic volcanic source.

6.8.2 Hill End Suite

An overall chemical similarity is seen between the average graywacke and the average mudrock of the Hill End suite (Table 6.10; Figure 6.19a,b). However graywackes are enriched in CaO, Na_2O, Sr and Zr due to the enrichment of feldspar and zircon, and the mudrocks are enriched in K_2O, Al_2O_3, Ba and Rb due to the enrichment of phyllosilicates and mica.

The average source rock composition of the Hill End suite is difficult to estimate because the volcanic rocks which supplied the detritus have now completely vanished. Compared to the average dacite (Le Maitre, 1976), the average Hill End suite composition is high in SiO_2 and low in Al_2O_3, CaO and Na_2O, but there is a close similarity between the two in TiO_2, FeO^t, MgO and to some extent in the K_2O content (Table 6.10). A remarkable similarity between the average Hill End suite and the average Silurian Goobarragandra dacite of New South Wales (Wyborn et al. 1981) can be observed particularly in the FeO^t, Al_2O_3, TiO_2, MgO, SiO_2, La, Nb, U, Ga, V and Rb content (Figure 6.19c,d). The most conspicuous difference is that the average Goobarragandra dacite is higher in Pb by a factor of 1.7 and the average Hill End suite composition is higher in Cr by a factor of 2.5. The high enrichment of Cr and to a lesser extent of Ni, Cu and Zn in the Hill End suite could be either due to the adsortion of these elements on phyllosilicates or due to the inheritance of phyllosilicates rich in Cr, Ni, Cu & Zn.

Table 6.10 Compositions of Average Hill End Suite Sedimentary Rocks and Average Source Rocks*

	(1)	(2)	(3)	(4)	(5)
SiO_2	74.38	70.33	72.38	65.66	71.13
TiO_2	0.66	0.54	0.60	0.59	0.56
Al_2O_3	12.25	15.61	13.92	16.07	13.89
Fe_2O_3	1.04	1.96	1.50	2.45	0.96
FeO	2.96	2.45	2.70	2.32	3.14
MnO	0.08	0.06	0.07	0.09	0.05
MgO	1.49	1.68	1.58	1.80	1.57
CaO	2.66	1.78	2.21	4.36	2.57
Na_2O	2.52	1.55	2.04	3.82	2.88
K_2O	1.82	3.91	2.87	2.19	3.07
P_2O_5	0.12	0.11	0.11	0.92	0.17
Ba	461	841	651		560
Rb	72	160	116		122
Sr	184	122	153		149
Pb	15	20	17.5		31.0
Th	11	18	14.5		17.4
U	3.0	3.4	3.2		3.2
Zr	233	199	216		191
Nb	9	9.8	9.4		9
Y	25	28	27		32
La	25	25	25		28
Ce	50	52	51		66
Nd	21	21	21		-
Sc	15	14	14		12
V	85	79	83		78
Cr	53	60	57		22
Co	11	10	11		-
Ni	13	19	16		13
Cu	11	17	14		11
Zn	69	82	76		60
Ga	13	17	15		16.2

* All averages recalculated on volatile free basis.
(1) Average Hill End suite graywacke, (29 samples).
(2) Average Hill End suite mudrock, (9 samples).
(3) Average Hill End suite composition (1:1 = 1 Graywackes : Mudrock).
(4) Average dacite (Le Maitre, 1976).
(5) Average Goobarragandra suite dacite, N.S.W. (Wyborn et al. 1981).

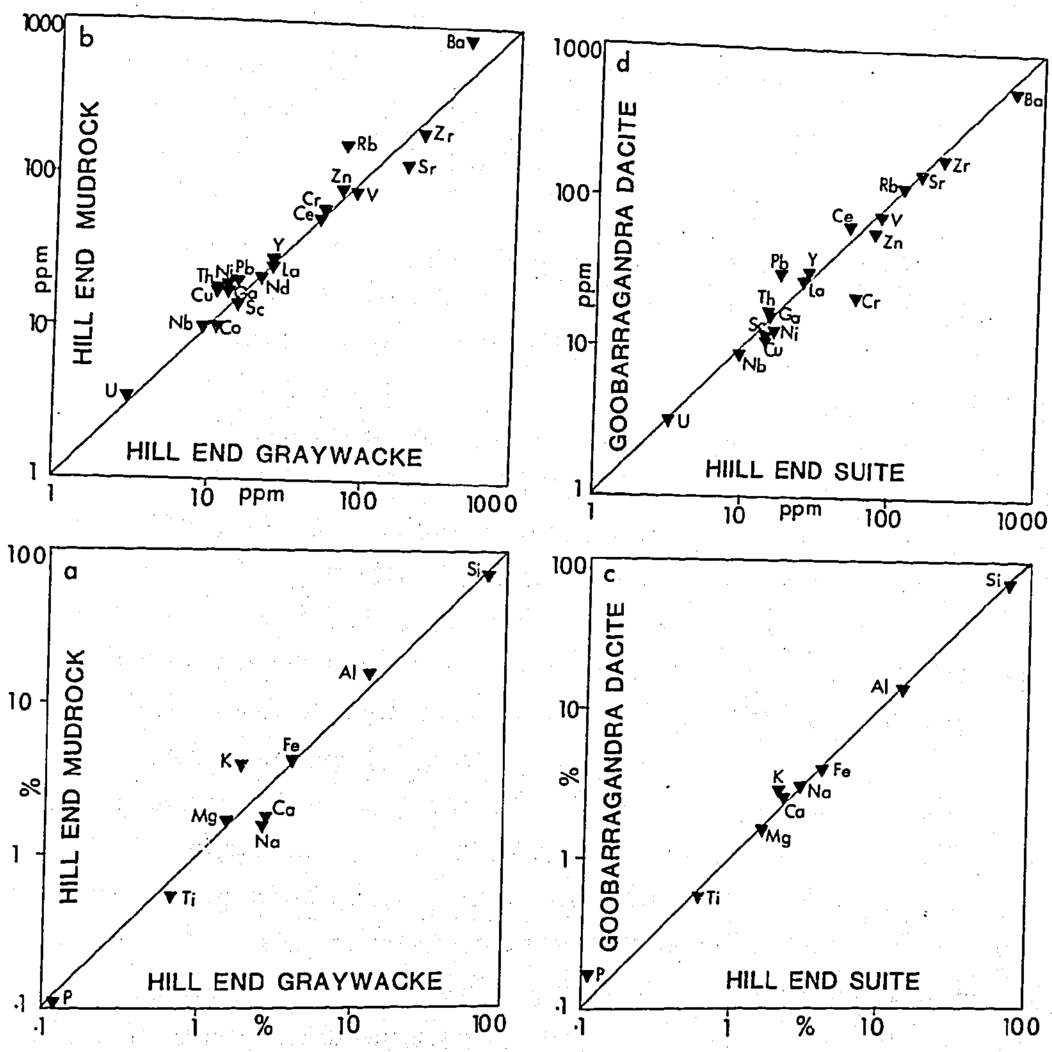


Figure 6.19 Comparison of the compositions of
(a,b): the average graywacke and mudrock of the Hill End suite.
(c,d): the average Hill End suite and the average Goobarragandra dacite, N.S.W. (Wyborn et al., 1981).

6.8.3 Hodgkinson Suite

A large difference is noticed in the average chemical compositions of graywackes and mudrocks of the Hodgkinson suite (Figure 6.20a,b). The graywackes are significantly high in SiO_2, Na_2O , CaO and Sr due to the enrichment of quartz and feldspar, and the mudrocks are high in Al_2O_3, FeO^t, MgO, K_2O and most trace elements due to abundant phyllosilicates. Elements Pb, Sc, V, Cr, Ni, and Zn show enrichment in mudrocks upto a factor of 2 whereas Th, U, Zr, Nb, Co and La show slight enrichment.

The average major element composition of the Hodgkinson suite is close to the average granodiorite (Le Maitre, 1976) and the average I- and S-type granitoids of the Lachlan Fold Belt, except for CaO and Na_2O which are significantly low in the sedimentary average (Table 6.11). The Precambrian Georgetown igneous rocks have been inferred to constitute the source rocks of the Hodgkinson sediments. A rough estimate of the bulk composition of the igneous rocks of the Georgetown area has been made by taking the mean of the averages of the Esmeralda, Forsyth and Robin Hood granites from Sheraton and Labonne (1978).

A geochemical comparison of the average Hodgkinson suite and the average Georgetown igneous rock reveals a close similarity between the two, particularly for the SiO_2, Al_2O_3, FeO^t, La, Ce, Nd, Y, V, Rb, Ni and Co content, (Figure 6.20c,d). The average Hodgkinson suite composition is significantly low in Na_2O, CaO and Sr, due to the loss of plagioclase during weathering, and is enriched in TiO_2, MgO, Cu and Zn, probably due to some contribution from volcanic sources. The slightly high Zr content in the sedimentary rocks is due to the enrichment of zircon grains during sedimentation.

6.8.4 Bendigo Suite

A wide difference was noted between the average graywacke and mudrock compositions of the Bendigo suite (Figure 6.21a,b; Table 6.12). Graywackes are significantly rich in SiO_2, Na_2O and Zr due to the abundance of quartz, feldspar and zircon grains, and the mudrocks are significantly high in Al_2O_3, FeO^t, K_2O, MgO, TiO_2 and most ferromagnesian and large cations due to the high abundance of phyllosilicates. The light rare earth elements (La, Ce, Nd), Y, Th and U show a remarkable similarity in the two lithologies.

Table 6.11 Compositions of the Average Hodgkinson Suite Sedimentary Rocks and Average Source Rocks

	(1)	(2)	(3)	(4)	(5)	(6)	(7)
SiO_2	78.55	66.20	72.23	66.75	68.13	69.18	70.80
TiO_2	0.45	0.66	0.55	0.55	0.44	0.53	0.34
Al_2O_3	11.08	19.11	14.94	15.90	14.47	14.23	14.74
Fe_2O_3	0.64	3.42	2.00	1.39	1.24	0.76	0.75
FeO	2.00	2.63	2.31	2.76	2.57	3.15	2.71
MnO	0.05	0.04	0.04	0.08	0.08	0.06	0.05
MgO	0.93	1.71	1.31	1.76	1.76	1.83	0.95
CaO	1.19	0.59	0.89	3.87	3.75	2.58	2.33
Na_2O	2.32	1.18	1.76	3.79	2.94	2.24	3.46
K_2O	2.71	4.33	3.49	2.76	3.04	3.60	3.72
P_2O_5	0.08	0.12	0.10	0.18	0.11	0.13	0.13
Ba	522	661	591		494	480	800
Rb	115	217	166		133	177	176
Sr	141	80	110		244	140	449
Pb	24	24	24		16	27	31
Th	19	28	24		16	19	17
U	3.9	6	4.9		3	3	4
Zr	180	189	185		142	167	147
Nb	11	16	14		9	11	10*
Y	25	33	29		28	32	24
La	33	42	38		28	31	34
Ce	73	87	80		63	69	64
Nd	25	33	29		23	25	24*
Sc	7	17	12		15	15	15*
V	48	100	74		73	73	73*
Cr	25	58	41.5		28	46	37*
Co	10	16	13		12	13	12
Ni	10	25	17.5		9	17	13*
Cu	8	42	25		11	11	11*
Zn	52	111	82		51	62	52
Ga	14	24	19		16	17	19

* Data not available for Georgetown Igneous rocks. Mean of I- & S-type granitoids.
(1) Average Hodgkinson suite graywacke, volatile free, (10 samples).
(2) Average Hodgkinson suite mudrock, volatile free, (2 samples).
(3) Average Hodgkinson suite composition (1 graywackes : 1 mudrock).
(4) Average granodiorite (Le Maitre, 1976).
(5) Average of 455 I-type granitoid, Lachlan Fold Belt (B.W. Chappell, per. comm.).
(6) Average of 243 S-type granitoid, Lachland Fold Belt (B.W. Chappell, per comm.).
(7) Average composition of igneous rocks of the Georgetown Massif, volatile free (Sheraton and Labonne, 1978).

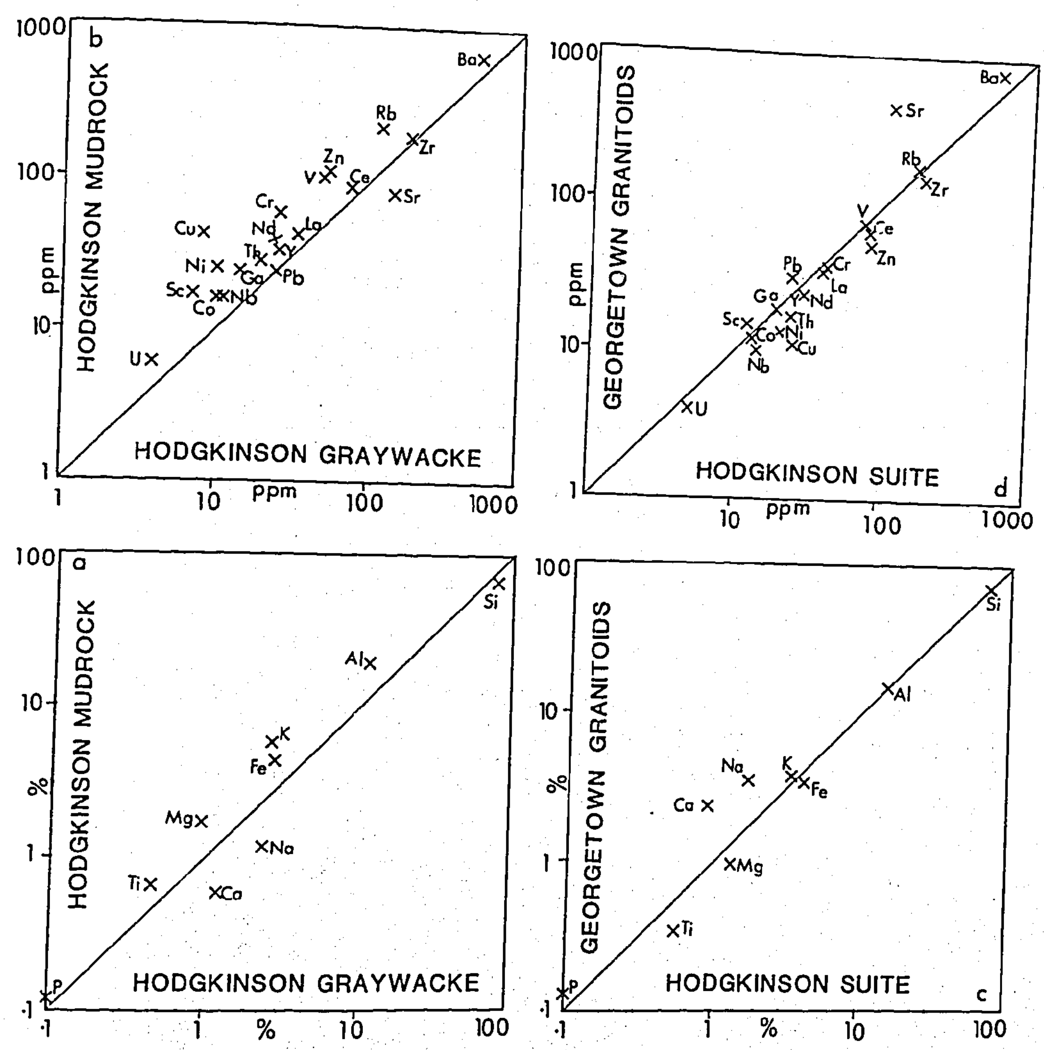


Figure 6.20 Comparison of the composition of
(a,b): the average graywacke and mudrock of the Hodgkinson suite.
(c,d): the average Hodgkinson suite and the Georgetown granitoids (Sheraton and Labonne, 1978).

The sedimentary rocks of the Robertson Bay Group of Antarctica have been suggested to form the provenance of the Ordovician sediments (which include the Bendigo Trough region) of Australia and New Zealand (Chapter 4; Nathan, 1976; Wyborn, 1977). The published data on the composition of the Robertson Bay Group are extremely meagre. The average composition of the Robertson Bay Group was computed using the graywacke and mudrock analyses given by Harrington et al. (1967) and Nathan (1976)(Table 6.12). A comparison between the average Robertson Bay Group and Bendigo suite compositions show that the CaO, Na_2O and Sr content is significantly high in the former due to the presence of more feldspar; and the Zr and Th content is higher in the latter due to the enrichment of heavy minerals (Figure 6.21c,d). A remarkable similarity was noticed in the SiO_2, TiO_2 and Ba content between the two. Slight enrichment of La, Ce and Co in the Bendigo suite and of Rb, Cr and Sc in the Robertson Bay Group is observed.

6.8.5 Cookman Suite

The highly matured Silurian sedimentary rocks of the Lachlan Fold Belt have been suggested to be derived from Ordovician rocks of the region (Packham, 1968; Wyborn, 1977; Chapter 4). Only one mudrock sample of the Cookman suite was analysed in the present work. Wyborn (1977) analysed two Silurian mudrock samples from the Snowy Mountain region of New South Wales. An average of all these samples was computed in order to have a better estimate of the average mudrock composition of the Cookman suite and similar rocks of the region.

A large difference in the average graywacke and mudrock compositions is observed (Figure 6.22a,b; Table 6.12). The graywackes are significantly high in SiO_2, Na_2O, CaO, Sr and Pb due to the high abundance of quartz and feldspar grains and the mudrocks are significantly high in Al_2O_3, FeO^t, MgO, TiO_2 and most trace elements, due to the high abundance of phyllosilicates. However, the light rare earth elements (La, Ce, Nd) and Y only show a slight enrichment in mudrocks compared to graywackes.

Because the Cookman sediments are derived from the Ordovician sediments, the Bendigo suite composition can represent the average source rock composition. A comparison of the average Bendigo and Cookman suite compositions shows that the Cookman suite average is higher in Sr and the Bendigo suite average is higher in Na_2O, CaO, MgO,

Table 6.12 Compositions of Average Bendigo and Cookman Sedimentary Suites and Source Rocks*

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	85.69	61.62	73.66	71.26	62.26	68.89	87.80	66.64	77.22
TiO_2	0.50	0.81	0.66	0.57	0.67	0.64	0.28	0.84	0.56
Al_2O_3	7.53	20.87	14.2	12.18	16.83	14.97	8.07	20.40	14.26
Fe_2O_3	0.56	2.66	1.61	1.29	0.84	1.10	0.54	2.26	1.40
FeO	1.63	4.33	2.98	3.03	5.47	4.39	0.49	1.60	1.05
MnO	0.02	0.05	0.03	0.04	0.02	0.03	0.03	0.03	0.03
MgO	1.01	3.52	2.27	2.12	3.68	2.99	0.40	1.67	1.04
CaO	0.19	0.23	0.21	2.06	1.05	1.61	0.10	0.05	0.08
Na_2O	1.39	0.54	0.97	1.32	1.21	1.31	0.91	0.23	0.57
K_2O	1.33	5.2	3.27	2.97	4.55	3.88	1.30	5.50	3.40
P_2O_5	0.13	0.14	0.14	0.14	0.16	0.15	0.08	0.09	0.09
Ba	262	855	559	588	547	567	246	725	485
Rb	64	244	153	165	199	182	58	251	154
Sr	40	36	38	75	112	94	88	45	66
Pb	13	26	20				19	13	16
Th	22	24	23	16.1	14.3	15.2	12.4	29	21
U	4.2	4.0	4.1				2.3	4.0	3.1
Zr	351	149	250	112	106	109	251	192	221
Nb	9	17	13				7	17	12
Y	30	36	33				25	30	28
La	34	36	35	35.5	25	30	34	48	41
Ce	77	81	79	80.7	52	66	67	99	83
Nd	27	29	28				31	43	37
Se	7	19	13	16.3	16.3	16.3	[illegible]	21	13
V	41	124	83				23	130	77
Cr	39	108	74	90	103	97	39	116	78
Co	8	22	15	13.3	14	13.6	2	6	4
Ni	11	51	31				4	25	15
Cu	7	41	24				5	16	10
Zn	35	128	82				17	73	45
Ga	9	29	19				7	29	18

* All average recalculated on volatile free.

(1) Average Bendigo suite graywacke, (7 samples).

(2) Average Bendigo suite mudrock, (2 samples).

(3) Average Bendigo suite composition (1 Graywacke : 1 Mudrock).

(4) Average Robertson Bay Group Graywacke (Harrington, et al. 1967, Nathan, 1976).

(5) Average Robertson Bay Group Mudrock (Harrington, et al. 1967; Nathan, 1976).

(6) Average Robertson Bay Group composition (1 Graywacke : 1 Mudrock).

(7) Average Cookman suite graywacke, (8 samples).

(8) Average Silurian mudrock, N.S.W. (1 sample Cookman suite; 7 samples of Silurian mudrocks of N.S.W.-Wyborn, 1977).

(9) Average Cookman suite composition (1 Graywacke : 1 Silurian mudrock).

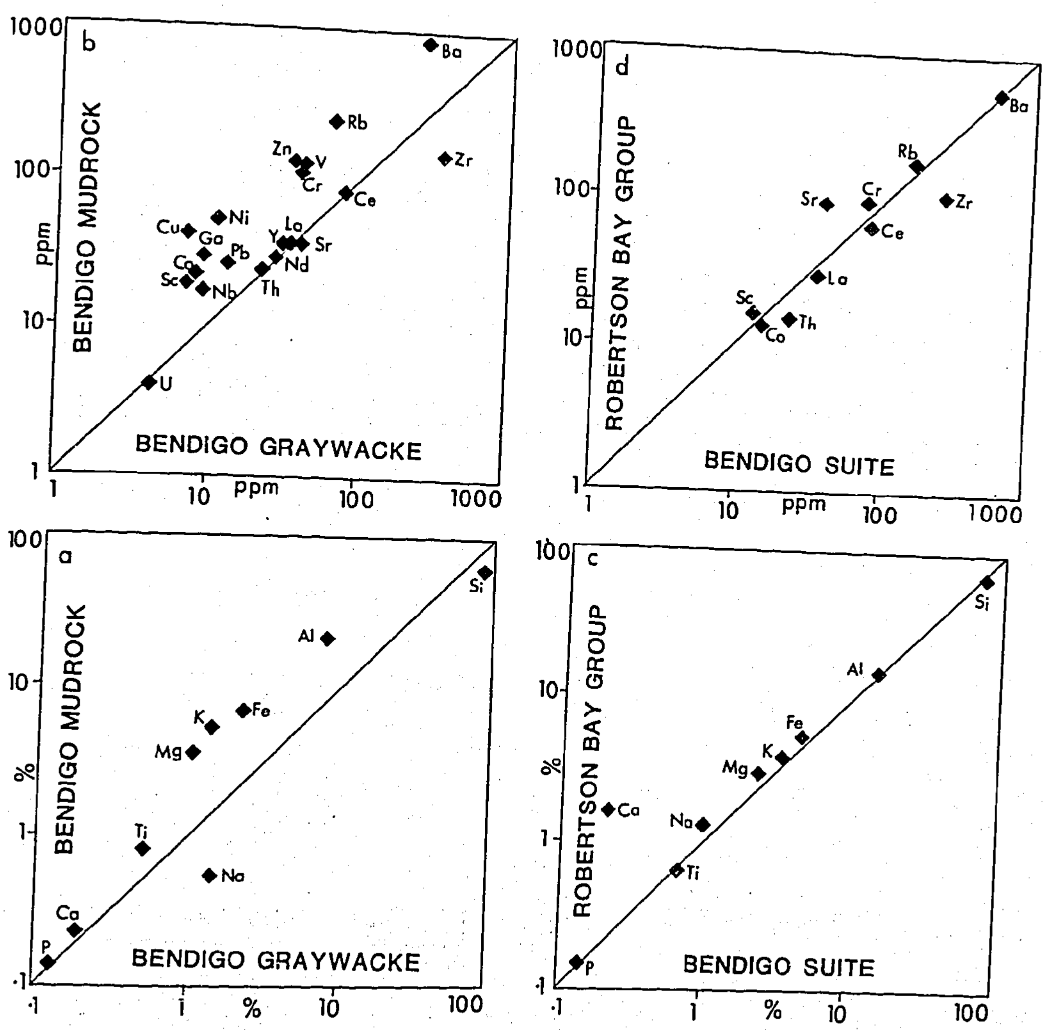


Figure 6.21 Comparison of the compositions of
(a,b): the average graywacke and mudrock of the Bendigo suite.
(c,d): the average Bendigo suite and the Robertson Bay Group (Harrington et al., 1967; Nathan, 1976).

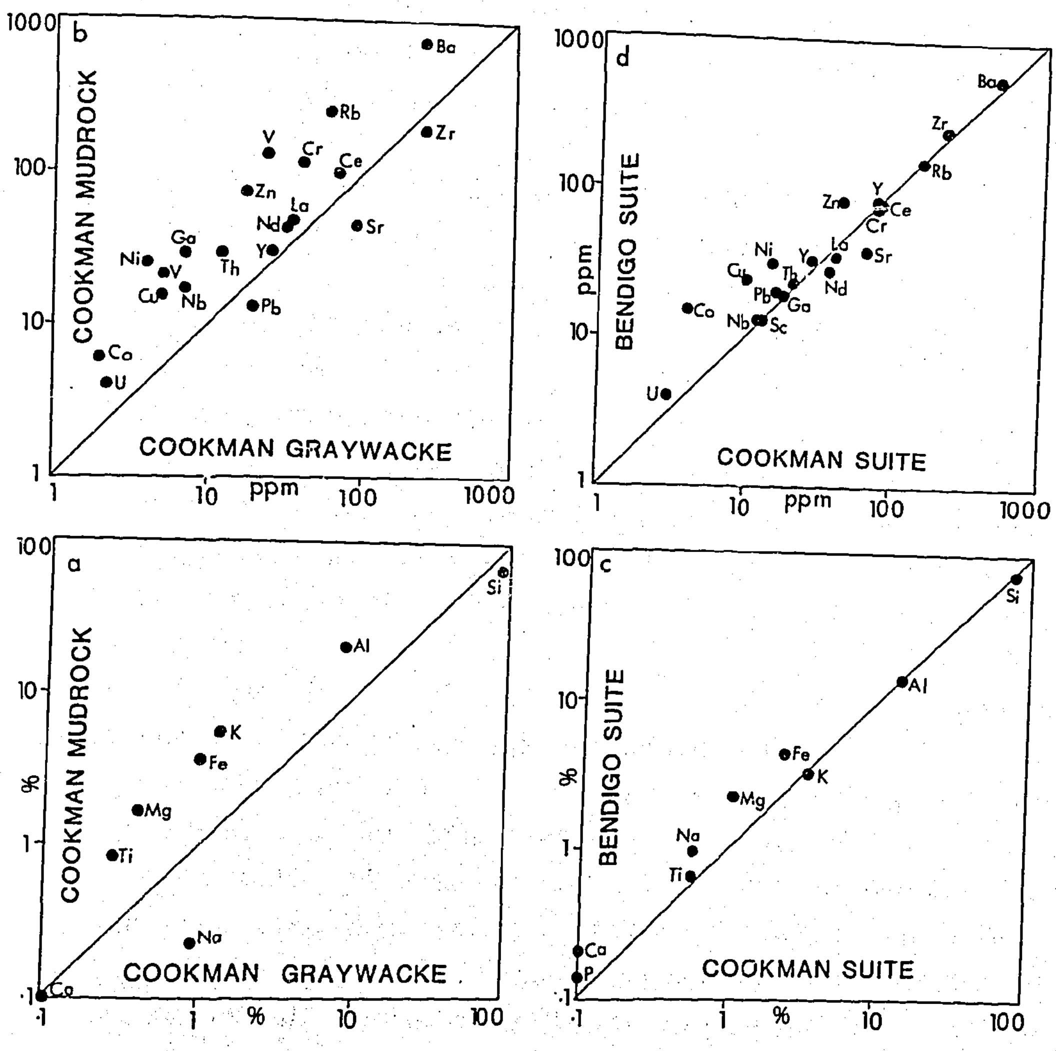


Figure 6.22 Comparison of the composition of
(a,b): the average graywacke and mudrock of the Cookman suite.
(c,d): the average Cookman and Bendigo suite.

FeO^t, MgO, Co, Cu, Ni and Zn (Figure 6.22c,d). SiO_2, Al_2O_3, K_2O, Ba, Rb, LREE, Y, Th, Sc, V and Cr exhibit similar abundances in the two suites. The reason for the slightly high abundance of Sr in the Cookman suite is not clear, probably it is due to the enrichment of K-feldspar. The average Bendigo and Cookman compositions are computed from unweighted data. However, a comparison of the weighted Cookman and Bendigo suite compositions gives a similar result.

6.9 MIGRATION AND REDISTRIBUTION OF ELEMENTS

The behaviour and redistribution of chemical elements during sedimentary cycles is complicated and not completely understood (Goldschmidt, 1954; Krauskopf, 1955; Nicholls and Loring, 1962; Tardy, 1975a,b; Turekian, 1977; Kronberg et al., 1979; Duddy, 1980; Nesbitt et al. 1980). Weathering, dissolution of primary minerals, authigenic formation of secondary phases, cation exchange and diagenesis influence the geochemical cycle of many elements during sedimentary processes. Lack of data on the individual phases of sediments render it extremely difficult to generalise on the behaviour of elements during the sedimentary cycle.

The redistribution of elements in clastic sedimentary rocks is deciphered on the basis of the relative abundances in graywackes and mudrocks and the comparison of average sedimentary suite and source rock compositions. In "immature" suites, having volcanic source rocks and minimal weathering conditions, e.g., the Tamworth and Hill End suites, the bulk compositions of graywackes and mudrocks are quite similar (Figures 6.18, 6.19). Graywacke compositions differ significantly from the associated mudrocks with the progressive increase in "maturity", weathering and recycling as in the case of the Hodgkinson, Bendigo and Cookman suites (Figure 6.20, 6.21, 6.22). The graywackes are high in SiO_2; Na_2O, CaO and Sr; and Zr due to the high abundance of quartz; feldspar; and zircon grains, respectively compared to mudrocks in most suites. Mudrocks, on the other hand, are high in Al_2O_3, K_2O, FeO^t, Ba, Rb, Ni, Cr, Zn, Cu and Ga compared to associated graywackes, due to the high abundance of phyllosilicates in each suite. The degree of enrichment of the elements in the various lithologies is very minor in the case of immature sediments like those of the Tamworth and Hill End suites but increases progressively with increasing maturity as in the case of the Hodgkinson, Bendigo and Cookman suites.

The small cations (Na, Ca, Sr) are in most cases depleted in the average clastic sedimentary composition compared to the average source composition. Thus, during the evolution of clastic sedimentary rocks, these elements are leached out of the source rocks and transported in solution. The degree of loss of these elements depends on the amount present in the source rocks and the weathering conditions; but in general increases with increasing maturity.

The increase in Al_2O_3 with increasing phyllosicate content in mudrocks is also accompanied by the increase in FeO^t and probably also in MgO. This could be due to the presence of iron-rich magnesium chlorites in the Bendigo suite mudrocks. Magnesium is known to decrease only slightly in weathering profiles and is transformed to phyllosilicates without much loss (Nesbitt et al. 1980). The relative amount of ferric and ferrous iron is a function of the oxidation state of the rock. During diagenesis ferric iron can be transferred to ferrous iron. However, the total iron decreases in graywackes and increases in mudrocks with increasing maturity. Iron is carried in suspension with phyllosilicates as well as small particles and colloids and deposited in quiet conditions with mudrocks in marine environments (Sharma, 1979).

Potassium is mainly concentrated in K-feldspar, mica and phyllosilicates. Large cations (Ba, Rb and Pb) follow K during sedimentary cycles (Puchelt, 1972, Tardy, 1975b). These elements are enriched in mudrocks compared to the graywackes in all suites, however, their total abundance in the sedimentary rocks remains similar to their source composition. These elements are released in the source region during weathering and are adsorbed on phyllosilicates (Nesbitt et al. 1980). Thus the abundance of large cations increases in mudrocks with increasing maturity.

Titanium occurs in resistate minerals, mica, phyllosilicates, pyroxene and volcanic material, or as opaque oxide (Spears and Kanaris-Sotiriou, 1976). Due to its occurrence in various forms, the redistribution of Ti is difficult to decipher. However, in graywackes, there is a decrease in TiO_2 content with increasing maturity. This trend along with the lack of positive correlation with resistate elements such as Zr suggests that most Ti is associated with pyroxene and other volcanic components. No definite trend is seen in mudrocks, however, the high TiO_2 content in matured mudrocks may be due to the presence of silt sized rutile needles associated with phyllosilicates.

The rare earth element abundance in average clastic sedimentary rocks is close to the average source rock estimate in each suite, suggesting their immobile nature. These elements are only slightly enriched in mudrocks compared to the associated graywackes. Light rare earth elements (La, Ce, Nd) and Y increase both in graywackes and mudrocks with increasing maturity. Large highly charged cations (Th, U, Nb, Zr) are also concentrated, mainly in the accessory minerals and phyllosilicates, and follow rare earth elements. These elements show an increasing abundance with increasing maturity, however, U can be lost because of oxidation of U^{4+} to U^{6+} under high weathering conditions. Th, U and Nb, like LREE are only slightly enriched in mudrocks compared to graywackes but Zr is significantly enriched in graywackes compared to the associated mudrocks in almost all suites, due to the retention of zircon grains in the sand size fraction. Thus, whereas Th and Nb remain almost constant Zr is slightly enriched in average sedimentary rocks compared to the source rock estimate. The exact behaviour of Zr during the sedimentary cycle and its distribution in resistate and hydrolysates is not completely known (Erlank et al. 1978). It can form a complex compound $[ZrO(CO_3)_2]^-$ or can occur as hydrated Zr oxide or as adsorbed zircon in iron hydroxide.

Chromium and nickel are mobile elements and migrate in detrital as well as non-detrital phases (Shiraki, 1978; Turekian, 1978). These elements are marked by their increased concentration in mudrocks compared to the graywackes in each suite and suggest that mechanical transportation of these elements is sub-ordinate to other processes of migration. Cr and Ni do not exhibit any definite trend in graywackes, but in mudrocks their abundance is increased with increasing maturity and they have high correlation coefficients with the mudrock maturity index (Table 6.3), indicating that Cr and Ni are not associated with volcanic detritus but rather were removed from solution and suspension by adsorption on phyllosilicates. The intensity of adsorption depends on temperature, pH, salanity of the solution (adsorbate) and other properties such as the composition, structure, grain size etc of the adsorbent. Kraus and Durkovic (1975) found that Cr and Ni are more abundant in mudrocks derived from non-volcanic sources than those derived from volcanic sources, probably due to increased weathering in non-volcanic regions. The high enrichment of Cr and Ni in mudrocks compared to the associated quartzose graywackes has also been noted in other regions (Logvinenko and Kosmachev, 1964; Van de Kamp et al. 1976).

Vanadium and scandium are dominantly associated with pyroxene and other volcanic material. In graywackes, V and Sc decrease in abundance with increasing maturity, while no definite trend is observed in mudrocks. Copper, zinc and cobalt generally exhibit a complex behaviour during sedimentary processes. These elements occur with volcanic detritus as well as adsorbed on phyllosilicates. These elements are mobile, decrease in abundance with increasing maturity in graywackes but can be enriched in mudrocks due to adsorption. A positive correlation between S, Zn and Cu suggests their presence in the sulphide phase (Tardy, 1975b). Ga is dominantly concentrated in phyllosilicates and increases in mudrocks but decreases in graywackes with increasing maturity.

CHAPTER 7
TECTONIC SETTING DISCRIMINATION USING GEOCHEMICAL CHARACTERISTICS OF SEDIMENTARY ROCKS

7.1 INTRODUCTION

Plate tectonics has emerged as the unifying theory to explain continental drift, sea-floor spreading, the evolution of island arcs continental margins and ocean floor. The history and evolution of mountain belts is also compatible with this theory (Coney, 1970; Dewey and Bird, 1970a). The concept of plate tectonics is now increasingly being used to explain the origin and evolution of sedimentary basins.

In the plate tectonic theory, the emphasis is on large scale horizontal movements of the lithosphere. The birth and development of a sedimentary basin requires a theory which embraces uplift of the source area and subsidence to form the basin. The vertical tectonics required to explain the origin of sedimentary basins is also inherent in the theory of plate tectonics in the form of attributes, such as crustal thickness, thermal regimes and isostatic adjustments. The vertical movement strongly influences the pattern of erosion and sedimentation on the earth's surface and the nature of basins is related to the plate tectonic setting of the region (Dickinson, 1974a; 1978).

Various igneous, metamorphic and sedimentary assemblages have been related to different plate tectonic settings. In igneous and metamorphic rocks, this is due to characteristic crustal processes acting on the astenosphere and lithosphere, and the controls are fairly well understood. Significant progress has also beeen achieved in relating the detrital composition of arenites to the tectonic settings and provenance types (Crook, 1974; Schwab, 1975; Dickinson and Suczek, 1979; Dickinson and Valloni, 1980; Valloni and Maynard, 1981). In these studies the uplift of the typical source region as a result of plate interactions and the subsequent accumulation of detritus in the accompanying basin has been emphasised. However, this paradigm does not take into account the intermediate processes such as climate, relief, physical sorting and diagenesis. The effect of plate tectonics on these variables has not yet been critically evaluated. An exception to this is the study of variation in diagenesis related to plate tectonics by Siever (1979).

In this chapter, an attempt has been made to relate plate tectonics to various variables acting during sedimentary processes. The tectonic settings of various sedimentary suites of eastern Australia have been deciphered on the basis of their geochemical characteristics. Then, mineralogical and geochemical parameters which can be used to discriminate various tectonic settings of sedimentary basins have been proposed.

7.2 TECTONIC CLASSIFICATION OF FLYSCH BASINS

The terminology of the geosynclinal belts has long been a matter of discussion. In classical theory, geosynclines are divided into the following two adjacent and parallel major belts: miogeosyncline and eugeosyncline (Kay, 1951). Many other names were also proposed for various other basins. Attempts were made to classify sedimentary basins in general and geosynclinal sequences in particular following an "actualistic" approach (Dietz, 1963; Mitchell and Reading, 1969, 1978; Dewey and Bird, 1970a,b; Dickinson, 1974a,b). However, a direct correspondence between the plate tectonic setting of modern basins and geosynclinal terminology was found to be elusive (Dickinson, 1974a; Schwab, 1974).

In the plate tectonic models, the junction between various plates can be described as divergent, convergent and strike-slip. Continental margins are either active (or leading) when they are situated at or near the plate junction or passive (or trailing) when situated within the lithospheric plates. The first-order classification of basins into leading and trailing edges is somewhat difficult and inadequate (Reading, 1974; Dickinson and Valloni, 1980). A three fold classification of the provenance type, into magmatic arc, recycled orogen and continental block, has also been proposed (Dickinson and Suczek, 1979).

In the present study, only flysch (orogenic) basins have been considered. Their diversity can be more easily explained by second or third order tectonic features. A simplified classification of the tectonic settings, based on the nature of the crust of the region and provenance type, has been proposed. The crustal nature is a function of plate interaction which in turn governs the isostatic movements, provenance type, and the position of the basin within the plate, on the plate boundary or on the continental margin. The flysch basins have been divided into four broad tectonic settings (Table 7.1).

The oceanic island arc, continental island arc and the Andean type settings represent the active margins and correspond to settings of orogenic volcanic rocks (Miyashiro, 1974; Ewart, 1976; Bailey, 1981). The "passive margin" type of tectonic settings have been tentatively divided into "East-Asian type" and "Atlantic type". The "East-Asian type" setting represents sedimentary basins adjacent to collision orogens and probably also some accretionary prisms (Moore, 1979; Velbel, 1980). The "Atlantic type" tectonic setting represents rifted continental margins developed along the edge of the continent.

The proposed classification of tectonic settings is not exhaustive. Particularly more work is needed to refine the 'passive margin' type of settings. The subduction complex may represent a distinct setting or may have overlapping characteristics with other settings. The transitions between various settings can also occur as sedimentary basins can change tectonic realms during their evolution, due to plate movements (Mitchel and Reading, 1969; Crook, 1980c).

7.3 TECTONIC SETTINGS OF SEDIMENATRY BASINS OF EASTERN AUSTRALIA

7.3.1 Tamworth Trough

The tectonic setting of the New England Fold Belt, which includes the Tamworth Trough sedimentary sequence has been discussed by a number of authors. A source terrain composed of tholeiitic andesites has been inferred for these rocks (Chappell, 1968; Leitch, 1974). In terms of plate tectonic setting, the Tamworth Trough has been interpreted as a fore-arc basin with an Upper Devonian - Middle Permian volcanic arc in the west (most of which is now buried), and an (?) Ordovician to Middle Permian subduction complex made up of pelagic sediments, volcaniclastics, pillow lavas and ophiolitic melange in the east (Korsh, 1977; Leitch, 1975; Crook, 1980b). Although, a volcanic arc has generally been accepted, its nature has remained uncertain. Marsden (1972) and Leitch (1975) have suggested that the arc could be of the Andean type developed on a crystalline basement. On the other hand, Scheibner (1973) and Crook (1980a,b) have envisaged an oceanic arc.

Andesitic volcanic rocks are widely associated with modern and fossil orogenic zones. A systematic change in the composition of andesites has been documented on passing from oceanic to continental

Table 7.1 Plate Tectonic Classification of Flysch Basins

Tectonic Setting	Dominant Depositional Basin(s)	Nature of Crust*	Provenance Type	Example
Oceanic Island Arc	Fore-arc	Oceanic island arc or island arc partly formed on thin continental crust	Undissected Magmatic Arc	Western North-Pacific; Aleutians; Lesser Antilles; Marianas
Continental Island Arc	Apical inter-arc, back arc, fore-arc	Island arc formed on well developed continental crust or on thin continental margin	Dissected Magmatic Arc-Recycled Orogen	Havre Trough; Puerto-Ricc shelf; Cascades-W. USA
Andean Type	Retro-arc foreland; faulted basins; rifted valleys	Thick continental margin; crystalline basement	Uplifted Basement	N. Chile; Eastern Americas
Passive Margins (a) East Asian Type	Marginal basin, remanant ocean basin	Thickened-Continental crust	Recycled & Collision Orogens	Bengal-Nicobar Fan and Nicobar Basin
(b) Atlantic Type	Rifted continental-margins (eugeoclines and abyssal plains)	Fractionated Basement	Craton-Interior	Atlantic Ocean

* Sedimentary basins adjacent to

orogenic types (McBirney, 1969; Ewart, 1976). Jakes and White (1972) have pointed out that calc-alkaline volcanic rocks of the continental margin have a higher Rb, Sr, Th, U and Zr content, and lower K/Rb and Th/U ratios at a given $Si0_2$ and K_20 content then equivalent rocks of the island arcs. Bailey (1981) has shown that certain geochemical parameters can be used to discriminate between the andesites of the oceanic island arc, continental island arc, and thick continental margin.

A comparison of the geochemical characteristics of the Tamworth suite graywackes with various orogenic andesites (Table 7.2) indicates that the sediments are similar to oceanic island arc andesites (variety "other" of Bailey, 1981). A remarkable resemblance can be noticed for La, Ce, Th,U, Th/U, Nb, K/Th, Zr/Y, Ni/Co, Sc/Ni, K/La, P/La and La/Y. The Tamworth Trough graywackes differ significantly from the continental and Andean type andesites in having significantly lower La, Ce, Th, Nb, Zr/Y, Ni/Co, La/Y and higher ratios of K/Th, Sc/Ni, K/La and P/La. Rare earth element characteristics also suggest an oceanic island arc tectonic setting for the Tamworth Trough (See Chapter 8).

Mineralogically, the Tamworth graywackes are characterised by low quartz, high feldspar and volcanic rock fragments. The detrital assemblage of $Q_8F_{41}L_{51}$ is similar to many ancient and modern oceanic island arc arenites and sands (Table 7.4; cf. Dickinson and Suczek, 1979; Valloni and Maynard, 1981).

The water depth of the fore-arc region depends on the position of the basin at the origin, and the relative rates of sedimentation and subsidence. Continental-margin arc-massif basins are commonly non-marine, whereas intra-oceanic arc-massif basins are probably dominantly marine (Dickinson, 1970, 1974a,b). The Devonian-Lower Carboniferous part of the Tamworth Trough is dominantly marine and thus represents an oceanic island arc tectonic setting. During the Upper Carboniferous-Lower Permian times, this island arc was cratonized and felsic volcanic material was supplied to the basin. This is reflected in the detrital characteristics and the high La, Th, U, Zr, Ba and Pb content of the Crow Mountain Creek beds (Chapter 6), and in the chemistry of the Permian volcanic rocks (Jakes and White, 1972).

Table 7.2 Geochemical Comparison of Graywackes of Eastern Australia with Andesites from Various Tectonic Settings+

	Oceanic Island Arc# Low K	Oceanic Island Arc# Others	Tamworth Suite^ψ	Continental Island Arc#	Hill End Suite^ψ	Andean Type#	Hodgkinson Suite^ψ
K (%)	0.51	1.2	0.91	1.37	1.45	1.95	2.1
P (%)	0.05	0.10	0.08	0.10	0.05	0.12	0.03
Rb	8.3	28	18	44	72	66	115
Ba	152	318	370	395	461	606	522
Sr	220	434	637	400	184	601	141
Pb	2.9	5	7	10.4	15	11.5	24
K/Rb	589	415	578	311	202	253	189
Ba/Sr	0.61	0.73	0.95	1.16	3.89	1.05	3.8
*La	3.0	11.7	9	17	25	28.5	33
*Ce	6.9	23.5	22	37	50	60.7	73
Th	0.72	1.95	2.27	5.36	11.37	6.0	18.8
U	0.37	0.62	1.10	1.6	2.48	1.25	3.9
*Th/U	1.7	2.7	2.18	3.6	4.76	3.3	4.8
Zr	63	111	96	117	233	181	180
Nb	0.81	5	2.0	9.4	8.6	10	11
K/Th	10500	5530	4055	2480	1344	3340	1252
Y	25	20	20	22	25	15	25
*Zr/Y	2.2	4.7	4.8	5.4	9.32	14.6	7.1
*Ni/Co	0.29	0.52	0.61	0.95	1.31	1.4	1.04
*Sc/Ni	3.4	2.0	2.3	1.1	1.4	0.55	0.77
*K/La	1950	1150	1058	814	605	715	700
*P/La	180	86	106	49	21	47	11.2
*La/Y	0.11	0.56	0.48	0.93	1.02	1.46	1.33

+ Abundances in ppm, unless otherwise indicated

* Most discriminating variables

From Bailey (1981)

ψ Mean element abundance of the suite. Element ratios are calculated from individual ratios not from the mean values. (Data from Tables 6.9-6.12).

7.3.2 Hill End Trough

The tectonic setting of the Hill End Trough has also been discussed by a number of authors. The suggestion that the Hill End Trough represents an inter-arc basin of the wholly intra-oceanic arc-trench system (Scheibner, 1973; Packham, 1968) has been disputed by Cas and Jones (1979) on the basis of the nature of Merrions Tuff lava flows and sedimentary fill. These authors have documented a similarity between the Hill End Trough environs and the southern apex of the Havre Trough region, where it impinges on the northern island of New Zealand.

A large difference between the geochemical characteristics (particularly in La, Ce, Th, U, Th/U, Zr/Y, and Sc/Ni) of the Hill End suite graywackes and the oceanic island arc andesites negates the intra-oceanic character of the Hill End Trough (Table 7.2). On the other hand a close similarity is observed in Nb, U, La/Y, Ni/Co and Sc/Ni ratios between the Hill End suite graywackes and the continental island arc andesites (Table 7.2). The above geochemical parameters also illustrate a large difference when compared with the Andean type volcanic rocks. The REE characteristics and the Sc/Ni vs La/Yb plot also support the continental island arc type of tectonic setting for the Hill End suite rocks (Chapter 8). The bulk composition of the Hill End suite is similar to the Goobarragandra felsic volcanic rocks, which have been suggested to be derived from the melting of continental material (Wyborn et al. 1981). Thus, the geochemical evidences suggest that the dominant part of the Hill End Trough evolved adjacent to an island arc formed on a well-developed continental crust, or on a thin continental margin. The nature of the crust could be somewhat similar to the modern crust of the southern island of New Zealand. The Sr^{87}/Sr^{86} ratio of 0.7062 reported for the Merrions Tuff lavas, is similar to such values of the rhyolitic lavas of New Zealand and supports the continental island arc character of the Hill End Trough (Cas et al. 1976; Ewart and Stipp, 1966).

The Hill End Trough developed as a result of rifting of the continental crust. Immediately after rifting, the abundant material was supplied by the fault bounded Ordovician sedimentary rocks, which are reflected in the quartzose nature of the Cookman suite. Thus during the Cookman deposition, the nature of the trough could be described as a peripheral basin developed adjacent to the recycled orogen. Later on and during the dominant part of its sedimentary history, it developed into an apical inter-arc basin adjoined to a microcontinent and could be assigned to the continental island arc type of tectonic setting.

7.3.3 Hodgkinson Basin

Two models have been proposed to explain the evolution of the Hodgkinson Basin. The first model envisages the active Cordilleran-type of margin on which the flysch sediments were emplaced in an arc-trench gap. This active arc is thought to have developed on a Precambrian crust in the west (Cooper et al. 1975; Henderson, 1980; Arnold in Arnold and Fawckner, 1980). According to the second model, during the Late Silurian a magmatic arc developed on the eastern margin of the craton, and the flysch sediments were deposited in a marginal basin formed due to rifting and crustal extension as subduction ceased (Fawckner in Arnold and Fawckner, 1980).

The Hodgkinson graywackes are too rich in quartz and K-feldspar grains, and too depleted in volcanic rock fragments and plagioclase to be derived from an active intra-oceanic arc. A comparison of the geochemical data exhibits a close similarity in the La, Ce and Zr content and the P/La, La/Y, Ni/Co, Sc/Ni ratios of the Hodgkinson graywackes and Andean type andesites (Table 7.2). The chondrite normalised rare earth patterns between the two also exhibit a similarity, in the form of the presence of a pronounced negative Eu anomaly and the significant enrichment of light rare earth over heavy rare earth elements (Chapter 8).

Thus, the geochemical evidences indicate that the Hodgkinson Basin developed on a thick continental margin of the Andean type. The geomorphic setting of the basin is not certain, probably it was some sort of retro-arc basin associated with an uplifted basement. In terms of the present flysch classification, the Hodgkinson Basin can be assigned to the Andean type of tectonic setting.

7.3.4 Bendigo Trough

The tectonic model for the development of the Ordovician sedimentary basins of southeastern Australia, of which the Bendigo Trough forms a part, is debatable. Cas et al. (1980) have drawn an analogy between the Ordovician paleogeography and the modern Andaman sea of the Indian Ocean. According to this model, the Bendigo Trough forms a part of the marginal sea behind an Ordovician island arc. The basement on which the Ordovician basin developed is also debatable. The Cambrian greenstone belt of the Heathcote Axis is dominantly of tholeiitic affinity and related to the oceanic substrata (Crawford and Keays, 1978; Crawford and Cameron, 1980). On the other hand, the evidence provided by the extensively developed Silurian-Devonian S-type granitoids of the Lachlan fold Belt indicates a pre-existing layer of meta-sedimentary rocks below the Ordovician flysch sequence (Wyborn, 1977; Wyborn and Chappell, 1979).

The Bendigo Trough can not be assigned to a definite tectonic setting with the present data. However, their recycled nature is clearly evident from their mature mineralogy and fractionated chemistry. It has been suggested that the quartz-rich type of arenites represent tectonically quiescent continental margins, like the modern Atlantic-type (Crook, 1974; Schwab, 1975). However, significantly mature and recycled sediments have also been reported from the accretionary prisms of Nias Island (Indonesia), and the Scotland Formation of Barbados (Moore, 1979; Velbel, 1980). This type of tectonic setting has been named as the East-Asian type in the present work and is similar to the setting envisaged by Cas et al. (1980) for the Ordovician rocks of southeastern Australia. The differences between the Atlantic type and the East-Asian type sediments are not well established, though the former are generally richer in K-feldspar because of their derivation from the craton (Dickinson and Volloni, 1980; Valloni and Maynard, 1981). However, K-feldspar is also common in the detrital assemblage of the Barbados sandstones (Velbel, 1980). Tentatively, the Bendigo Trough can be assigned to the passive margin, representing the recycled orogen provenance, and probably the East-Asian type of tectonic setting.

7.4 TECTONIC CONTROL ON GEOCHEMICAL VARIABLES

The chemical composition of sedimentary rocks is a function of the complex interplay of various variables, such as, source rocks, weathering, relief, physical sorting and diagenesis. Tectonism has been advocated as the primary control on sedimentary composition (Pettijohn et al. 1972; Blatt et al. 1980). The relationship between tectonic setting and the attributes of the composition of sedimentary rocks are shown in Figure 7.1 and Table 7.3.

7.4.1. Source Rocks

The nature of source rocks is the most important attribute governing the diversity of composition of clastic sedimentary rocks. Plate interaction governs the relationship between the provenance type (in the form of plutonism and volcanism) and the tectonic setting of sedimentary basins. In convergent plate margins, one plate is subducted below another plate. Due to the melting of the descending lithospheric slab, calc-alkaline magma is genetrated to form the principal provenance for the sediments. In the oceanic island arc tectonic setting, the detritus is dominated by microlitic rock fragments and plagioclase grains derived from andesites. The sediments formed in this tectonic setting are rich in ferromagnesian elements (Fe, Mg, Ti, V, Sc, Co, Cu), and small cations (Ca, Na, Sr), because of abundant volcanic material and plagioclase grains, and are depleted in Si, lithophile elements (Zr, Nb, Th, U, Hf & Y) including the light rare earth elements (La, Ce, Nd), compared to the upper crust. The continental island arc volcanic rocks formed on a well-developed crust and the detritus is mainly felsic in nature, resulting in the increased abundance of Si, Th, U, Zr, Nb, Y, Hf and rare earth elements compared to the oceanic arcs. The well developed crust of the continental margin or continental island arc can also contribute detritus in varying proportions.

In the Andean type of tectonic setting, crystalline rocks of the thick continental margin form the dominant source rocks with a minor contribution from the volcanic arc. The graywackes are quartzo-feldspathic in nature with a high abundance of mica and K-feldspar. This results in the high abundance of K, Rb, Pb, Th, U, Zr, Nb and rare earth elements. In the pasive margin settings, the sediments are derived from the extensive weathering of heterogeneous rocks of the craton or from uplifted orogenic sediments. The sediments are geochemically fractionated and exhibit enrichment of Zr, Hf, Nb and rare earth elements. Thus, with the change of tectonic setting from oceanic island arc to continental island arc to Andean type to passive margins, there is a corresponding change in source rocks from andesite to dacite to granite-gneiss to sedimentary rocks.

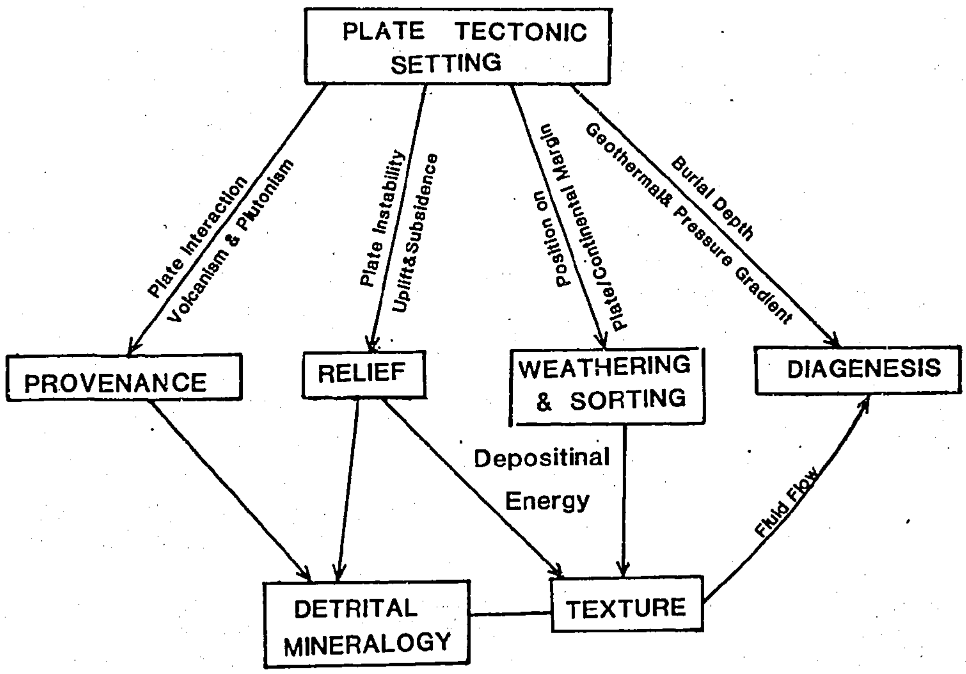


Figure 7.1 Relationship between attributes of plate tectonic setting and compositional variables.

Table 7.3 Variation in Compositional Variables with Tectonic Setting of the Sedimentary Basins

Tectonic Setting	Dominant Source Rocks	Relief	Weathering & Physical Sorting	Digenetic Modifications
Oceanic Island Arc	Andesite	V. high	Minimal	Complex and extensive
Continental Island Arc	Dacite	High	Low	Extensive
Andean Type	Granite-gneiss	Moderate	Moderate	Common and moderate
Passive Margin	Sedimentary-metasedimentary rocks	Subdued	High	Simple

7.4.2 Relief

The tectonic stability/instability in the form of volcanism and plutonism along the plate/continental margin, governs the relief of the source area. In the oceanic and continental island arc settings, high relief is retained due to crustal interaction in the form of volcanism and plutonism. In the Andean type setting, the continental margin maintains a moderate to high relief. On the other hand, in the Atlantic type tectonic setting, the relief is subdued due to the tectonic stability of the region. In East-Asian settings, relief varies, and is probably only moderate but can be high due to continental collision. Thus, in general, the relief changes with tectonic setting and is an important parameter in the composition of sedimentary rocks because it (relief) directly affects the weathering processes in the source region, which in turn govern geochemical fractionation (see below).

7.4.3. Weathering

Though some studies have been done on climatic changes and tectonic evolution (e.g. Mackenzie and Pigott, 1981), the relation between the two is very poorly understood. In the present section, the effect of weathering conditions of the source region on detrital composition and geochemical fractionation is examined briefly and no attempt has been made to envisage a global pattern of climatic changes with tectonic setting. This avenue of research is very interesting and can form an excellent project for future research.

The role of weathering in element mobility has been documented in some detail (e.g. Garrels and Mackenzie, 1971; Kronberg et al. 1979; Nesbitt et al. 1980). Weathering affects the composition of mudrocks to a great extent. In oceanic and continental island arc tectonic settings, due to the high relief maintained by volcanism and plutonism, the weathering conditions are minimal, and thus unstable grains are retained in detritus, resulting in only a slight geochemical fractionation of clastic sediments. In the Andean type of tectonic setting, relief is reduced and weathering conditions are increased, resulting in significant element mobility. Small cations (Na, Ca, Sr) are lost in solution and large cations (K, Rb, Ba), Al-group (Al, Ga) and some ferromagnesian elements (Ni, Cr, Zn) are enriched in the mudrocks, due to the abundance of phyllosilicates and adsorption processes. In the passive margin settings, the relative tectonic stability and low relief permit extensive weathering in the source region, thus resulting in the significant loss of small cations and the enrichment of large cations, Al-group and some ferromagnesian elements in mudrocks.

The relative differences in the composition of graywackes and mudrocks, and the different element mobility due to weathering, can be attributed to the position of the basin relative to the plate/continental margin and thus ultimately to the tectonic setting of the sedimentary basin. The intensity of loss of small cations, and the enrichment in mudrocks of large cations, Al-group, and some ferromagnesian elements (Cr, Ni, Zr), increases with geochemical fractionation as a result of the change in tectonic setting from oceanic island arc, to continental island arc to Andean type to the passive margins (see also Chapter 9, Section 9.2).

7.4.4 Physical Processes

Conglomerates (coarse grained), graywackes (medium grained) and mudrocks (fine grained) are formed as a result of decreasing depositional energy. In general, mudrocks are more abundant in the Andean type and passive margin sequences (Hodgkinson and Bendigo suites) compared to the arc related basins (Tamworth and Hill End sequences). The increasing abundance of fine grained sedimentary rocks can be explained as a result of the increasing tectonic stability of a sedimentary basin. Thus, the depositional energy to some extent is governed by the position of the basir on the plate margin/boundary.

The following redistribution of chemical elements takes place due to physical sorting:

(a) Increase of SiO_2 in graywackes because of the enrichment of quartz.

(b) Increase of Na, Sr and sometimes Ca in graywackes due to the enrichment of feldspar in the medium sand size fraction.

(c) Increase of Zr in graywackes due to the retention of heavy minerals in the medium sand size fraction.

The above mentioned redistribution of elements increases from oceanic island arc to continental island arc to Andean type to passive margin settings because of increasing tectonic stability and probably also increasing transportation during sedimentation.

7.4.5 Diagenesis

Siever (1979) has provided a detailed account of plate tectonic control on the diagenesis of sedimentary basins. Diagenetic variables such as detrital mineralogy, fluid flow, burial features and geothermal pressure gradients are governed by regional tectonics, volcanism, plutonism, heat flow and the transport of formation water, which in fact are attributes of the plate tectonic setting of the sedimentary basin.

The oceanic and continental island arc basins are regions of low heat flow, rapid subsidence and burial. Mafic minerals are abundant and diagenesis results in their complex and extensive alterations, e.g., the formation of zeolite, prehnite and pumpellyite minerals and the albitisation of Ca-plagioclase. A transition from shallow zeolite through prehnite-pumpellyite to greenschist facies of burial metamorphism is commonly observed in these sequences. The sedimentary basins of the passive margins are characterised by a lowered heat-flow, a reduced geothermal gradient and slower subsidence and burial. The detrital mineralogy of clastics in fairly stable. Diagenesis in these regions is simple and results mainly in the formation of chlorite-illite and sometimes carbonate and quartz as the cementing agents. Diagenesis in Andean type sedimentary basins is intermediate between the arc-related and passive margin tectonic settings.

Thus the nature of diagenesis in sedimentary rocks is dependant on the provenance and texture, which in turn are governed by the prediagenetic and preburial tectonic setting of the basins (Figure 7.3; Hayes, 1979).

7.5 TECTONIC SETTING DISCRIMINATION USING MINERAL COMPOSITION

7.5.1. Arenites

The detrital composition of arenites as indicators of provenance type and tectonic setting has already been discussed in some detail (Crook, 1974; Schwab, 1975; Potter, 1978; Dickinson and Suczek, 1979; Dickinson and Valloni, 1980; Valloni and Maynard, 1981). However, complexities can arise due to large variations in geomorphic settings and provenance type. The same geomorphic setting can develop in different tectonic settings, e.g., a fore-arc basin can form adjacent to an oceanic island arc, a continental island arc or a thick to thin continental margin, with varied detrital composition. On the other hand, detritus of the same provenance type can be contributed (either in the same proportion or in different proportions) to various geomorphic settings, e.g., a magmatic arc can contribute detritus to fore-arc, back arc, inter-arc or trench-slope basins. Inconsistencies in using detrital framework modes of arenites as unequivocal indicators of plate tectonic settings have been noted in many regions (Moore 1979; Velbel 1980, and Zuffa et al. 1980). Schwab (1981) has described various factors, such as contrasting modes of dispersal, in transit change in mineralogy, and lack of data from transitional continental margins which affect the relationship between detrital composition and plate tectonic settings.

In the present study, the emphasis is on the nature of the crust of the source terrain and its relation to the adjacent sedimentary basin. Data on framework modes of the graywacke suites of eastern Australia, have been compared with the published modes of arenites (Table 7.4; Figures 7.2 and 7.3).

Most modern and ancient oceanic island arc sediments are very distinctive and are characterised by an extremely low abundance of quartz and high abundance of plagioclase and volcanic rock fragments. The arenites are of the feldspatho-lithic type, mainly derived from andesites and occupy very restricted fields on all discriminatory plots (Figures 7.2 and 7.3). The continental island arc type sediments are more quartzose than those of the oceanic island arc (Figure 7.2) and are mainly derived from felsic volcanic sources. The arenites of the Andean type setting are quartzo-feldspathic in nature and are mainly derived from crystalline sources. The QFL and QpLvLs plots clearly discriminate between oceanic island arc, continental island arc and the Andean type settings.

Arenites of the passive margins, though generally more quartzose than other arenites, show a much larger variation in their mineralogical characteristics. The Bendigo and Cookman suite samples are similar to the Eocene arenites of Apennine, Italy (Sestini, 1970) and the Carboniferous graywackes of Arkansas (Graham et al. 1976). The last two examples have been assigned to the collision orogen type of provenance and grouped here under East-Asian type of tectonic setting. The QFL plot does not discriminate between matured arenites. The Atlantic type and Bengel-Nicobar fan samples plot in the Andean type

Table 7.4 Mean Detrital Modes of Arenites and Sands Representing Various Tectonic Settings

	N	Q	F	L	Qp	Lv	Ls	P/F	Lv/L
Oceanic Island Arc									
1. Tamworth Suite*	11	8	41	51	5	92	3	0.94	0.97
2. Upper Paleozoic, N.S.W.**	69	3	29	68	0	100	0	1	1
3. Atka Basin, Alska**	27	7	34	59	6	92	2	0.97	0.98
4. Modern Oceanic Island Arc***	85	11	34	55	5	90	5	0.91	0.95
5. Modern Fore Arc#	20	8	17	75	-	-	-	0.87	0.99
Continental Island Arc									
6. Hill End suite*	29	54	17	28	16	55	29	0.88	0.67
7. Modern Back-Arc#	53	20	29	51	-	-	-	0.61	0.84
8. Modern Continental-margin Arc***	40	20	41	39	11	79	10	0.75	0.89
9. Lr. Cret. Lagoda Petrofacies**	32	48	23	29	6	68	26	0.88	0.73
10. Middle Tertiary Sandstone, Washington**	127	38	32	30	24	52	24	0.87	0.68
11. Insular Sands, northern Puerto-Rico Shelf**	27	21	31	48	13	56	31	0.85	0.83
Andean-Type									
12. Hodgkinson suite*	21	71	18	11	60	16	24	0.52	0.42
13. Salton Basin California**	7	46	47	7	-	-	-	0.59	0.71
14. Santa Ynez California**	24	50	47	3	-	-	-	0.56	0.46
15. Sierra Madre Basin+	?	50	33	17	-	-	-	0.39	-
16. Salinian Block California***	64	49	43	8	50	19	31	0.53	0.38
17. Modern Leading Edge-Strike Slip#	50	34	39	27	-	-	-	0.65	0.33
18. Transform Arc Orogen***	35	31	45	24	27	26	47	0.63	0.36
Passive Margins									
19. Bendigo Suite*	9	94	3	3	-	-	-	0.96	-
20. Cookman Suite*	8	87	1	12	20	2	78	1.0	.03
21. Carboniferous Oachita Mt. Arkansas**	12	79	3	18	39	3	58	0.75	0.04
22. Apennine Eocene, Italy**	?	90	5	5	58	-	42	-	-
23. Bengal Nicobar Fan**	22	58	28	14	6	4	90	0.71	0.04
24. Modern rifted Continental-margins***	155	76	18	6	-	-	-	0.25	-
25. Atlantic Ocean#	29	66	23	12	-	-	-	0.30	0.13

Notes:

N Number of samples

Data adopted from:

* present work

** Dickinson and Suczek (1979)

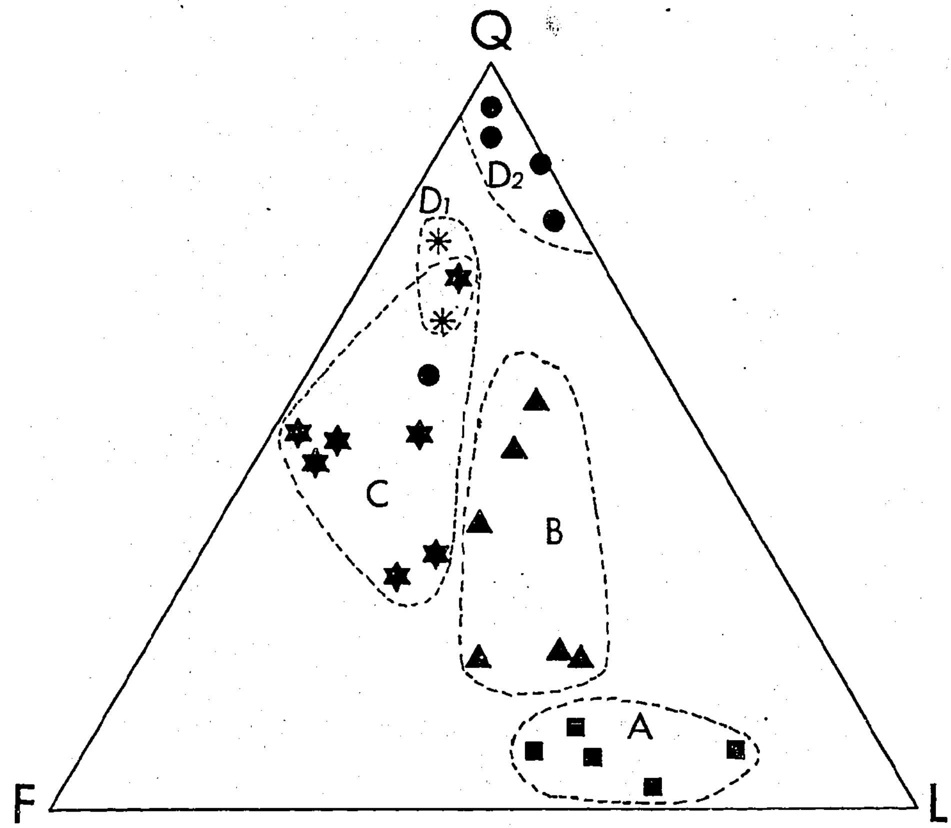
*** Dickinson and Valloni (1980)

\# Valloni and Maynard (1981)

\+ Dickinson et al. (1979)

Figure 7.2 QFL and QpLvLs plots of arenites and sands for tectonic setting discrimination (Data adopted from Table 7.4). Dotted lines mark the dominant field for each tectonic setting. The field of Atlantic type on the QpLvLs plot is adopted from Ingersoll and Suczek (1979).

- ▣ Oceanic Island Arc (A)
- △ Continental Island Arc (B)
- ✡ Andean Type (C)
- Passive Margins (D)
  - ● East-Asian Type (D_1)
  - ✻ Atlantic Type (D_2)


Q
D2
D1
C
B
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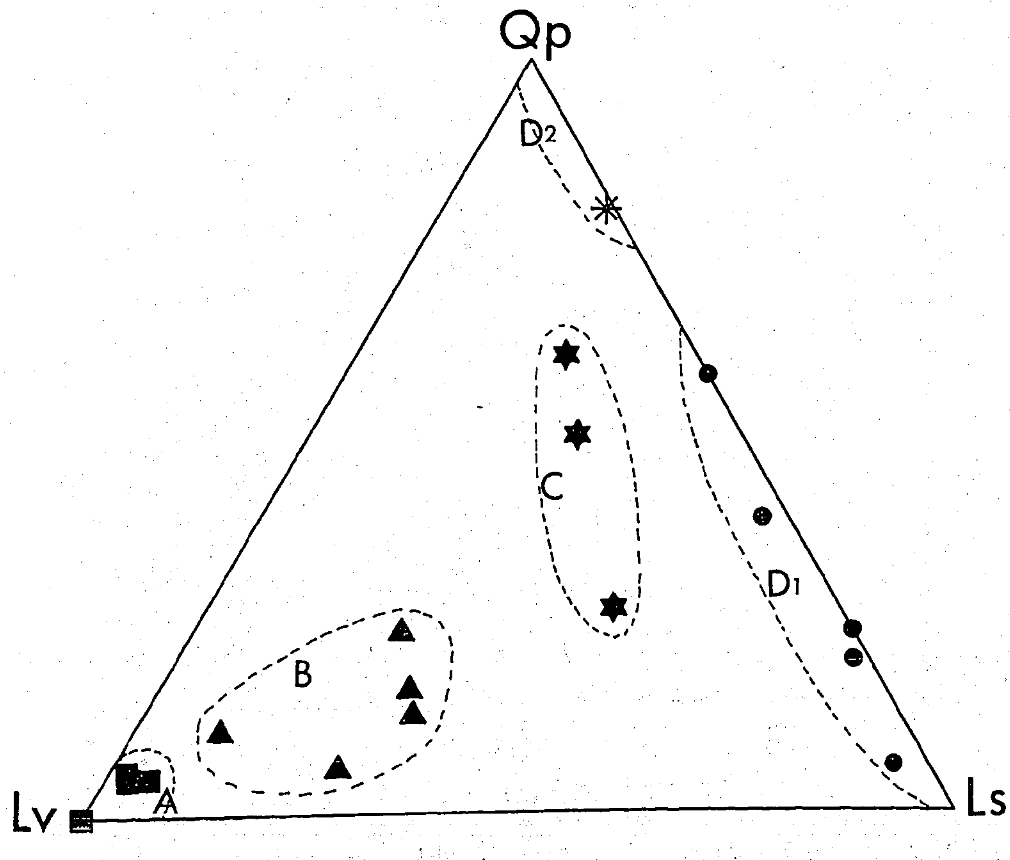
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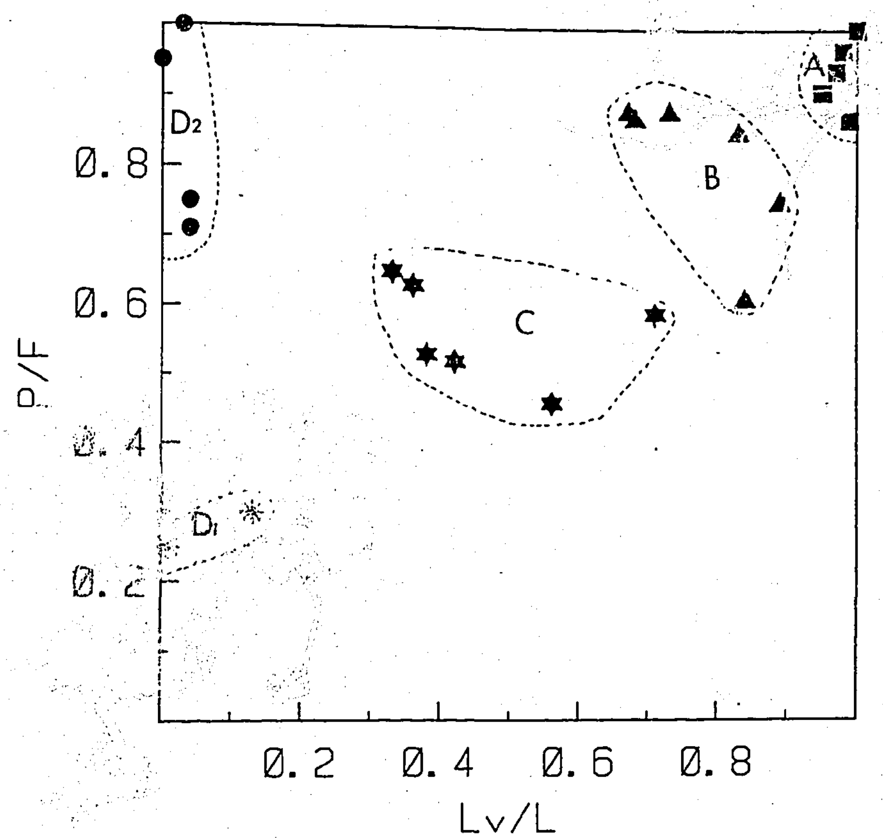


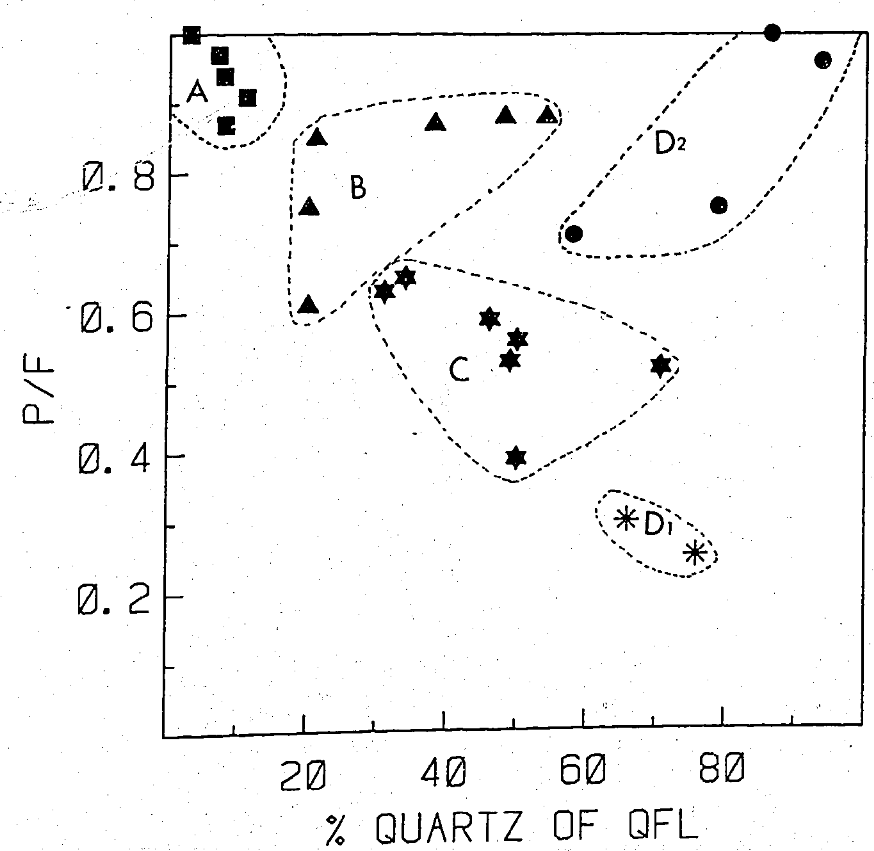


Figure 7.3 P/F versus Lv/L, and P/F versus Quartz plots (Data from Table 7.4). Symbols and fields as in Figure 7.2. Note the marked difference in the P/F ratio between the Atlantic and East-Asian type arenites.

Table 7.5 Detrital mineralogical characteristics of arenites and sands from various tectonic settings*

	N		Q	F	L	Qp	Lv	Ls	P/F	Lv/L
Oceanic Island Arc	212	X̄	7	31	62	4	93	3	0.94	0.98
		±L	0.2	0.7	1.2	0.1	2.3	0.1	0.02	0.02
Continental Island Arc	308	X̄	34	30	36	18	59	23	0.81	0.75
		±L	0.6	0.5	0.4	0.5	1.0	0.5	0.01	0.01
Andean Type	202	X̄	45	40	15	45	21	34	0.58	0.39
		±L	0.7	0.7	0.4	1.8	0.7	1.2	0.01	0.01
Passive Margin										
East Asian Type#	52	X̄	74	13	13	29	3	68	0.81	.03
		±L	2.2	1.4	0.7	1.4	0.2	3.9	0.02	-
Atlantic Type##	184	X̄	74	19	7	80	1	19	0.26	.02
		±L	5.3	1.1	0.3	6.4	0.7	6.5	0.02	-

Notes:

N Number of samples

* Weighted mean (X̄) from Table 7.4; uncertainties (±L) represent 95% confidence limits on the means

\# Data from 19-23 of Table 7.4

\## Data from 24-25 of Table 7.4; QpLvLs adopted from QpLvmLsm of Ingersoll and Suczek (1979) field (Figure 7.2). However the QpLvLs plot shows that most Atlantic type samples plot near the Qp pole whereas the East-Asian type samples plot near the Ls pole (Figure 7.2; also Ingersoll and Suczek, 1979). (The Bendigo suite data are not plotted on the QpLvLs plot of Figure 7.2, because of the extremely small fraction of these modes in the graywackes). The P/F ratio discriminates between East-Asian and Atlantic type sands (Table 7.4; Figure 7.3). The Atlantic type sands contain common K-feldspar because of their derivation from the craton and thus have a low P/F ratio. In contrast, most feldspar is plagioclase in East-Asian type sands because of their derivation from orogenic zones, and thus have a high P/F ratio.

The data derived from this study and from literature shows that detrital characteristics can be related to the tectonic setting of the basin (Table 7.5). The QFL, QpLvLs, P/F and Lv/L parameters successfully discriminate oceanic island arc, continental island arc and Andean type settings. The P/F ratio is also very useful in discriminating between East-Asian and Atlantic type arenites. However, complexities can arise when detritus is mixed from various sources. More work is also needed to characterise passive margin type arenites.

7.5.2 Mudrocks

How can mudrock mineralogy be related to the tectonic setting of sedimentary basins? Although in modern ocean basins the distribution of clay minerals has been related to climatic conditions of the adjacent land mass (Griffin et al. 1968; Rateev et al. 1968), it has been contended that the mineralogy of mud and mudrocks is controlled by the source rock and the climate at the provenance (Weaver 1978; Potter et al. 1980; Blatt et al. 1980). Source rocks and weathering are dependant on the tectonic setting of the sedimentary basin (Section 7.2). The present attempt to characterise mudrocks on the basis of mineralogy, is an extension of the study of the associated graywackes (Section 7.5.1.).

The mudrock suites of eastern Australia were grouped into various tectonic settings, the mean values of the mineralogical parameters for each tectonic setting are given in Table 7.6. A plot of phyllosilicate content versus the phyllosilicate/feldspar ratio shows that there is an overlap in the characteristics of mudrocks (Figure 7.4), but some useful generalisations can be made from the data. The mudrocks of the oceanic

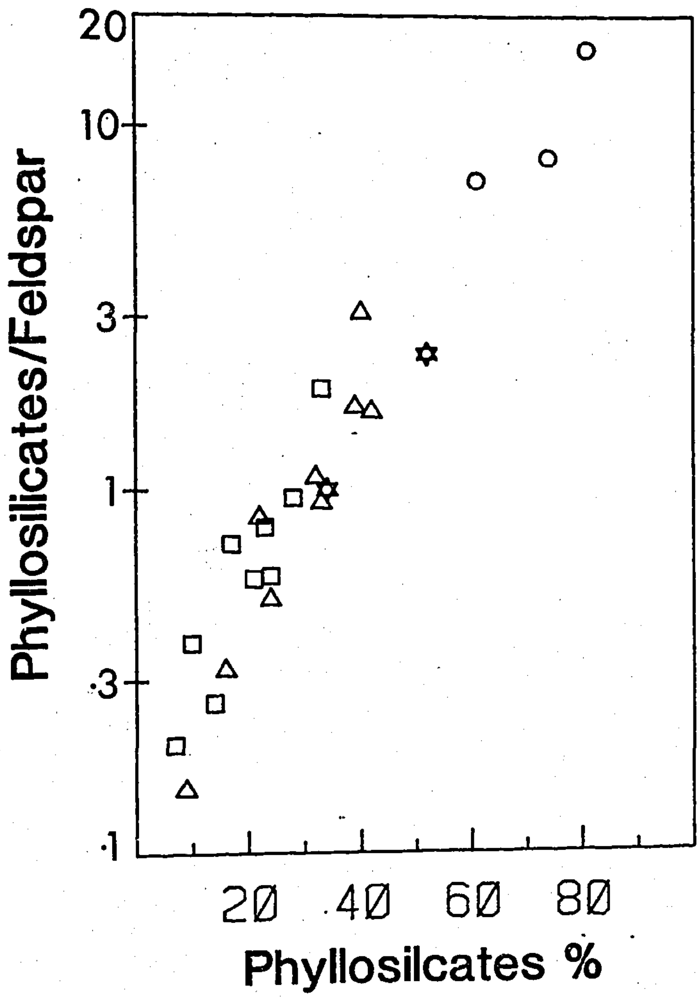


Figure 7.4 Plot of phyllosilicate versus the phyllosilicate/feldspar ratio for mudrock suites of eastern Australia. Note the overlapping of fields of various suites, but the linear relation suggests an increase in phyllosilicates with the decrease in feldspar. Also note log-scale along the Y-axis.

□	Tamworth suite
△	Hill End suite
✡	Hodgkinson suite
○	Bendigo & Cookman suites

Table 7.6 Mineralogical Characteristics of Mudrocks of Various Tectonic Settings*

	N		Quartz#	Feldspar#	ΣPhyllosilicates#	ΣPhyllosilicates/Feldspar ψ	ΣPhyllosilicates/Quartz ψ	Mudrock
Oceanic** Island Arc	9	$\bar{X}$	46	32	20	0.69	0.47	Tectic Mud.
		$\pm L$	8	8	6	0.4	0.2	
Continental Island Arc**	9	$\bar{X}$	35	33	28	1.13	0.79	Tectic to Phyllo-tectic Mudrocks
		$\pm L$	5	11	9	0.6	0.3	
Andean Type**	2	$\bar{X}$	26	28	41	1.68	1.68	Phyllo-tectic Mudrocks
Passive Margin**	3	$\bar{X}$	17	8	76	10.5	4.6	Phyllic Mudrocks

Notes:

* Mean values ($\bar{X}$); uncertainties ($\pm L$) represent 95% confidence limits on means

N Number of samples

\# In percent

ψ Means of the individual ratios

** Data source (Table 5.1): Oceanic Island Arc - Tamworth Suite
Continental Island Arc - Hill End Suite
Andean Type - Hodgkinson Suite
Passive Margin - Bendigo and Cookman Suites

and continental island arcs contain abundant feldspar, and in general are low in phyllosilicates, and phyllosilicate/feldspar ratio, suggesting volcanic sources and low weathering conditions. Distinction between oceanic and continental island arc mudrocks is not perfect, though the former are mainly tectic type mudrocks and the latter range from the tectic to phyllo-tectic type of mudrocks. The Andean type mudrocks are also of the phyllo-tectic type. The data is insufficient, but probably they can be discriminated from the continental island arc types by their high phyllosilicate/quartz ratio (Table 7.6). The passive margin mudrocks are characterised by a high phyllosilicate content, high phyllosilicate/feldspar ratio and low feldspar and quartz content, indicating their recycled nature and the high weathering conditions in the source region. The mudrocks are of the phyllic type.

The above inferences are only tentative because of the small data set (specially in the Andean and passive margin type settings), and the lack of comparable data on the whole rock mineralogy of mudrocks in other areas. However, the approach is reasonable and worth pursuing. Suchecki et al. (1977) following a similar approach, have related clay mineralogy of the <2μm silicate fraction to the Cambro-Ordovician continental margin of Western Newfoundland.

7.6 RESIDENCE TIME OF ELEMENTS

During sedimentary cycles, the chemical elements are redistributed in various rock types, transferred into clastics without much change, lost in solution or sometimes gained. The behaviour of an element during the sedimentary cycle can be judged to some extent by its residence time in sea water. The residence time of an element is defined as the ratio of the total quantity of the element in seawater to its rate of river input (Holland, 1978).

McLennan (1981b) has proposed a plot (Figure 7.5) of the log residence times of elements versus the log ratio of concentration in seawater/concentration in the upper continental crust (log[SW]/[UC]), which suggests that elements like Na, Ca, Sr, Rb, K, and B have high residence time and high log [SW]/[UC]. These elements are significantly modified during sedimentary processes (Chapter 7). On the other hand, elements with a low log [SW]/[UC] ratio have low residence times and thus are good indicators of source rock and tectonic settings. These

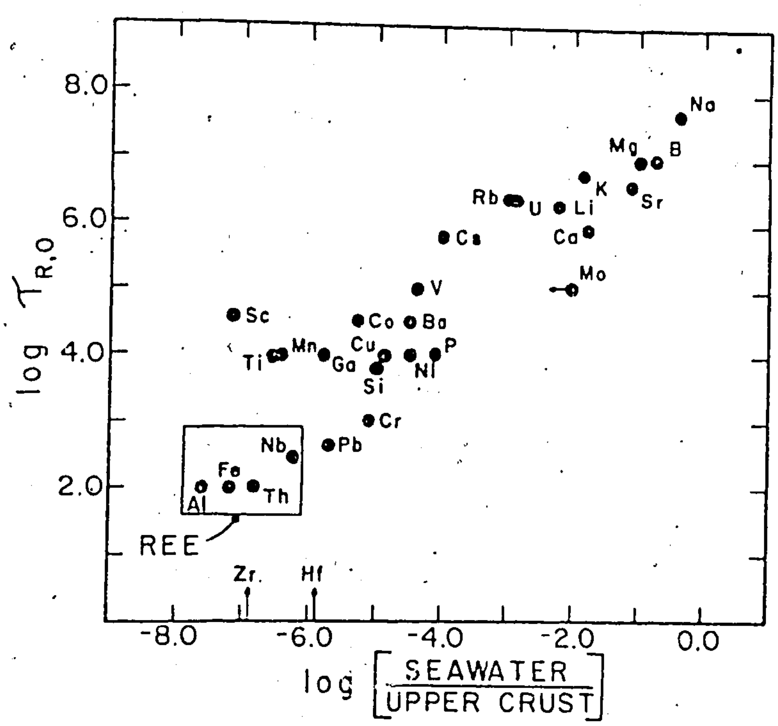


Figure 7.5 Plot of log residence time in sea water (log $\tau_{R,O}$) versus log [concentration in seawater/concentration in upper continental crust] for elements (after McLennan, 1981b).

elements, which include the Ti-group (Ti, Zr, Hf), Al-groups (Al, Ga), REE, Y, Th, Sc, Fe and Nb, are mainly redistributed amongst the clastic lithologies. Elements like V, Cr, Ni, Co and Cu have intermediate characteristics. In coarse-medium grained rocks, they may indicate the source rock type, but in fine grained sedimentary rocks (mudrocks), they may be significantly enriched due to their association with phyllosilicates.

7.7 TECTONIC SETTING DISCRIMINATION USING MAJOR ELEMENT GEOCHEMISTRY OF ARENITES

7.7.1 Geochemical Parameters

The major elements in arenites undergo some changes during sedimentary processes, e.g., in most cases SiO_2 is enriched, and Na_2O and CaO are lost in solution. Thus, the bulk major element chemistry gives clue of the provenance as well as weathering conditions, both of which are controlled by the tectonic setting of the basin.

Published analyses of arenites and modern sands are compared with the present data of graywacke suites from eastern Australia and grouped into various tectonic settings (Tables 7.7 to 7.10). The tectonic setting of some of these published suites is not well constrained. The most discriminating parameters are (total Fe as Fe_2O_3) $Fe_2O_3^t$+MgO %, TiO_2 %, and Al_2O_3/SiO_2, K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ ratios. Fe and Ti are useful because of their low mobility. Although Mg has a high residence time in sea water, it has been suggested to remain unchanged in graywackes during burial because of the low permeability of these rocks (Blatt et al. 1980).

Plots of $Fe_2O_3^t$+MgO versus TiO_2, Al_2O_3/SiO_2, K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ show that though the overlapping of fields occur in most plots, arenites representing each tectonic setting occupy quite distinct fields (Figure 7.6). In general, there is a decrease in $Fe_2O_3^t$+MgO, TiO_2, Al_2O_3/SiO_2 and an increase in K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ as the nature of arenites changes from oceanic island arc to continental island arc to Andean type to the passive margin type.

The oceanic island arc arenites are most distinctive and are characterised by high Fe_2O^t+MgO (range 8-14%); high TiO_2 (range 0.8-1.4%); high Al_2O_3/SiO_2 (range 0.24 - 0.33); low K_2O/Na_2O (range 0.2-0.4); and low $Al_2O_3/(CaO+Na_2O)$ (range 1-2) (Figure 7.6). Examples of

Table 7.7 Average Chemical Composition of Arenites and Sands of the Oceanic Island Arc Tectonic Setting#

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	59.20	57.56	59.22	62.00	58.49	58.0	57.34	66.19	63.45
TiO_2	0.87	1.17	0.93	-	1.41	0.88	1.06	0.60	0.83
Al_2O_3	16.37	16.53	20.37	15.00	16.95	18.1	16.49	15.32	17.50
Fe_2O_3	1.73	1.74	2.68	7.7*	1.31	2.3	8.82*	8.69*	6.31*
FeO	5.02	7.69	2.62	-	7.70	4.6	-	-	-
MnO	0.26	0.17	0.09	-	0.13	0.11	0.14	0.14	0.12
MgO	2.74	3.9	2.91	3.8	4.06	3.28	4.87	4.80	2.70
CaO	7.62	5.28	6.53	6.7	3.67	5.93	5.14	5.06	2.67
Na_2O	4.78	5.05	2.42	3.8	4.60	4.00	4.13	4.07	4.88
K_2O	1.16	0.70	1.91	1.4	1.67	2.58	1.75	1.72	1.33
P_2O_5	0.18	0.24	0.31	-	0.31	0.22	0.29	0.29	0.20
$Fe_2O_3^*$+MgO	10.03	14.18	8.5	11.5	13.92	13.34	13.69	8.7	7.01
Al_2O_3/SiO_2	0.28	0.29	0.34	0.24	0.29	0.31	0.29	0.23	0.28
K_2O/Na_2O	0.24	0.14	0.78	0.37	0.36	0.65	0.42	0.22	0.23
$Al_2O_3/(Na_2O+CaO)$	1.30	1.60	2.28	1.43	2.05	1.82	1.77	1.91	2.31

\# All averages are recalculated on volatile free basis.
* Total Fe as Fe_2O_3.
(1) Tamworth suite, present work, (N= 11).
(2) Baldwin Formation (Chappell, 1968) (N = 10)
(3) Napere graywacke, Aure Trough, Papua New Guinea (Edwards, 1950), (N=1).
(4) Fore-arc sand (Maynard et al., 1980) (N = 9).
(5) Volcanic graywacke, Taringatura, New Zealand (Coombs, 1954) (N=1).
(6) Jurassic tuffaceous graywacke, Oregon (Dickinson, 1962) (N=6).
(7) Central Saridina graywacke, Italy (Ricci and Sabatini, 1976) (N=29).
(8) Uyak Complex graywacke, Alaska (Connelly, 1978) (N=11).
(9) Cape Current graywackes, Alaska (Connelly, 1978) (N=4).
N Number of samples.

Table 7.8 Average Chemical Composition of Arenites and Sands of the Continental Island Arc Tectonic Setting#

	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)
SiO_2	74.38	69.0	71.5	66.6	72.92	70.1	73.5	69.63	68.69
TiO_2	0.66	-	0.6	0.69	0.61	0.5	0.6	0.63	0.83
Al_2O_3	12.25	14.0	14.7	15.9	12.29	14.0	14.8	14.09	14.41
Fe_2O_3	1.04	4.5*	1.0	2.2	5.73*	1.2	1.5	1.67	4.87*
FeO	2.96	-	2.6	3.1	-	3.1	2.9	3.65	-
MnO	0.08	-	0.1	0.04	0.11	0.1	0.1	0.10	0.10
MgO	1.49	2.4	1.2	2.8	1.72	2.3	1.6	2.19	2.07
CaO	2.66	4.4	1.9	3.0	2.49	2.5	1.0	2.61	3.52
Na_2O	2.52	3.6	3.6	3.0	3.15	3.7	2.5	3.02	3.00
K_2O	1.82	2.0	2.5	2.4	0.83	1.8	1.4	2.09	2.18
P_2O_5	0.12	-	0.2	0.19	0.17	0.1	0.1	0.21	-
$Fe_2O_3^*$+MgO	5.81	6.9	5.09	5.64	7.45	6.94	6.32	7.91	6.94
Al_2O_3/SiO_2	0.16	0.20	0.21	0.24	0.17	0.20	0.20	0.21	0.21
K_2O/Na_2O	0.72	0.55	0.69	0.80	0.26	0.48	0.56	0.69	0.73
$Al_2O_3/(Na_2O+CaO)$	2.36	1.75	2.67	2.65	2.18	2.28	3.79	2.76	2.21

\# All averages recalculated on volatile free basis
* Total Fe as Fe_2O_3
(10) Hill End suite, present work (N=29)
(11) Modern Back -arc Sand (Maynard et al. 1980) (N=27)
(12) Alpine Facies, New Zealand (Reed, 1957) (N=14)
(13) Middle Eocene Tyee graywackes, Oregon (Coleman, 1972) (N=3)
(14) Kodiak Formation graywackes, Alaska (Connelly, 1978) (N=4)
(15) Franciscan graywackes, California (Bailey et al. 1964) (N=21)
(16) Culm graywackes, Harz Mountains (Huckenholz, 1963) (N=20)
(17) Average graywacke (Pettijohn, 1963) (N=61)
(18) Average Columbia river sand (Whetten et al. 1969) (N=68)
N Number of samples

Table 7.9 Average Chemical Composition of Arenites and Sands of the Andean type Tectonic Setting#

	(19)	(20)	(21)	(22)	(23)	(24)	(25)
SiO_2	78.55	69.0	71.98	71.66	72.72	80.18	72.96
TiO_2	0.45	-	0.45	0.39	0.66	0.31	0.51
Al_2O_3	11.08	15.0	13.27	14.13	12.97	9.04	14.76
Fe_2O_3	0.64	4.1*	1.84	1.75	5.12*	1.56	0.73
FeO	2.00	-	1.71	1.17	-	0.73	2.32
MnO	0.05	-	0.06	0.05	0.08	0.28	0.05
MgO	0.93	1.9	1.79	1.24	1.55	0.52	0.69
CaO	1.19	4.2	2.76	3.17	1.65	2.81	1.59
Na_2O	2.32	3.8	3.17	3.05	2.84	1.56	2.62
K_2O	2.71	2.6	2.84	3.28	2.27	2.91	3.67
P_2O_5	0.08	-	0.14	0.06	-	0.1	0.03
Fe_2O_3*+MgO	3.79	6.0	5.5	4.2	6.67	2.89	3.99
Al_2O_3/SiO_2	0.14	0.22	0.18	0.20	0.18	0.11	0.21
K_2O/Na_2O	1.17	0.68	0.89	1.08	0.80	1.86	1.40
$Al_2O_3/(Na_2O+CaO)$	3.15	1.88	2.23	2.27	2.88	2.07	3.51

\# All averages recalculated on volatile free basis
* Total Fe as Fe_2O_3

(19) Hodgkinson suite, present work (N=10)
(20) Modern Leading Edge sand (Maynard et al. 1980) (N=15)
(21) Eocene-Oligocene sandstones Santa Ynez, California (Van de Kamp et al. 1976) (N=26)
(22) Holocene sand, Salton Basin, California (Van de Kamp et al. 1976) (N=6)
(23) Rensselaer graywacke, New York (Ondrick and Griffiths, 1969) (N=119)
(24) Average Askose (Pettijohn, 1963) (N=32)
(25) Modern rhyolite sand (Webb and Potter, 1969) (N=4)

N Number of Samples

Table 7.10 Average Chemical Composition of Arenites and Sands of the Passive Margin Tectonic Setting#

	(26)	(27)	(28)	(29)	(30)	(31)	(32)	(33)	(34)
SiO_2	85.69	87.80	78.0	88.82	74.23	86.25	72.90	96.60	71.50
TiO_2	0.50	0.28	-	0.39	0.69	0.76	0.33	0.20	1.21
Al_2O_3	7.53	8.07	9.8	5.88	12.55	6.17	8.93	1.10	13.40
Fe_2O_3	0.56	0.54	2.9*	0.39	0.91	1.52*	4.19	0.40	1.30
FeO	1.63	0.49	-	1.35	3.79	-	1.54	0.20	3.60
MnO	0.02	0.03	-	0.02	0.06	-	0.11	-	0.10
MgO	1.01	0.40	1.3	0.83	2.39	1.17	2.65	0.10	1.00
CaO	0.19	0.10	4.1	0.39	0.90	1.07	6.84	1.60	1.00
Na_2O	1.39	0.91	1.9	0.69	1.51	1.03	0.99	0.10	2.80
K_2O	1.33	1.30	2.0	1.18	2.76	1.99	1.43	0.20	1.60
P_2O_5	0.13	0.08	-	0.09	0.20	0.08	0.11	-	0.14
Fe_2O_3*+Mgo	3.38	1.48	4.2	2.72	7.51	2.69	8.55	0.62	6.30
Al_2O_3/SiO_2	0.09	0.09	0.13	0.07	0.17	0.08	0.12	.001	0.19
K_2O/Na_2O	0.96	1.42	1.2	1.71	1.82	1.93	1.44	2.0	0.57
$Al_2O_3/(Na_2O+CaO)$	4.76	7.99	1.6	5.4	5.23	2.93	1.14	0.64	3.52

\# All averages recalculated on volatile free basis
* Total Fe as Fe_2O_3

(26) Bendigo suite, present work (N=8)
(27) Cookman suite, present work (N=7)
(28) Modern Trailing Edge sand (Maynard et al. 1980) (N=29)
(29) Quartz-rich graywacke, mainly from Tasman Geosyncline (Crook, 1974) (N=24)
(30) Greenland Graywacke, New Zealand (Nathan, 1976) (N=6)
(31) Cambrian-Quaternary sand, North American platform (Ronov and Migdisov, 1971)
(32) Average Lithic-Arenite (Pettijohn, 1963) (N=20)
(33) Average Quartz-Arenite (Pettijohn, 1963) (N=26)
(34) Greenish-grey Charny Sandstone, Canada (Middleton, 1972) (N=4)
N Number of samples

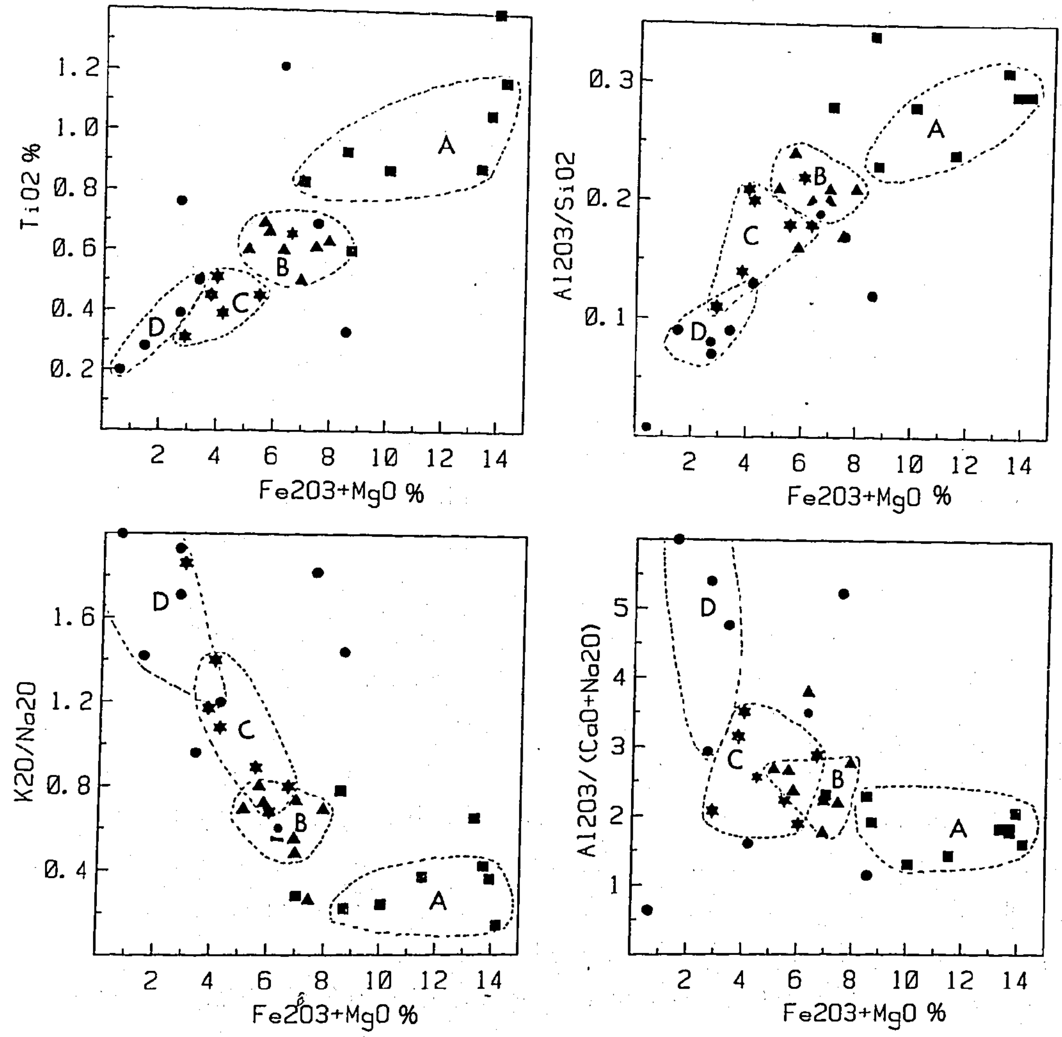


Figure 7.6 Major element tectonic setting discrimination plots for arenites - plot of TiO_2, Al_2O_3/SiO_2, K_2O/Na_2O, and $Al_2O_3/(CaO+Na_2O)$ versus Fe_2O_3+MgO (Total Fe as Fe_2O_3). Data for various arenites are from Tables 7.7 to 7.10. Note the excellent discrimination of various arenites and sands.

- ■ Oceanic Island Arc (A)
- ▲ Continental Island Arc (B)
- ✱ Andean Type (C)
- ● Passive Margins (D)

arenites of this tectonic setting are common in the Circum-Pacific region (Table 7.7), they are dominantly derived from andesites. The modern fore-arc sands are geochemically similar to other arenites of this tectonic setting. An oceanic island arc setting is assigned to the Uyak Complex and the Cape Current arenites of Alaska (Connelly, 1976). On most major element discriminatory plots, these fall at the boundary of oceanic and continental island arc fields.

Continental island arc arenites are most clearly discriminated from oceanic island arc types by their lower $Fe_2O_3{}^t$+MgO (range 5-8%); lower TiO_2 (range 0.5 - 0.7%); lower Al_2O_3/SiO_2 (range 0.15 - 0.20); higher K_2O/Na_2O (range 0.4 - 0.8); and higher $Al_2O_3/(CaO+Na_2O)$ (range 0.5-2.5) (Figure 7.6). Examples of arenites of this tectonic setting are also common in the Circum-Pacific region (Table 7.8). Deep-sea sands of the back-arc region can be assigned to this category on the basis of similar geochemical characteristics. The Culm graywackes of Germany (Hüchenholz, 1963); the Franciscan graywackes of California (Bailey et al. 1964); the modern Columbia river sands (Whetten et al. 1969) and the average graywacke (Pettijohn, 1963) are also grouped into this category. These arenites are mainly derived from a wide range of sources but have a signifcant contribution from felsic volcanic rocks.

Arenites of the Andean type tectonic setting can be discriminated from those of the continental island arc by their lower $Fe_2O_3{}^t$+MgO (range 2-5%); lower TiO_2 (range 0.25-0.45%); lower Al_2O_3/SiO_2 (range 0.1 - 0.2); and higher K_2O/Na_2O (Figure 7.6). These arenites are mainly derived from granite-gneisses and examples are Tertiary arkose of Santa Ynez (Van de Kamp et al. 1976); Rensselaer graywackes, New York (?) (Ondrick and Griffiths, 1969); modern rhyolitic sands of Mexico (Webb and Potter, 1969); and Holocene Sands of Salton Basin, California (Van de Kamp et al. 1976). The average modern deep sea sands of the leading edge are similar in geochemical characteristics to arenites of this category, (Maynard et al. 1980) except for being slightly higher in Al_2O_3/SiO_2 and lower K_2O/Na_2O ratios. The average arkose has geochemical characteristics similar to arenites of this class, except for being higher in K_2O/Na_2O ratio and lower in Al_2O_3/SiO_2 ratios. The problematic Cambrian Charny Sandstone of Quebec has also some characteristics, such as $Fe_2O_3{}^t$+MgO; Al_2O/SiO_2 and $Al_2O_3/(CaO+Na_2O)$ ratios, similar to the arenites and sands of this category (see discusssion on Charny Sandstone in Section 7.7.2).

Table 7.11 Average Chemical Composition of Arenites of Various Tectonic Settings#

	Oceanic Island Arc[1]		Continental Island Arc[2]		Andean Type[3]		Passive Margin[4]	
	$\bar{X}$	±sd	$\bar{X}$	±sd	$\bar{X}$	±sd	$\bar{X}$	±sd
SiO_2	58.83	1.6	70.69	2.6	73.86	4.0	81.95	6.2
TiO_2	1.06	0.2	0.64	0.1	0.46	0.1	0.49	0.2
Al_2O_3	17.11	1.7	14.04	1.1	12.89	2.1	8.41	2.2
Fe_2O_3	1.95	0.5	1.43	0.5	1.30	0.5	1.32	1.6
FeO	5.52	2.1	3.05	0.4	1.58	0.9	1.76	1.2
MnO	0.15	-	0.10	-	0.10	-	0.05	-
MgO	3.65	0.7	1.97	0.5	1.23	0.5	1.39	0.8
CaO	5.83	1.3	2.68	0.9	2.48	1.0	1.89	2.3
Na_2O	4.10	0.8	3.12	0.4	2.77	0.7	1.07	0.6
K_2O	1.60	0.6	1.89	0.5	2.90	0.5	1.71	0.6
P_2O_5	0.26	0.1	0.16	0.1	0.09	-	0.12	-
$Fe_2O_3^*$+MgO	11.73		6.79		4.63		2.89$^{\psi}$	
Al_2O_3/SiO_2	0.29		0.20		0.18		0.10	
K_2O/Na_2O	0.39		0.61		0.99		1.60	
$Al_2O_3/(CaO+Na_2O)$	1.72		2.42		2.56		4.15$^{\psi\psi}$	

Notes

All averages ($\bar{X}$) on volatile free basis. Uncertainties (sd) represent 1 standard deviation

* Total Fe as Fe_2O_3

(1) Unweighted average of 1-7 of Table 7.7

(2) Unweighted average of 10-18 of Table 7.8

(3) Unweighted average of 19-25 of Table 7.9

(4) Unweighted average of 26-32 of Table 7.10

ψ Typical value - calculated without 30 & 32 of Table 7.10

$\psi\psi$ Typical value - average of individual ratios from Table 7.10

Arenites of the passive margins exhibit a large variation in their characteristics, especially in the K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ ratios (Figure 7.6). Their characteristics slightly overlap with those of Andean type arenites but they can be discriminated by their lower $Fe_2O_3{}^t$+MgO, Al_2O_3/SiO_2 and higher K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ ratios (Figure 7.6). All these features indicate their highly recycled nature. Examples of this tectonic setting are common in southeastern Australia, New Zealand (Nathan, 1976) and North America (Schwab, 1975). The Ordovician graywackes of the Greenland Group, New Zealand (Nathan, 1976) are significantly high in $Fe_2O_3{}^t$+ MgO, TiO_2 and Al_2O_3/SiO ratio. However their K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ ratios are typical of arenites of this class. Modern deep sea sands of the trailing margins have geochemical characteristics similar to arenites of this class, except for being lower in $Al_2O_3/(CaO+Na_2O)$ ratio, probably due to the presence of biogenic carbonates. Except for having higher MgO and CaO content, the average lithic arenite (Pettijohn, 1963) has geochemical characteristics quite similar to arenites of this tectonic setting. The average Cambrian-Quaternary sand of the North American platform (Ronov and Migdisov, 1971) is also similar in composition to the arenites of this tectonic setting, except for being higher in TiO_2 and CaO. The average quartz-arenite (Pettijohn, 1963) is an extremely fractionated example of this tectonic setting.

The average major element composition of arenites representing each tectonic setting is given in Table 7.11. The most discriminating parameters are $Fe_2O_3{}^t$+MgO; TiO_2 and Al_2O_3/SiO_2 and give excellent clues to the nature of the source rocks. The discriminating plots of these parameters are especially useful for medium grained arenites. The parameters may not hold good for very fine grained arenites.

7.7.2 Discriminant Function Analysis

Discriminant functions for sandstones were given by Middleton (1962) to distinguish the following tectonic settings: miogeosyncline, eugeosyncline and taphrogeosyncline. These tectonic regimes have since been shown to be inadequate in describing the variation in basin types (Dickinson, 1974a). Geochemical discriminant functions have been developed to distinguish various graywacke suites in eastern Australia (Chapter 6). In this section, these discriminant functions have been

Table 7.12 Tectonic Setting Classification of Various Arenite Suites on the Basis of Discriminant Analysis

Expected Tectonic Setting	Discriminant Scores		Assigned to
	Function I	Function II	
Oceanic Island Arc			
Tamworth Suite	3.22	0.53	Oceanic Island Arc
Baldwin Formation	4.12	0.62	Oceanic Island Arc
Aure Trough, PNG	1.98	3.70	Oceanic Island Arc
Modern Fore-arc Sand	2.62	-1.50	Oceanic Island Arc
Taringatura, New Zealand	4.04	0.79	Oceanic Island Arc
Jurassic Oregon	3.32	1.42	Oceanic Island Arc
Saridina Italy	3.36	0.97	Oceanic Island Arc
Uyak Complex, Alaska	2.01	-1.07	Oceanic Island Arc
Cape Current, Alaska	2.66	-0.30	?Oceanic Island Arc
Continental Island Arc			
Hill End Suite	-0.13	-0.35	Continental Island Arc
Modern Back-Arc Sand	1.40	-1.98	Continental Island Arc
Alpine Facies, New Zealand	1.14	-0.66	Continental Island Arc
Tyee, Oregon	1.20	-1.38	Continental Island Arc
Kodiak, Alaska	0.78	-0.14	Continental Island Arc
Franciscan, California	0.96	0.55	Continental Island Arc
Harz, Germany	-0.12	0.92	Continental Island Arc
Average Graywacke	1.14	0.17	Continental Island Arc
Columbia River Sand	0.40	0.05	Continental Island Arc
Andean Type			
Hodgkinson Suite	-0.88	-1.89	Andean Type
Modern Leading Edge Sand	1.47	-4.91	Andean Type
Santa Ynez, California#	0.48	-0.57	Continental Island Arc
Salton Basin Sand, California	-0.20	-3.00	Andean Type
Rensselaer, New York	1.01	-5.35	Andean Type
Average Arkose	-1.90	-0.98	Andean Type
Modern Ryolitic Sand	-0.76	-4.21	Andean Type
Passive Margin			
Bendigo Suite	-1.65	1.58	Passive Margin
Quartz-rich graywacke	-2.56	0.26	Passive Margin
Modern Trailing Edge Sand#	-0.13	-2.98	Andean Type
Cookman Suite	-2.67	0.20	Passive Margin
Greenland, New Zealand	-1.57	2.27	Passive Margin
Cambrian-Quaternary Sand	-1.25	2.58	Passive Margin
Av. Lithic Arenite	-1.01	2.67	Passive Margin
Charny Sandstone, Quebec#	-0.52	0.13	Continental Island Arc
Av. Quartz Arenite	-3.21	1.64	Passive Margin

#Misclassified

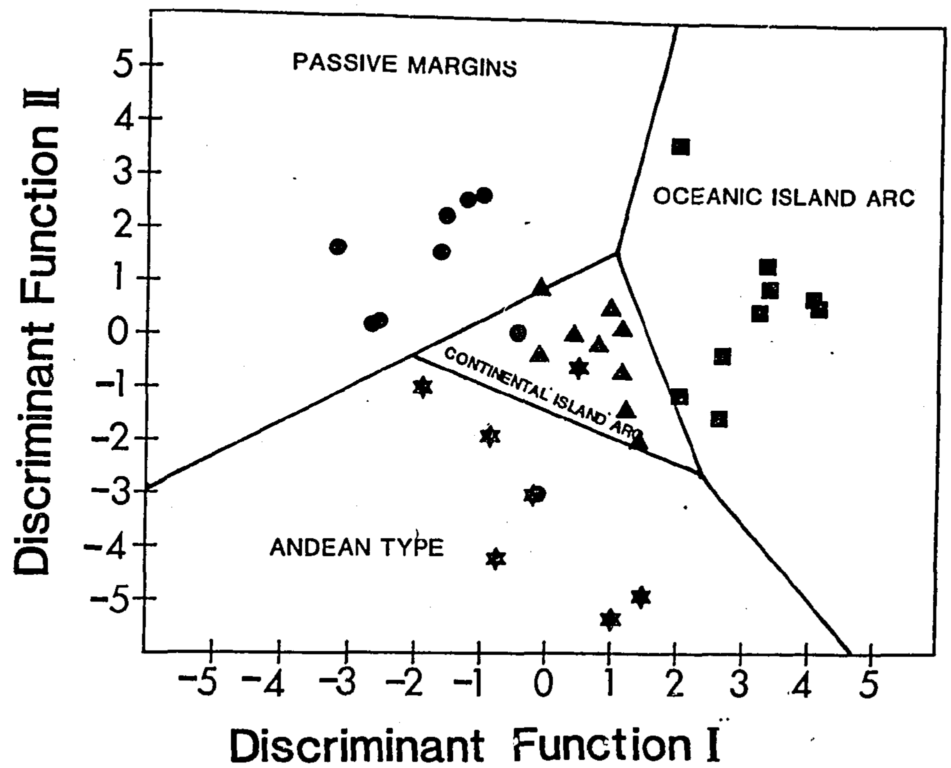


Figure 7.7 Plot of discriminant scores along Function I versus II for various arenites and sands (data from Table 7.12). Note the excellent discrimination of various tectonic settings. The territorial map is adopted from Figure 6.12, and is based on data from eastern Australia.

- Oceanic Island Arc
- Continental Island Arc
- Andean Type
- Passive Margins

used to assign tectonic settings to the published analyses of arenites (Tables 7.7 to 7.10). The first two discriminant functions are the most significant (Table 6.3). Discriminant scores for the published analyses were calculated using the unstandardised function coefficients (Table 6.4). The results are given in Table 7.12, and plotted on the territorial map obtained through the computer using data of eastern Australia (Figure 7.7).

Various arenites, mainly from the Circum-Pacific region, plot in the field of the Tamworth Trough suite. Modern sands from fore-arc regions also plot in this field. This field is characteristic of the oceanic island arc tectonic setting. The Uyak Complex graywackes plot at the boundary of the oceanic and continental island arcs.

Modern back-arc sands; Alpine facies graywackes, New Zealand; Tyee graywackes, Oregon; Kodiak sandstones, Alaska; Franciscan graywackes, California; Culm graywackes, Germany; Columbia river sand; and the average graywacke plot in the field occupied by the Hill End suite samples. This territory is characteristic of the continental island arc type of arenites.

Modern sands from leading edges; Salton Basin sand, California; Rensselaer graywackes, New York; modern rhyolitic sands, Mexico; and average arkose plot in the field of the Hodgkinson suite graywackes. This field is characteristic of the Andean type of arenites (Figure 7.7). There is one misclassification in this group. The Santa Ynez arkoses of California are mainly derived from granites and gneisses of the uplifted basement provenance (Van de Kamp et al. 1976; Dickinson and Suczek, 1979) and can be assigned to the Andean type tectonic setting, as also shown by the geochemical parameters (Figure 7.6). However, on the basis of discriminant functions, they are assigned to the continental island arc type of setting. It has been suggested that the volcanics present in the source region were preferentially lost in solution during the Santa Ynez sedimentation (Van de Kamp et al. 1976). Probably, this volcanic component which is otherwise difficult to detect, causes these arenites to fall in the continental island arc field.

The average quartz-rich graywacke; Greenland graywackes, New Zealand; average Cambrian-Quaternary sands, North American platform; the average lithic arenite; and the average quartz arenite plot in the field occupied by the Bendigo and Cookman suite samples (Figure 7.7).

This territory characterises the passive continental margins. However, modern deep sea sands of the trailing margins plot in the Andean field. This may be due to the high CaO content in modern sands and suggests that there may be differences in the characteristics of modern and ancient arenites within one tectonic setting.

The genesis of the Charny Sandstone of Quebec has been a matter of discussion in recent years. Granites and gneisses have been inferred to form the source rocks for these sediments (Weber and Middleton, 1961; Middleton, 1972). According to plate tectonic models, the Charny Sandstone were deposited on the passive margins (R.G. Walker, per. com.). The high TiO_2 and $Fe_2O_3^t$+MgO content of these sandstones, indicates some contribution from volcanic sources, and probably causes the grouping of these samples with the continental island arc arenites. Due to extensive post-depositional chemical changes (e.g. Ogunyomi et al. 1981), the original nature of these sediments may be difficult to decipher on the basis of major elements.

The results of the discriminant analysis are consistent with the tectonic setting discrimination achieved using geochemical parameters (Section 7.7.1). On the basis of discriminant analysis, about 90% of examples are correctly classified to their expected tectonic setting (Table 7.12). Thus, this approach is successful and rewarding. However, the disadvantage is that the unknown has to belong to one of the four settings. Also, as there could be transitions in the tectonic settings, an overlap of samples into various territorial fields will not be unexpected.

7.8 TECTONIC SETTING DISCRIMINATION USING MAJOR ELEMENT GEOCHEMISTRY OF MUDROCKS

There have been very few attempts to correlate the major element geochemistry of mudrocks to the provenance type. Bjørlykke (1974) has suggested that the $(Al_2O_3+K_2O)/(MgO+Na_2O)$ ratio can be used to detect the volcanic arc provenance in the Ordovician mudrocks of Norway. However, this ratio was found to be less discrimating in the present work. The behaviour of chemical elements is more complex, because of adsorption and fixation processes operating during the formation and diagenesis of mudrocks.

Figure 7.13 Average Chemical Composition of Mud and Mudrocks From Various Tectonic Settings and Estimates of Average Mudrock Compositions#

	Oceanic Island Arc					Continental Island Arc						
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
SiO_2	67.63	59.69	68.23	63.63	62.50	70.33	60.14	55.43	68.51	65.94	64.35	62.95
TiO_2	0.72	1.03	0.69	1.14	0.56	0.54	0.79	2.78	0.65	0.88	0.86	0.83
Al_2O_3	15.92	18.05	15.90	18.02	15.60	15.61	18.43	18.62	17.27	20.72	17.70	17.90
Fe_2O_3	2.86	2.23	2.36	-	4.52	1.96	3.80	2.78	1.74	1.69	2.68	2.99
FeO	2.77	4.26	4.91	7.41*	1.92	2.45	3.16	6.63	3.28	3.38	4.08	3.95
MnO	0.07	0.09	0.07	0.18	-	0.06	-	0.11	0.08	0.01	0.10	0.10
MgO	2.02	3.42	1.13	2.51	3.05	1.68	2.71	5.90	1.99	2.09	2.64	2.77
CaO	2.94	6.73	1.88	1.60	6.78	1.78	6.50	0.96	0.80	0.81	1.84	2.35
Na_2O	2.55	2.49	2.60	2.74	2.03	1.55	1.24	2.46	2.26	1.59	1.93	1.71
K_2O	2.34	1.71	2.04	2.62	3.05	3.91	3.05	4.17	3.37	2.62	3.61	3.84
P_2O_5	0.22	0.31	0.22	0.15	0.22	0.11	0.2	0.21	0.10	0.05	0.21	0.06
K_2O/Na_2O	0.92	0.69	0.78	0.96	1.50	2.52	2.45	1.70	1.49	1.65	1.87	2.25
$\frac{Al_2O_3}{(CaO+Na_2O)}$	2.90	1.96	3.55	3.36	1.77	4.68	2.38	5.43	5.64	8.63	4.71	4.42

\# All averages recalculated on volatile free basis
* Total Fe as FeO
N Number of samples
(1) Average Tamworth suite mudrock - present work (N = 9)
(2) Average mudrock, Aura Trough, Papua New Guinea (Edwards, 1950) - (3 samples, 1 analysis)
(3) Mesozoic Shale, Papua New Guniea (Van Moort, 1971) (N= 20)
(4) Average mud, Gulf of Paria (Hirst, 1962a,b) (N = 11)
(5) Average Mesozoic - Cenozoic Shale (Clarke, 1924)
(6) Average Hill End Suite mudrock - present work (N = 11)
(7) Average mudrock, Great Caucasus Geosyncline, (Ronov et al., 1966) (N = 455)
(8) Tanner mudrock, Harz Mountain, Germany (Huckenholz, 1963) (N= 1)
(9) Average Paleozoic-Mesozoic Geosynclinal mudrock, Japan (Katada et al., 1977) (N = 394)
(10) Average Wilcox Formation mudrock, Louisiana (Van Moort, 1971) (N = 19)
(11) Average Pelitic rock (Shaw, 1956) (N = 155)
(12) Average Worldwide Shale (Wedepohl, 1971).

	Andean Type					Passive Margin		
	(13)	(14)	(15)	(16)	(17)	(18)	(19)	(20)
SiO_2	66.20	61.69	63.62	64.80	59.0	64.13	63.06	63.60
TiO_2	0.66	0.90	1.02	0.86	0.9	0.83	0.86	1.06
Al_2O_3	19.11	18.82	20.44	17.66	17.8	20.64	18.83	23.71
Fe_2O_3	3.42	4.85	1.54	4.31	-	2.66	1.17	-
FeO	2.63	3.08	5.54	3.21	6.1*	2.97	5.76	4.54*
MnO	0.04	0.08	0.07	-	0.1	0.04	0.05	0.12
MgO	1.71	2.93	2.11	2.48	2.1	2.60	3.60	1.25
CaO	0.59	2.07	0.40	1.51	1.2	0.14	0.56	0.69
Na_2O	1.18	1.68	1.21	1.08	1.1	0.39	1.14	0.49
K_2O	4.33	3.76	3.85	3.88	3.5	5.35	4.79	4.43
P_2O_5	0.12	0.14	0.15	0.22	0.15	0.12	0.19	0.14
K_2O/Na_2O	3.65	2.23	3.18	3.6	3.18	15.13	4.21	9.04
$Al_2O_3/(Na_2O+CaO)$	10.79	5.02	12.70	6.82	7.74	38.94	11.08	20.09

* Total Fe as FeO
(13) Average Hodgkinson suite mudrock - present work (N = 2).
(14) Average Santa Ynez mudrock, California (Van de Kamp et al., 1976) (N = 13).
(15) Average Littleton Formation pelite. New Hampshire (Shaw, 1956) (N = 18).
(16) Average Paleozoic shale (Clarke, 1924).
(17) Average Post-Archean shale (McLennan, 1981b).
(18) Average Bendigo-Cookman suite mudrock - present work (N = 3).
(19) Average Ordovician Greenland mudrock, New Zealand (Nathan, 1976) (N = 5).
(20) Average Carboniferous Shale, Great Britain (Nicholls and Loring, 1962; Hirst and Kaye, 1971) (N = 19).

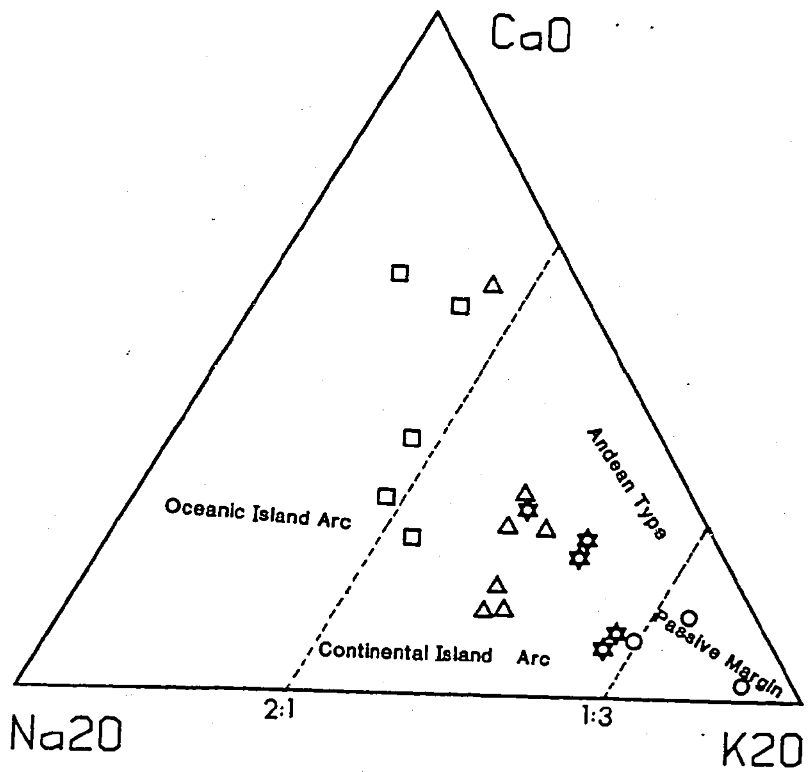


Figure 7.8 $CaO-Na_2O-K_2O$ plot of mudrocks for tectonic setting discrimination (data from Table 7.13).

□	Oceanic Island Arc
△	Continental Island Arc
✡	Andean Type
O	Passive Margins

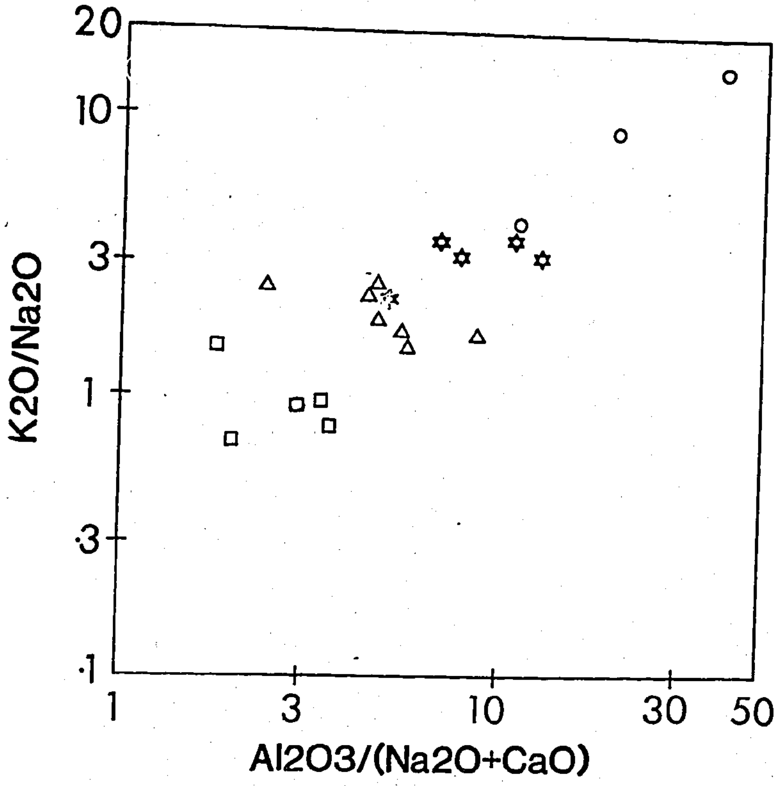


Figure 7.9 Plot of K_2O/Na_2O versus $Al_2O/(CaO+Na_2O)$ of mudrocks for tectonic setting discrimination (Log-log scale; data from Table 7.13). Note the increase in K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ with the change in tectonic setting from oceanic island arc to continental island arc to Andean type to the passive margins. Symbols as in Figure 7.8.

There are very few good quality published analyses of mudrocks. The average compositions of the various published mudrock suites are compared with the mudrock compositions of Australia and grouped into various settings (Table 7.13). The most discriminating elements are Ca, Na, K and Al. They reflect the nature of the source rock and the weathering conditions. A plot of $CaO-Na_2O-K_2O$ shows that there is an increase in K_2O and a decrease in Na_2O and CaO, with the change in tectonic setting (Figure 7.8) and three broad groups representing oceanic island arc, continental island arc - Andean type; and passive margins can be distinguished. The oceanic island arc mudrocks are mainly tectic type, the continental island arc and Andean type are phyllo-tectic type and those of passive margins are phyllic type mudrocks.

Tectonic setting discrimination is achieved by a plot of K_2O/Na_2O versus $Al_2O_3/(Na_2O+CaO)$ (Figure 7.9). Mudrock suites of Australia and Papua New Guinea derived from andesites, represent the oceanic island arc tectonic setting, and are characterised by the K_2O/Na_2O ratio of less than 1 and $Al_2O_3/(CaO+Na_2O)$ ratio between 2 and 3. The Gulf of Paria mud has compositional characteristics of this tectonic setting. The composition of the average Mesozoic-Cenozoic mudrock (Clarke, 1924) is also similar to oceanic island arc mudrocks. These similarities are not clearly understood but may represent the high volcanic component in the Gulf of Paria and in the average Mesozoic-Cenozoic mudrocks.

The mudrocks of the Hill End, Caucaus Geosyncline, and Paleozoic-Mesozoic Geosyncline of Japan represent the continental island arc setting and are discriminated from the oceanic island arc by their higher K_2O/Na_2O (range 1.5-2.0) and $Al_2O_3/(CaO+Na_2O)$ (range 4-5) ratios. The average composition of the Great Caucaus Geosynclinal mudrocks is slightly higher in CaO compared to other mudrocks of this group. Estimates of the composition of average pelite (Shaw, 1956) and average worldwide shale (Wedepohl, 1971) are similar to the composition of mudrocks of the continental island arc tectonic setting.

The mudrocks of the Hodgkinson suite represent the Andean type tectonic setting and are characterised by a K_2O/Na_2O ratio of more than 3 and an $Al_2O_3/(Na_2O+CaO)$ ratio of more than 8. The average Littleton formation pelites which have been derived from granite-gneisses, show geochemical characteristics similar to the Hodgkinson suite mudrocks

Table 7.14 Average Chemical Composition of Mudrocks of Various Tectonic Settings*

	Oceanic Island Arc 1)		Continental Island Arc 2)		Andean Type 3)		Passive Margin 4)	
	$\bar{X}$	±s.d	$\bar{X}$	±s.d	$\bar{X}$	±s.d	$\bar{X}$	±s.d
SiO_2	65.18	4.8	66.23	4.4	64.91	1.82	63.59	0.8
TiO_2	0.83	0.2	0.74	0.1	0.84	0.25	0.85	0.02
Al_2O_3	16.62	1.2	18.00	2.1	19.78	0.9	19.74	1.28
Fe_2O_3	2.48	0.3	2.30	1.0	2.48	1.3	1.92	1.1
FeO	3.98	1.1	3.07	0.4	4.10	2.1	4.37	1.9
MnO	0.07	0.01	0.04	0.04	0.05	0.02	0.04	-
MgO	2.19	1.2	2.12	0.4	1.91	0.3	3.1	0.7
CaO	3.85	2.5	2.40	2.7	0.50	0.1	0.35	0.3
Na_2O	2.54	0.1	1.66	0.4	1.20	0.02	0.77	0.5
K_2O	2.03	0.1	3.23	0.5	4.09	0.3	5.07	0.4
P_2O_5	0.25	0.05	0.16	0.06	0.14	0.02	0.16	0.05
K_2O/Na_2O	0.80		1.94		3.41		6.58	
$Al_2O/CaO+Na_2O)$	2.60		4.43		11.64		17.63	

* All averages ($\bar{X}$) on volatile free basis; Uncertainties (± s.d) represent 1 Standard Deviation.

1) Unweighted average of 1,2,3 of table 7.13
2) Unweighted average of 6,7,9,10 of Table 7.13
3) Unweighted average of 13 & 15 of Table 7.13
4) Unweighted average of 18 & 19 of Table 7.13

(Table 7.13; Figures 7.8, 7.9). The Santa Ynez mudrocks assigned to the Andean type tectonic setting (Van de Kamp et al., 1976) have characteristics of the continental island arc type mudrocks (Figure 7.9). The geochemistry of the Santa Ynez arenites also suggests a continental island arc tectonic setting. The average Wilcox Formation mudrock of Louisiana (Van Moort, 1971) has characteristics intermediate between the Andean type and the continental island arc and probably represent a misclassification in the present discrimination. Mudrocks of the Andean type tectonic setting are similar in composition to estimates of average Paleozoic shale (Clark, 1924) and average Post-Archean Shale (McLennan, 1981b). The distinction between the Andean type and the continental island arc type of mudrocks is not very clear but the former are probably slightly higher in K_20/Na_20 and $Al_20/(Na_2O+CaO)$ ratios (Figure 7.9).

The Ordovician-Silurian mudrocks of southeastern Australia represent the passive margin tectonic setting. They are highly depleted in Ca0 and Na_20, and are characterised by high K_20/Na_20 and $Al_20_3/(Ca0+Na_20)$ ratios (Figure 7.9). The comparable Ordovician mudrocks of the Greenland Group (New Zealand), are higher in Na_20 and Ca0 and exhibit slightly lower K_20/Na_20 and $Al_20_3/(Ca0+Na_20)$ ratios. Mudrocks of the passive margins are highly matured and recycled, as reflected in their geochemical similarity with the Carboniferious fluvial mudrocks of Great Britain (Figures 7.8, 7.9).

Thus, the major element composition of mudrocks can be used to decipher the provenance type and the tectonic setting of sedimentary basins. The average composition of mudrocks representing the various tectonic settings are given in Table 7.14. However, more data are needed to refine the discriminating parameters and plots, as tectonic settings of many mudrock suites used in the present work, are not well constrained.

7.9 TECTONIC SETTING DISCRIMINATION USING TRACE ELEMENT GEOCHEMISTRY OF ARENITES

7.9.1 Introduction

Immobile trace elements have widely been used to discriminate magma types and tectonic settings (e.g. Bailey, 1981 and references therein). Such studies have remained neglected in sedimentary rocks. In this section, trace element parameters and plots which can be used to

Table 7.15 Trace Element Characteristics of Arenites from Various Tectonic Settings 1)2)3)

	Oceanic Island Arc 4)		Continental Island Arc 4)		Andean Type 4)		Passive Margin 4)	
	X̄	±L	X̄	±L	X̄	±L	X̄	±L
Ba	370	233	444	64	522	100	253	64
Rb	18	10.7	67	10	115	8	61	19
Sr	637	516	250	86	141	30	66	22
*Pb	6.9	1.4	15.1	1.1	24.0	1.1	16.0	3.4
K (%)	0.91	0.43	1.37	0.21	2.19	0.32	1.06	0.32
K/Rb	578	92	219	28	189	20	178	20
*Rb/Sr	0.05	0.05	0.65	0.33	0.89	0.24	1.19	0.40
Ba/Rb	21.3	5.0	7.5	1.3	4.5	0.8	4.7	1.1
Ba/Sr	0.95	0.6	3.55	1.4	3.8	0.7	4.7	1.3
*Th	2.27	0.7	11.1	1.1	18.8	3.0	16.7	3.5
U	1.09	0.21	2.53	0.24	3.90	0.5	3.20	0.8
*Zr	96	20	229	27	179	33	298	80
*Hf†	2.1	0.6	6.3	2.0	6.8	-	10.1	-
*Nb	2.0	0.4	8.5	0.8	10.7	1.4	7.9	1.9
Y	19.5	5.6	24.2	2.2	24.9	3.6	27.3	5.3
*K/Th	4055	1526	1296	250	1252	360	681	194
K/U	8682	4438	5631	867	5956	1560	3950	1382
*Th/U	2.1	0.78	4.6	0.45	4.8	0.38	5.6	0.7
*Zr/Hf	45.7	-	36.3	-	26.3	-	29.5	-
*Zr/Th	48.0	13.4	21.5	2.4	9.5	0.7	19.1	5.8
Zr/Nb	49.3	10.2	31.5	9.9	16.7	1.8	37.2	8.0
Zr/Y	5.67	1.94	9.6	0.8	7.2	0.4	12.4	4.0
Nb/Y	0.11	0.03	0.36	0.04	0.43	0.04	0.30	0.06
*La	8.72	2.5	24.4	2.3	33.0	4.5	33.5	5.8
*Ce	22.53	5.9	50.5	4.3	72.7	9.8	71.9	11.5
*Nd	11.36	2.9	20.8	1.6	25.4	3.4	29.0	5.03
*La/Y	0.48	0.12	1.02	0.07	1.33	0.09	1.31	0.26
*La/Th	4.26	1.2	2.36	0.3	1.77	0.10	2.20	0.47
*La/Sc	0.55	0.22	1.82	0.3	4.55	0.8	6.25	1.35
*Th/Sc	0.15	0.08	0.85	0.13	2.59	0.5	3.06	0.8
*Ti (%)	0.48	0.12	0.39	0.06	0.26	0.02	0.22	0.06
*Ti/Zr	56.8#	21.4	19.7	4.3	15.3	2.4	6.74#	0.9
*Sc	19.5	5.2	14.8	1.7	8.0	1.1	6.0	1.4
*V	131	40	89	13.7	48	5.9	31	9.9
Cr	37	13	51	6.5	26	4.9	39	8.5
*Co	18	6.3	12	2.7	10	1.7	5	2.4
Ni	11	5.1	13	2.0	10	2.5	8	4.4
Cu	23	13.1	11	3.3	8	3.1	6	2.6
*Zn	89	18.6	74	9.8	52	8.6	26	12
Ga	17	1.9	13	1.3	14	1.5	8	1.6
Ni/Co	0.62	0.16	1.22	0.25	1.04	0.19	1.42	0.41
Sc/Ni	2.30	0.86	1.44	0.29	0.77	0.10	1.90	0.94
*Sc/Cr	0.57	0.16	0.32	0.06	0.30	0.02	0.16	0.02
V/Ni	14.0	4.19	8.1	1.52	5.0	0.79	7.55	2.8

Notes:
* Most sensitive discriminator of tectonic setting.
1) All data in ppm unless otherwise indicated.
2) Mean values (X̄), uncertainties (±L) represented 95% confidence limits on the means.
3) Mean ratios are means of the individual ratios.
4) Data source: Oceanic Island Arc - Tamworth Suite (11 samples);
Continental Island Arc - Hill End Suite and (29); Crow Mountain Creek Beds (3)(32 samples in all);
Andean Type - Hodgkinson Suite (10 samples);
Passive Margin - Bendigo Suite (7); Cookman Suite (8) (15 samples in all).
\# One sample each with extremely high value excluded.
† Hf values from Bhatia and Taylor (1981).

infer the provenance type and the tectonic setting of sedimentary rocks have been proposed. The data base for this discussion are analyses of graywacke suites representing the following tectonic settings of eastern Australia: Oceanic island arc (Tamworth suite); Continental island arc (Hill End suite and Crow Mountain Creek Beds); Andean Type (Hodgkinson suite); and Passive margins (Bendigo and Cookman suites). Unfortunately, due to the lack of comparable data in literature, the valadity of these parameters in other regions can not be evaluated.

Elements La, Ce, Y, Th, Zr, Hf, Nb and Ti are most suited for provenance type and tectonic setting discrimination because of their low mobility and low residence time in seawater. Elements Co, V and Sc are also useful because of their high discriminating strength and moderate mobility. The concentration of individual elements is sometimes influenced by changes of concentration in other constituents. However, ratios of elements are not subjected to such changes unless one of the constituents is changed. Thus, ratios of elements are useful for genetic considerations.

Mean trace element abundances and the element ratios along with estimates of uncertainties for arenites of various tectonic settings are presented in Table 7.15. The most discriminating parameters are marked with a star. In general, there is a systematic increase in LREE (La, Ce, Nd); Hf, Ba/Sr, Rb/Sr, La/Y and Ni/Co, and a decrease in ferromagnesian elements (Sc, V, Cu, Co, Zn) and the Ba/Rb, K/Th, K/U ratios from oceanic island arc to continental island arc to Andean type to passive margin type arenites, concommitant with change in provenance from andesite to dacite to granite-gneiss to sedimentary rocks. There is also an increase in Ba, Rb, Pb, Th, U and Nb from oceanic island arc to continental-island arc to the Andean type arenites. Variation in some of the trace element characteristics (e.g. Ba/Sr, Rb/Sr) is similar to the variation seen in andesites in passing from oceanic island arc to continental island arc to the Andean type tectonic settings (Bailey, 1981).

The following are the most discriminatory plots:

7.9.2 La-Th

A high positive correlation coefficient (n = 0.79) between La and Th in graywackes of eastern Australia suggests that these elements

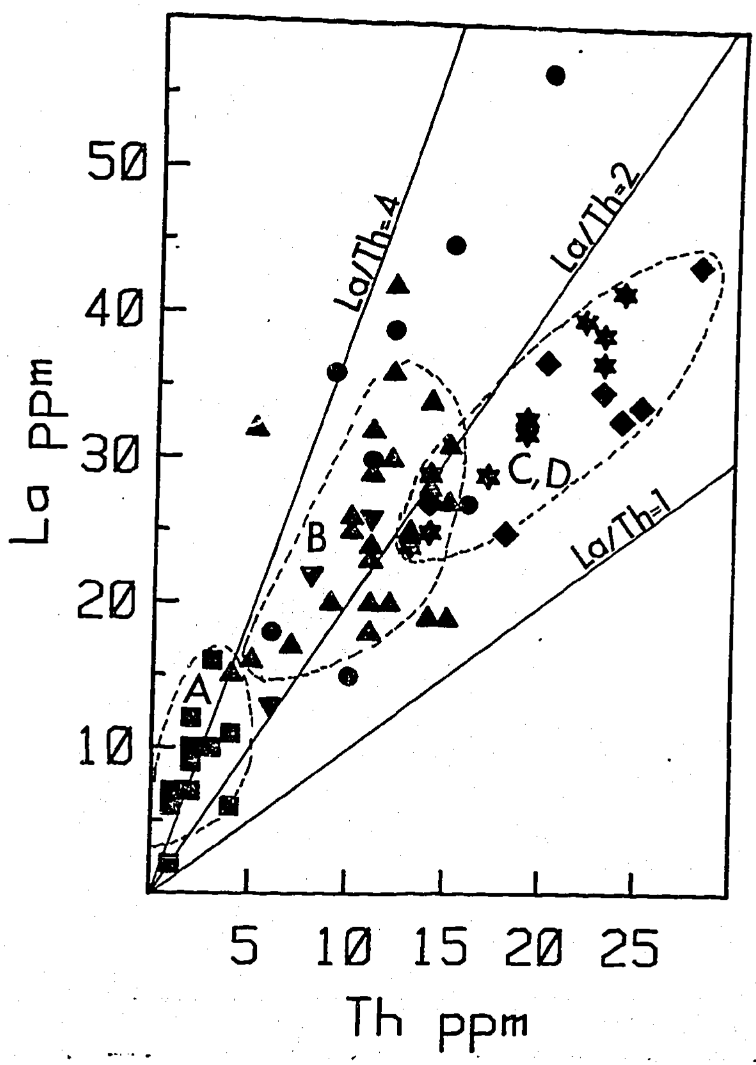
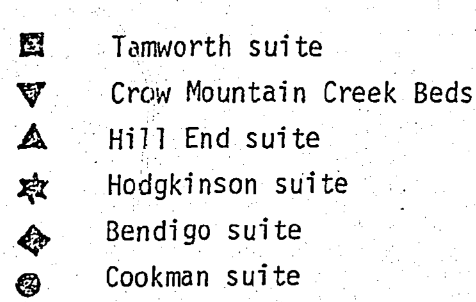


Figure 7.10 La-Th plot of arenites for tectonic setting discrimination. Dotted lines represent the dominant fields for the various tectonic settings:
A - Oceanic island arc (Tamworth suite);
B - Continental island arc (Hill End suite; Crow Mountain Creek Beds);
C - Andean type (Hodgkinson suite);
D - Passive margins (Bendigo and Cookman suites).
Note the lack of discrimination between C & D on this plot.



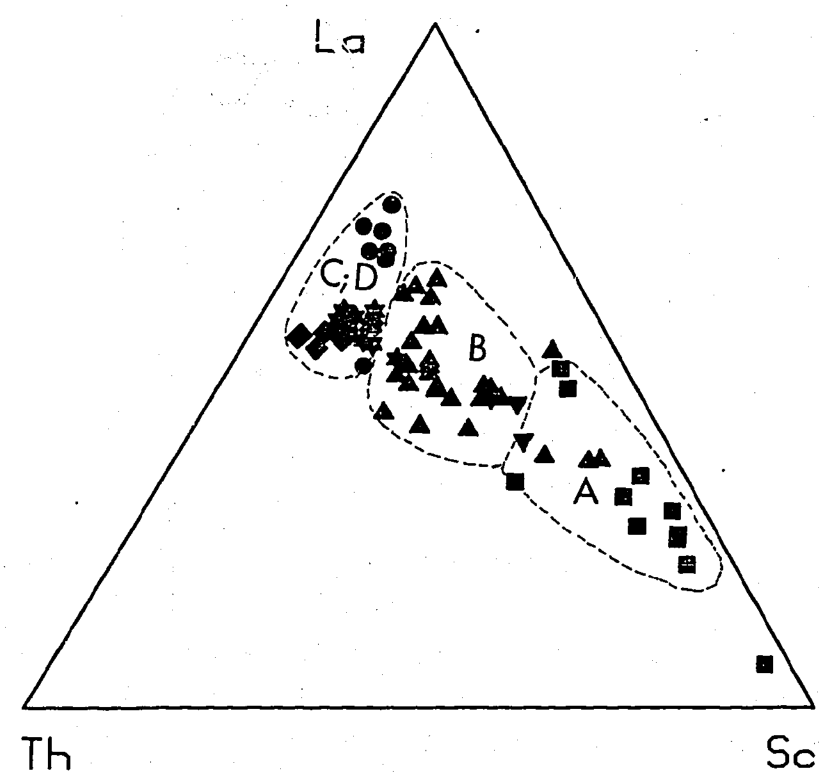


Figure 7.11 La-Th-Sc plot of arenites for tectonic setting discrimination, based on data of eastern Australia. Symbols and fields as in Figure 7.10. Note the lack of discrimination between Andean and passive margin type arenites on this plot.

behave coherently (Table 6.1). On the basis of preliminary data, the La-Th plot was suggested to discriminate provenance type and tectonic setting (Bhatia and Taylor, 1981; Appendix F). A plot of La versus Th for the complete data set shows that there is an increase in La and Th abundances in arenites as the tectonic setting changes. Three broad fields each representing oceanic island arc, continental island arc and Andean type-passive margins respectively are recognised (Figure 7.10). A large variation is seen in the passive margin arenites and discrimination between the Andean and the passive margin type arenites is not possible on this plot. The average La/Th ratio decreases from 4.2 ± 1.2 for the oceanic island arc, to 2.4 ± 0.3 for the continental island arc, to 1.8 ± 0.1 for the Andean type arenites. Compared to the Bendigo suite, the Cookman suite arenites exhibit a higher La/Th ratio, probably reflecting minor volcanic detritus in the former.

7.9.3 La-Th-Sc

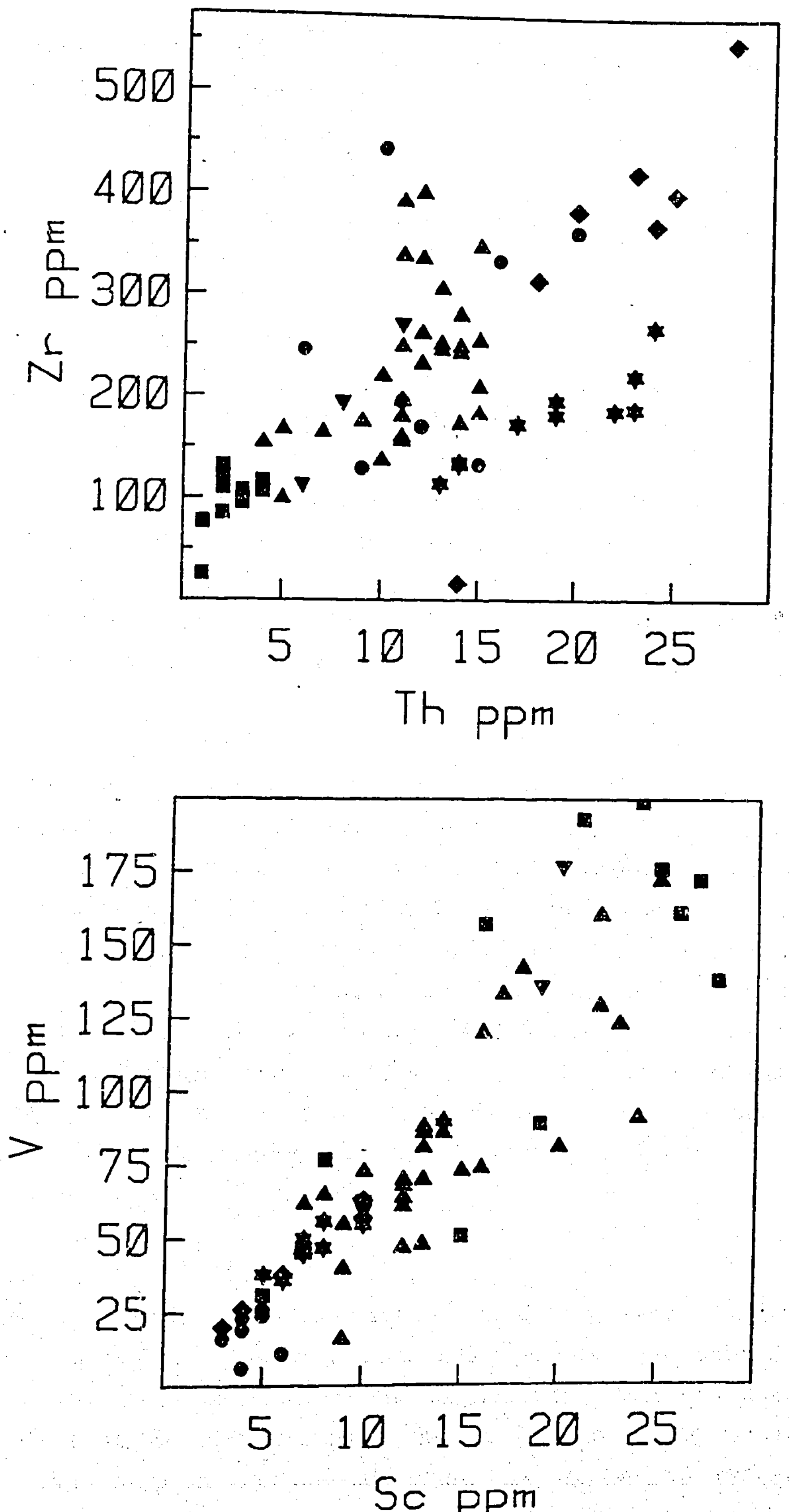
The La-Th-Sc triangular plot shows that distinct fields can be successfully delineated for oceanic island arc and continental island arc arenites. A combined field for Andean type - passive margin arenites is also distinct (Figure 7.11). Oceanic island arc samples plot near the Sc pole in this diagram, indicating a low La/Sc ratio (average La/Sc = 0.55 ± 0.2), whereas the Andean type-passive margin samples plot near the La pole, indicating a high La/Sc ratio (La/Sc > 4). Continental island arc arenites plot in between the two fields and have an intermediate La/Sc ratio (average La/Sc = 1.8 ± 0.3). This plot is useful in characterising oceanic and continental island arc suites and in discriminating them from the Andean type-passive margin arenites, but fails to distinguish between Andean and passive margin type arenites.

7.9.4 Th-Zr

A high positive correlation (r = 0.62) is noted between Th and Zr in arenites (Table 6.1). In general, there is an increase in Th and Zr from oceanic island arc to continental island arc to passive margin arenites (Figure 7.12a). Large variation is seen in the Th and Zr content of passive margin arenites, this is probably due to variation in grain size. However, the most significant use of this plot lies in separating the Andean type and passive margin samples due to

Figure 7.12 Th versus Zr, and Sc versus V plots for various graywackes. Note the lower Zr content and the lower Zr/Th ratio in the Andean type (Hodgkinson suite) graywackes, compared to the passive margin graywackes (Bendigo and Cookman suites). The Andean type graywackes are also characterised by a higher V and Sc content compared to the passive margin graywackes.

- ▣ Tamworth suite
- ▽ Crow Mountain Creek Beds
- △ Hill End suite
- ✡ Hodgkinson suite
- ◇ Bendigo suite
- ● Cookman suite


500
400
300
200
100
Zr ppm
5
10
15
20
25
Th ppm
175
150
125
100
75
50
25
V ppm
5
10
15
20
25
Sc ppm

differences in their Zr abundance and Zr/Th ratio. The average Zr/Th ratio for Andean type arenites is 9.5 ± 0.7 in comparison to the average Zr/Th ratio of 21.5 ± 2.4 and 19.1 ± 5.8 for continental island arc and passive margin arenites, respectively (Table 7.15). Oceanic island arc arenites are generally characterised by a low abundance of Zr and Th and a high Zr/Th ratio (average Zr/Th = 48.0 ± 13.4).

7.9.5 V-Sc

Vanadium and scandium are ferromagnesian trace elements, which chiefly reside with the mafic component of arenites. There is a decrease in the V and Sc abundance with the change in tectonic setting from oceanic island arc to continental island arc to Andean type to passive margin (Figure 7.12b). Though a large variation is seen in the abundance of these elements in some suites (especially in continental island arc type), the fields for each tectonic setting are quite distinct. The plot also shows that the passive margin suite samples can be discriminated from the Andean type by their lower V and Sc abundance.

7.9.6 Ti/Zr - La/Sc

A plot of Ti/Zr versus La/Sc shows excellent discrimination of the various arenite types and tectonic settings (Figure 7.13a). Oceanic island arc samples are characterised by Ti/Zr ratio of generally more than 40 and La/Sc ratio of less than 1. Continental island arc samples, are in general characterised by Ti/Zr ratio between 10 and 35, and La/Sc ratio between 1 and 3. Andean type arenites can be discriminated from the continental island arc type by their higher La/Sc ratio, which ranges from 3 to 6. Though passive margin arenites show large variation in the La/Sc ratio, they can be distinguished from arenites of other tectonic settings by their Ti/Zr ratio of generally less than 10 and a high La/Sc ratio (generally between 3 and 9).

7.9.7 La/Y - Sc/Cr

The La/Y ratio gives the enrichment of light rare earth elements (represented by La) over heavy rare earth elements (represented by Y). Sc/Cr is the ratio of two compatible elements, with Cr being more compatible than Sc. In general, the La/Y ratio increases from the oceanic island arc to continental island arc to Andean type-passive margin sediments. The Sc/Cr ratio decreases from the oceanic island arc

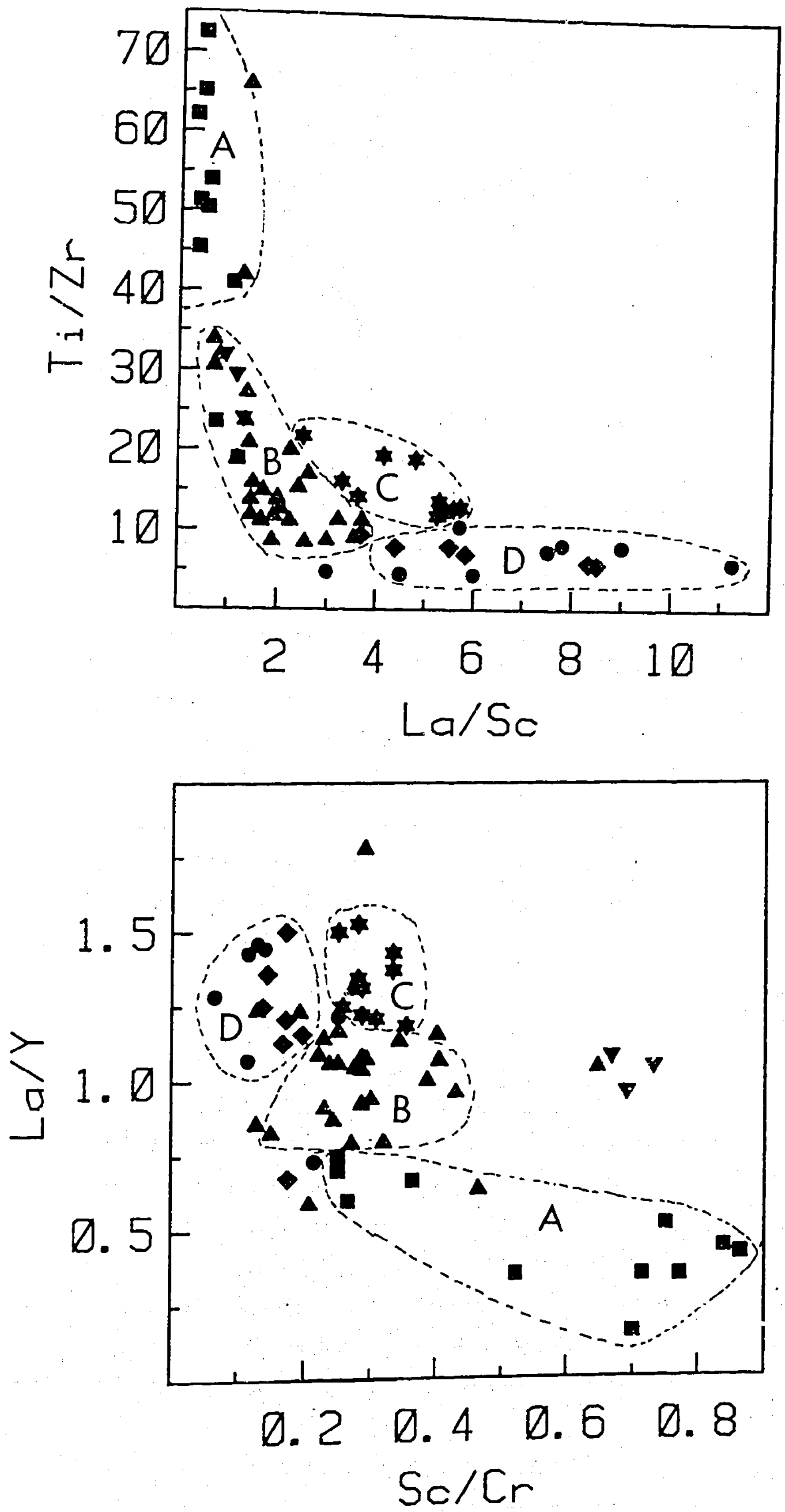


Figure 7.13 La/Sc versus Ti/Zr, and Sc/Cr versus La/Y plots of arenites for tectonic setting discrimination. Symbols and fields as in Figure 7.10.

to continental island arc - Andean type to passive margin type of arenites (Table 7.15).

On the plot of La/Y versus Sc/Cr, the arenites of various tectonic settings occupy quite distinct fields with very little overlap (Figure 7.13b). Oceanic island arc rocks are characterised by low La/Y (generally less than 0.5) and Sc/Cr (generally less than 0.6) ratio. Continental island arc arenites are discriminated by their La/Y ratio generally between 0.5 and 1.0, and their Sc/Cr ratio generally between 0.2 to 0.4. Andean type arenites can be discriminated from the continental island arc type, by their high La/Y ratio, which is generally between 1 to 1.5. The passive margin arenites have a La/Y ratio similar to that of the Andean type, but can be discriminated by their lower Sc/Cr ratio, which is generally less than 0.2.

7.9.8 Th-Sc-Zr and Th-Co-Zr

Like the La/Sc ratio, the Th/Sc ratio is also very useful in tectonic setting discrimination. There is an increase in Th/Sc from oceanic island arc to continental island arc to Andean type-passive margin arenites (Table 7.15). This ratio does not discrimate successfully between Andean type and passive margin type arenites. However, the Zr/Th ratio is very useful in discriminating between these two settings (Section 7.9.4). Co behaves coherently with Sc. Thus the following two triangular plots of these elements show excellent discrimination (Figure 7.14):

Th-Sc-Zr/10 and

Th-Co-Zr/10

The scaling factor has been used to bring the fields into the middle of the diagram without altering their relative positions. On these plots, oceanic island arc type arenites, characterized by high Th/Sc and Th/Co ratios, plot close to the Sc and Co poles. Andean type arenites, characterized by low Th/Sc and Th/Co ratios, plot near the Th pole. Passive margin arenites, characterized by high Zr/Th ratio, mainly plot near the Zr pole. Continental island arc arenites plot in between the three fields on both these plots (Figure 7.14).

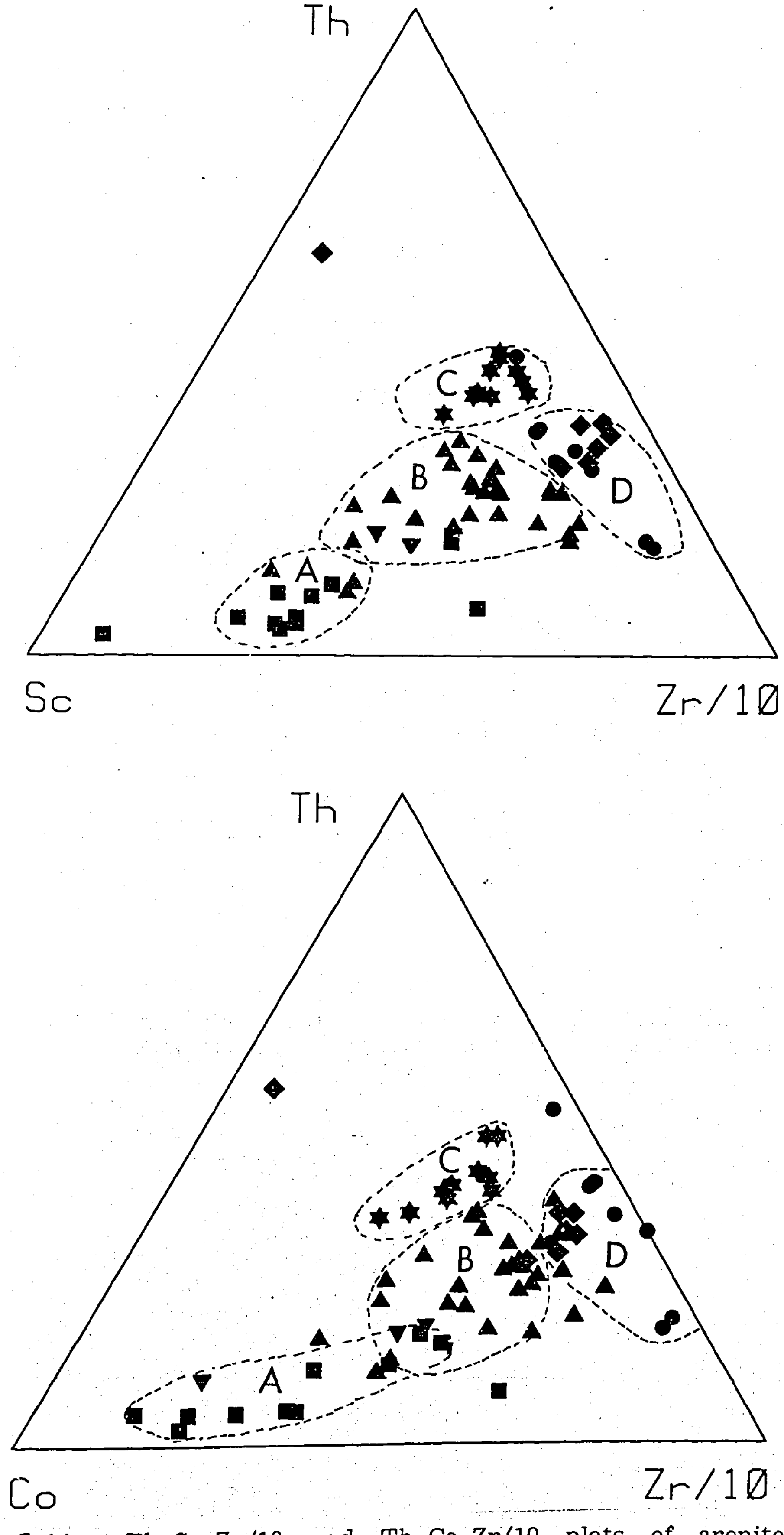


Figure 7.14 Th-Sc-Zr/10 and Th-Co-Zr/10 plots of arenites for tectonic setting discrimination. Note the excellent discrimination of various tectonic settings. Symbols and fields as in Figure 7.10.

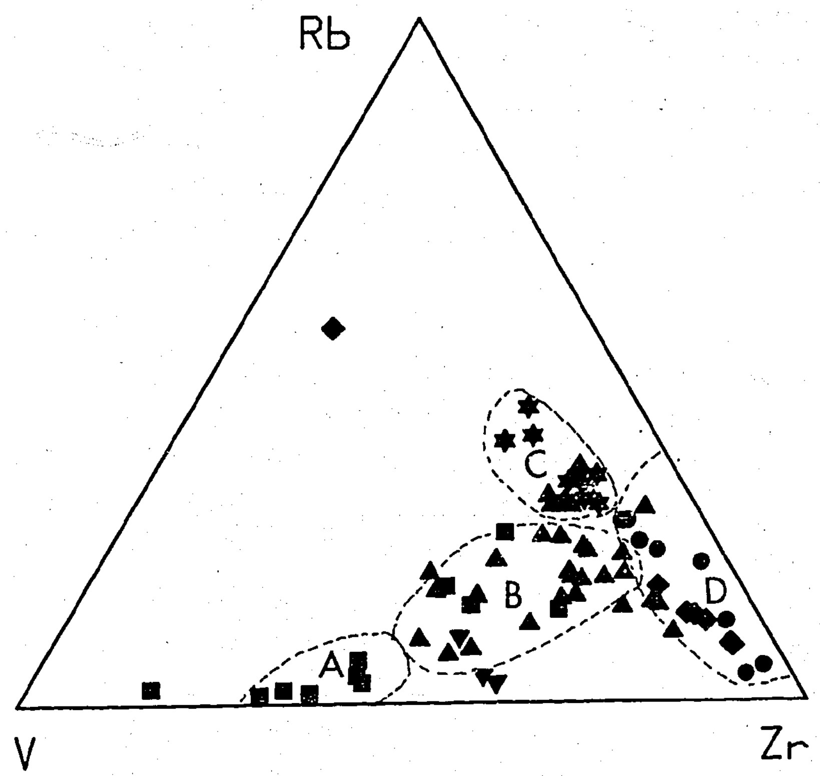


Figure 7.15 Rb-V-Zr plot of arenites for tectonic setting discrimination. Symbols and fields as in Figure 7.10.

7.9.9 Rb-V-Zr

A triangular plot similar to the Th-Sc-Zr plot using Rb, V and Zr as three end members discriminates between arenites of various tectonic settings (Figure 7.15). Oceanic island arc arenites plot near the V pole; the Andean type near the Rb pole and the passive margin type near the Zr pole. Continental island arc graywackes plot in between the three fields. The significant feature of this plot is that it can discriminate between Andean and passive margin type arenites. However, this plot should be used with caution, because the Rb abundance can be significantly modified during sedimentary processes.

7.9.10 Summary

Trace element parameters and discriminatory plots discussed in this section, can be used to characterise the provenance type and the tectonic setting of arenites. Although a large number of trace elements can be used, the immobile trace elements (La, Th, U, Zr, Nb, Y, Sc, Co and Ti) are most useful. The proposed method of characterising the tectonic setting for arenites is shown in the form of a flow-diagram (Figure 7.16), and the characteristic parameters for each tectonic setting are repeated in Table 7.16. Oceanic island arc arenites are identified by extremely low abundances of La, Th, U, Zr, Nb; low Th/U and high La/Sc, La/Th, Ti/Zr, Zr/Th ratios. Continental island arc type arenites are characterised by increased abundances of La, Th, U, Zr and Nb, and can be identified by the La-Th-Sc and La/Sc versus Ti/Zr plots. Andean and passive margin type arenites are discriminated by the Th-Sc-Zr/10 and Th-Co-Zr/10 plots and associated parameters (e.g. Th/Zr; Th/Sc). The most important characteristic of passive margin type arenites is the increased abundance of Zr in them compared to the Andean type arenites. Discriminant parameters and diagrams proposed in this section are not meant to be the basis of a pigeon-hole classification scheme, as transitional sedimentary tectonic settings and mixed provenance types are not unexpected. Rather, a comparison of the geochemical data of sedimentary suites in other regions with the geochemical characteristics of various tectonic settings given here (Tables 7.15 and 7.16) can be used to constrain their provenance type and tectonic setting.

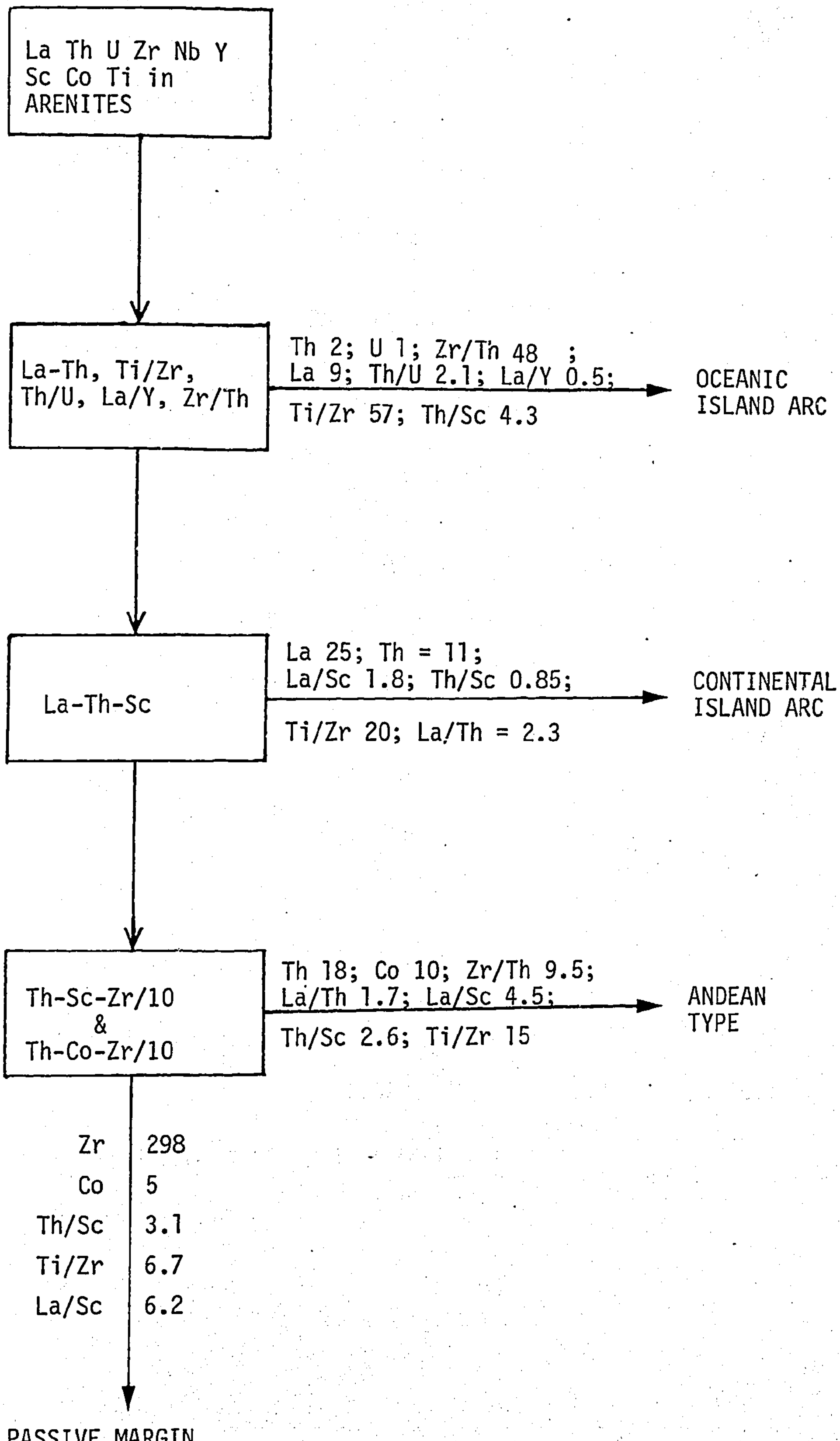


Figure 7.16 Flow diagram illustrating the proposed method of characterising the tectonic setting of arenites. (All abundances in ppm).

Table 7.16 Trace Element Parameters of Arenites for Tectonic Setting Discrimination*

	Oceanic Island Arc	Contiental Island Arc	Andean Type	Passive Margin
Th	2.3	11.1	18.8	15.7
U	1.1	2.5	3.9	3.2
Hf	2.1	6.3	6.8	10.1
Th/U	2.1	4.6	4.8	5.6
Zr	96	229	179	298
La	8.7	24	33	33
La/Y	0.48	1.0	1.3	1.3
La/Sc	0.55	1.82	4.6	6.3
Th/Sc	0.15	0.85	2.6	3.1
Sc	20	15	8	6
Co	18	12	10	5
Zr/Th	48	22	10	19
Ti/Zr	57	20	15	7
Sc/Cr	0.57	0.32	0.30	0.16

* Data condensed from Table 7.15. (Mean Values)

All abundances in ppm.

7.10 TECTONIC SETTING DISCRIMINATION USING TRACE ELEMENT GEOCHEMISTRY OF MUDROCKS

7.10.1 Introduction

Weathering plays a significant role in the formation of fine grained clastic sedimentary rocks, especially those formed due to recycling. The abundance of many trace elements is thus controlled by adsorption and fixation processes. Thus the most useful elements in mudrocks, for provenance type and tectonic setting discrimination, are those which remain relatively unaffected by these processes, e.g., REE, Nb, Zr, Th, Y, Hf and possibly Sc. In the present section, critical geochemical parameters and plots of mudrocks are proposed for the tectonic setting discrimination. The data base is as follows: oceanic island arc (Tamworth suite); continental island arc (Hill End suite; Crow Mountain Creek Beds); Andean type (Hodgkinson suite); passive margin (Bendigo and Cookman suites; Ordovician pelites from Snowy Mountain region, N.S.W.). The trace element characteristics of mudrocks of each tectonic setting are given in Table 7.17. There are only two samples of the Andean type setting in the present data set, and on many plots, it is difficult to distinguish these from the passive margin type. In such cases, Andean type-passive margin tectonic settings have been referred together. In general, there is an increase in Rb, LREE (La, Ce, Nd), Th, Y, Nb, Cr, Ni, and Rb/Sr, Ba/Sr, La/Sc, Th/U and Th/Sc ratios, and a decrease in Sr, and Ba/Rb, Zr/Nb, Zr/Th, Sc/Ni, V/Ni and Sc/Ni ratios in mudrocks with the change in tectonic setting from oceanic island arc to continental island arc to the Andean type-passive margin (Table 7.17).

The following are the most discriminatory plots.

7.10.2 Th-Sc-Zr

The Th-Sc-Zr/10 plot of arenites gives an excellent discrimination of provenance type and tectonic setting. However, in mudrocks it discriminates only to a limited extent (Figure 7.17). Mudrocks of the oceanic and continental island arcs, plot close to their respective field as delineated on the basis of arenites. However, all Andean type and passive margin mudrocks plot in the Andean type field. The distinction between continental island arc and Andean-passive margin type mudrocks is also not well established on this plot, as evident by the close

Table 7.17 Trace Element Characteristics of Mudrocks from Various Tectonic Settings 1)2)3)

	Oceanic Island Arc 4)		Continental Island Arc 4)		Andean Type 4)5)	Passive Margin 4)	
	X̄	±L	X̄	±L	X̄	X̄	±L
Ba	692	319	713	258	660	786	159
Rb	67	21.3	139	33	216	235	41
Sr	287	103	194	104	80	65	41
*Pb	8.1	1.9	18.8	3.6	29.5	20.5	10.2
*K (%)	1.82	0.69	2.73	1.10	3.30	4.13	0.80
K/Rb	339	143	199	26	157	177	7.5
*Rb/Sr	0.29	0.15	1.31	0.7	2.9	5.82	2.0
Ba/Rb	11.7	6.1	5.2	1.54	3.1	3.39	0.43
*Ba/Sr	2.4	1.1	6.28	3.0	8.7	17.59	5.3
*Th	5.5	1.13	16.2	2.6	27.5	22	8.5
*U	2.36	0.95	3.17	0.45	6.0	3.6	0.56
Zr	130	14.7	185	40	189	179	32
Hf†	3.5	-	6.6	-	6.4	5.7	-
*Nb	3.7	0.94	9.0	1.5	16.5	15.8	1.73
Y	22.0	3.8	26.5	3.9	33.0	30.3	3.7
K/Th	3866	1481	1643	299	1225	1611	442
K/U	10425	3727	8421	1508	6199	11586	1441
*Th/U	2.81	0.92	5.15	0.6	5.0	6.7	0.76
Zr/Hf	37.7	-	28.0	-	29.5	31.4	-
*Zr/Th	27.7	12.2	11.58	2.0	6.88	7.37	1.51
*Zr/Nb	38.7	11.29	20.98	3.9	11.47	9.95	3.1
Zr/Y	5.79	1.7	7.08	1.4	5.76	6.14	1.08
*Nb/Y	0.17	0.05	0.35	0.09	0.50	0.54	0.04
*La	18	7.2	24.4	3.6	42	33.7	6.3
Ce	37	16.7	53.0	9.0	87	73.3	18.7
Nd	19	7.3	21.4	1.7	33.0	28.2	4.5
La/Y	0.82	0.25	0.93	0.11	1.27	1.11	0.18
La/Th	3.9	1.3	1.58	0.3	1.52	1.45	0.20
*La/Sc	1.0	0.4	1.78	0.3	2.5	1.92	0.23
Th/Sc	0.29	0.07	1.17	0.23	1.61	1.39	0.15
Ti (%)	0.42	0.04	0.32	0.03	0.37	0.43	0.14
Ti/Zr	33.0	4.39	18.8	3.7	19.6	26.9	3.4
Sc	20	1.7	14.1	1.7	17	17.2	3.28
V	159	52	84	12.3	99	102	15.8
*Cr	39	6.9	55	12.5	58	100	13.3
Co	15	3.6	11	2.9	16	14.0	3.9
*Ni	15	4.1	18	5.7	26	35.5	8.1
Cu	44	13	20	6.5	42	30	20.8
Zn	104	30.0	85	16.5	111	94	21.6
Ga	19	2.23	17	1.65	25	23	3.6
Ni/Co	1.08	0.29	1.74	0.51	1.59	2.7	0.65
*Sc/Ni	1.70	0.7	0.96	0.26	0.75	0.45	0.05
Sc/Cr	0.53	0.12	0.27	0.04	0.29	0.18	0.01
V/Ni	10.9	2.53	5.5	1.35	4.4	2.87	0.6
Cr/V	0.29	0.07	0.67	0.12	0.58	1.00	0.14

Notes:
* Most sensitive discriminator of tectonic setting.
1) All data in ppm unless otherwise indicated.
2) Mean values (X̄) and uncertainties (+L) represent 95% condience limits on the means
3) Mean ratios are means of the individual ratios.
4) Data from: Oceanic Island Arc - Tamworth Suite; (9 samples in all);
Continental Island Arc - Hill End Suite (9) and Crow Mountain Creek Beds (3) (12 samples in all);
Andean Type - Hodgkinson Suite - (2 samples);
Passive Margin - Bendigo Suite (2); Cookman Suite (1); Ordovician, Snowy Mt. (7); (Wyborn, 1977); (10 samples in all).
5) Uncertainties not given due to very small data set.
† Hf values from Bhatia and Taylor (1981).

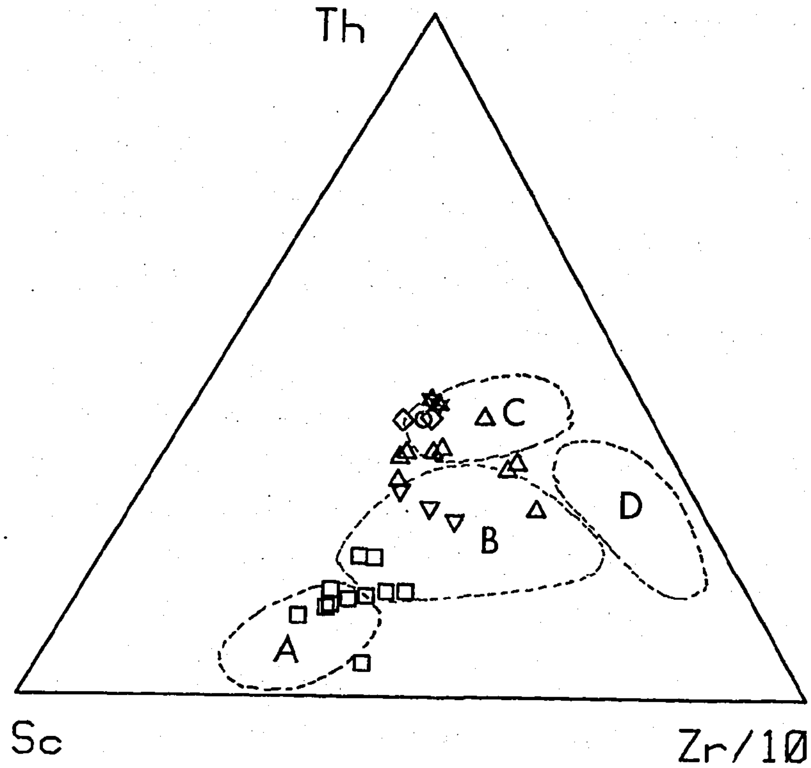


Figure 7.17 Th-Sc-Zr/10 plot of mudrocks for tectonic setting discrimination. Fields representing the various tectonic settings (A-D) are based on arenite data, and are adopted from Figure 7.14. Note that the passive margin mudrocks plot in the Andean field.

- □ Tamworth suite
- ▽ Crow Mountain Creek Beds
- △ Hill End suite
- ✡ Hodgkinson suite
- ◇ Bendigo suite
- ○ Cookman suite

clustering of many samples from three settings. However, this plot can help in discriminating between oceanic and continental island arc type mudrocks.

7.10.3 La-Th

As in arenites, generally there is an increase in the La and Th abundance in mudrocks as the tectonic setting changes from oceanic island arc to continental island arc to Andean type-passive margins. However, the fields of arenites and mudrocks within each tectonic setting may vary slightly (Figure 7.18). Oceanic island arc mudrocks show a large variation in the La/Th ratio, but it is generally more than 2 and high compared to other mudrocks. The La/Th ratio for all other mudrocks is generally between 1 and 2. The three fields are quite distinct, though minor overlapping does exist on this plot.

7.10.4 Nb-Zr/Th

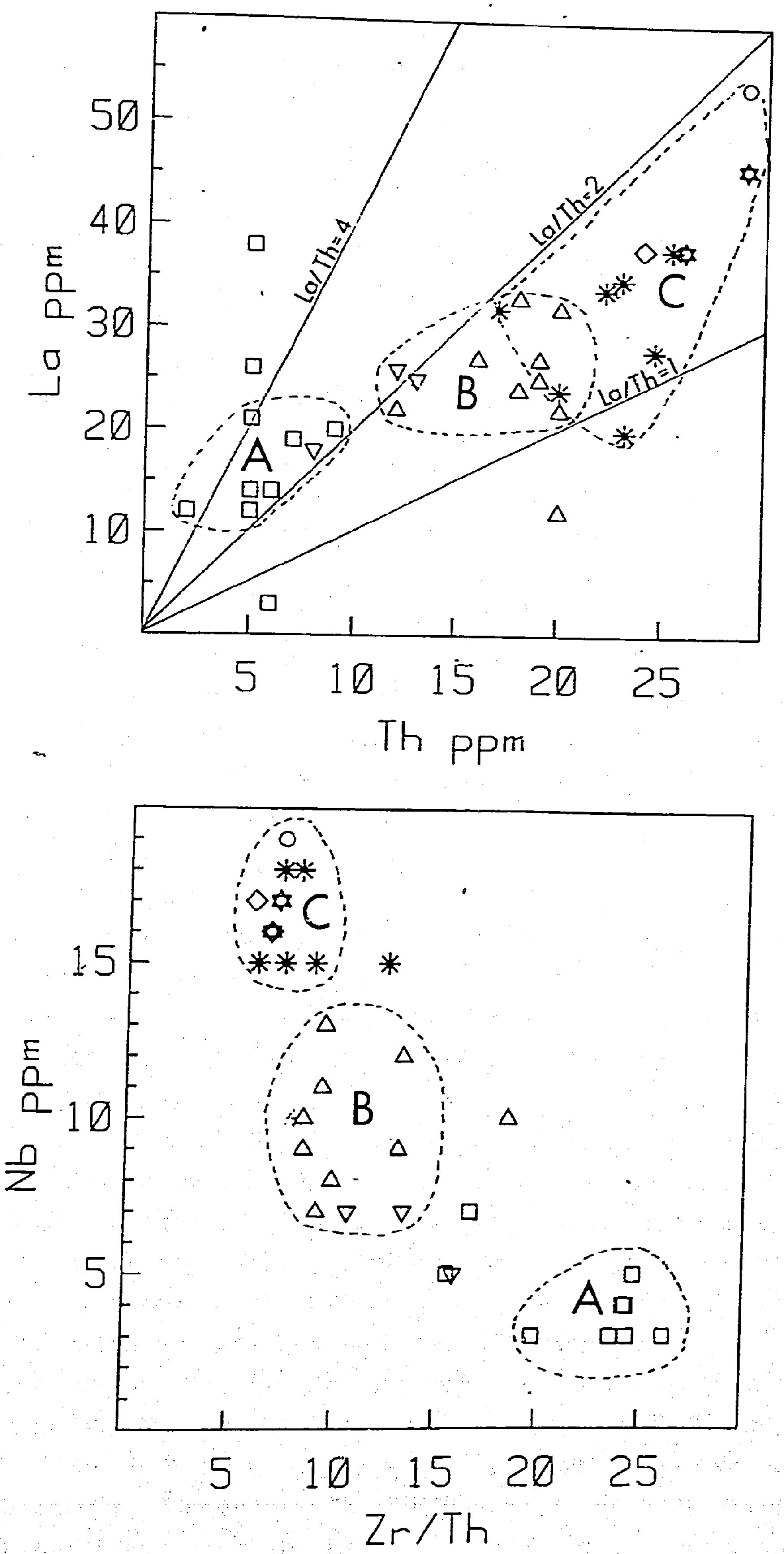
The Nb versus Zr/Th plot shows an excellent discrimination of various mudrock types representing various tectonic settings (7.18). Oceanic island arc mudrocks are characterised by generally less than 5 ppm Nb content and Zr/Th ratio ≅ 25, whereas continental island arc type mudrocks are generally characterised by 6-13 ppm Nb and a Zr/Th ratio between 8 and 16. Andean and passive margin type mudrocks have a Zr/Th ratio of generally less than 10, but more importantly are characterised by a Nb content of generally more than 15 ppm.

7.10.5 Th-Nb/Y

As suggested by their high positive correlation coefficient (r = 0.94, Table 6.2) Th and Nb behave coherently in mudrocks. A plot of Nb/Y versus Th in mudrocks is very useful in discriminating provenance types and tectonic settings (Figure 7.19). Oceanic island arc mudrocks are characterised by a Th content of less than 8 ppm and Nb/Y generally less than 0.25. Continental island arc mudrocks are characterised by a Th content between 10 and 20 ppm, and Nb/Y ratio between 0.2 and 0.4. Andean type and passive margin mudrocks are characterised by a Th content of generally more than 20 ppm and a Nb/Y ratio of more than 0.4. The three tectonic settings occupy quite distinct fields with very little overlapping on this plot.

Figure 7.18 La versus Th, and Nb versus Zr/Th plots of mudrocks, for tectonic setting discrimination. Note that the samples representing various tectonic settings occupy distinct fields, but the data is not enough to discriminate between Andean and passive margin type mudrocks. The fields are : A - Oceanic island arc (Tamworth suite) B- Continental island arc (Hill End suite and Crow Mountain Creek Beds) C - Andean and passive margin type (Bendigo and Cookman suites; Ordovician mudrocks of the Snowy Mountains).

□	Tamworth suite
▽	Crow Mountain Creek Beds
△	Hill End suite
✡	Hodgkinson suite
◇	Bendigo suite
○	Cookman suite
✻	Ordovician mudrocks. Snowy Mountains (data from Wyborn,1977)


La ppm
Th ppm
La/Th=4
La/Th=2
La/Th=1
A
B
C
Nb ppm
Zr/Th
5
10
15
20
25
50
40
30

7.10.6 La/Sc - Nb/Y

The La/Sc ratio is a useful parameter to discriminate between oceanic and continental island arc type mudrocks. A plot of La/Sc versus Nb/Y ratios (Figure 7.19) shows that oceanic island arc, continental island arc and Andean Type- passive margin settings can be discriminated on the basis of these two parameters quite successfully.

7.10.7 Nb-Th/U

The Th/U ratio shows a good discrimination of mudrocks of various tectonic settings. Broadly there is an increase in Nb and the Th/U ratio as the tectonic setting changes from oceanic island arc to continental island arc to the passive margin (Figure 7.20). Like associated arenites, oceanic island arc mudrocks have a Th/U ratio of less than 3. In arenites of other tectonic settings, the Th/U ratio remains uniform between 4 and 5 (Table 7.15; Bhatia and Taylor, 1981). However, in mudrocks a large variation is seen in the Th/U ratio. It is generally between 4-6 in continental island arc mudrocks and in the passive margins types it is commonly more than 6. More data are needed to understand the Th/U ratio in Andean type mudrocks.

7.10.8 Summary

Trace element characteristics of mudrocks, especially those of Andean type and passive margins, differ from their associated arenites. Hence, a separate set of criteria for mudrocks is given for tectonic setting discrimination. Immobile trace elements (La, Th, U, Zr, Nb, Y) are most useful for tectonic setting discrimination. However elements Ba, Rb, Sr, Cr and Ni also contribute significantly, especially in separating Andean type mudrocks from those of the passive margins. A discrimination scheme in the form of a flow-diagram is given in Figure 7.21 and the characteristic parameters for mudrocks of each tectonic setting are repeated in Table 7.18. Oceanic island arc mudrocks are similar to associated arenites and can be characterised by the low abundance of La, Th, U, Zr, Nb and low Th/U and Nb/Y ratios. Continental island arc mudrocks can be recognized on Nb-Zr/Th, Nb/Y-Th and La/Sc-Nb/Y plots. Andean type and passive margin mudrocks are recognised by higher Nb, Th, Nb/Y and low Zr/Th ratios compared to continental island arc mudrocks.

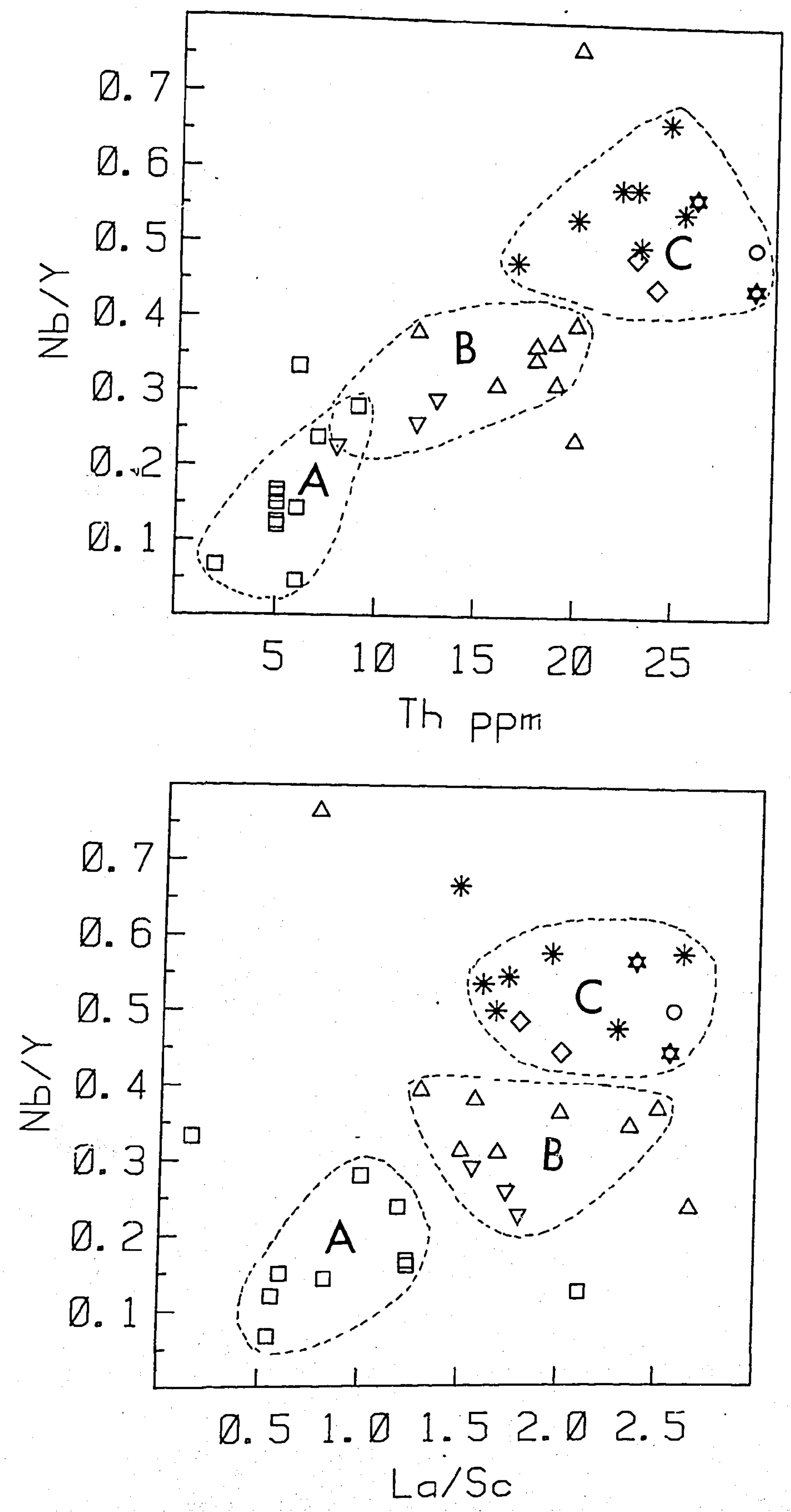


Figure 7.19 Tectonic setting discrimination plots of La/Sc, and Th versus Nb/Y in mudrocks. Note the excellent discrimination of various mudrocks. Symbols and fields as in Figure 7.18.

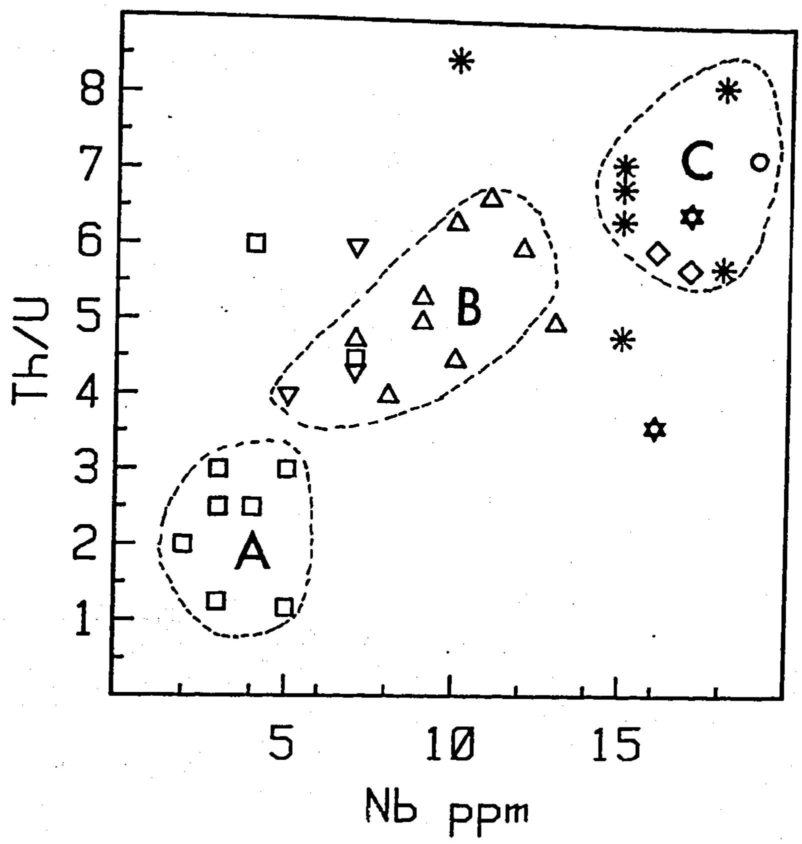


Figure 7.20 Nb versus Th/U plot of mudrocks representing various tectonic settings. Symbols and fields as in Figure 7.18.

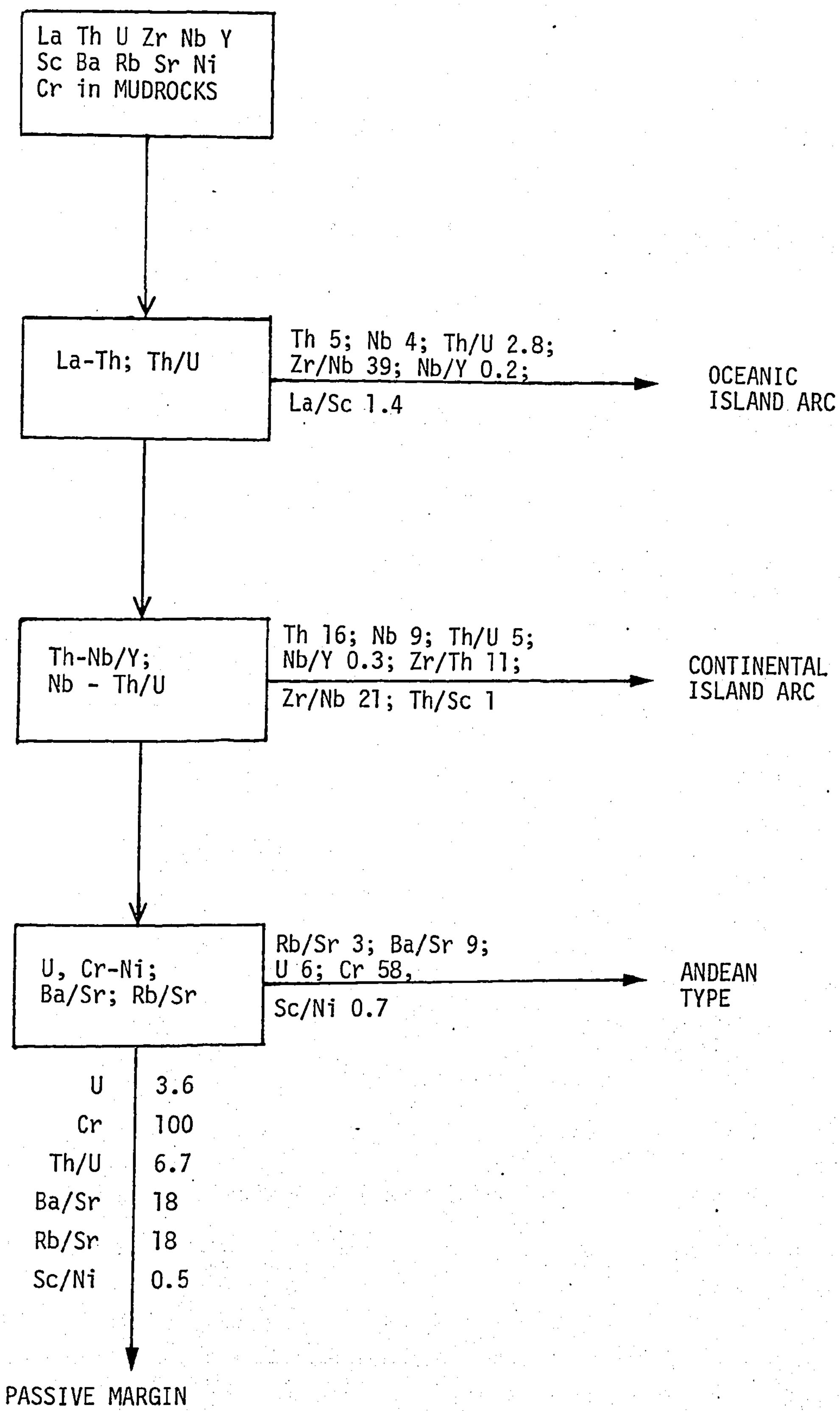


Figure 7.21 Flow diagram illustrating the proposed method of characterising tectonic setting of mudrocks. (All abundances in ppm).

Table 7.18 Trace Element Parameters of Mudrocks for Tectonic Setting Discriminantion*

	Oceanic Island Arc	Continental Island Arc	Andean Type	Passive Margin
Th	5.5	16.2	28	22
U	2.4	3.2	6.0	3.6
Nb	3.7	9.0	16.5	15.8
Th/U	2.8	5.2	5.0	6.7
Zr/Th	28	12	7	7
Zr/Nb	38	21	11	10
Nb/Y	0.17	0.35	0.50	0.54
La	18	24	42	34
La/Sc	1.0	1.8	2.5	1.9
Cr	39	55	58	100
Ni	15	18	26	36
Sc/Ni	1.7	0.96	0.75	0.45
Rb/Sr	0.29	1.31	2.9	5.8
Ba/Sr	2.5	6.3	8.7	17.6

* Data condensed from Table 7.17. (Mean Values)

All abundances in ppm.

The data is not enough but probably passive margin mudrocks can be distinguished from the Andean type by their higher Cr, Ni, and Rb/Sr, Ba/Sr, Th/U ratios and lower U, Sc/Ni and V/Ni ratios. These features reflect the higher redistribution of elements in passive margin settings, due to higher weathering conditions. The average U content in passive margin mudrocks is 3.6 ppm compared to 6 ppm U in the Andean type. The low value in the passive margins could be due to oxidation of U^{4+} to U^{6+} and its removal as soluble $[UO_2]^{2-}$ during sedimentation, resulting in high Th/U and also K/U ratios (Table 7.17). The high Rb/Sr and Ba/Sr ratios in passive margin mudrocks are also due to the loss of Sr during sedimentation. The high Cr and Ni content in passive margin mudrocks is probably due to the enrichment of these elements with phyllosilicates, with increasing weathering and recycling, resulting in higher Cr/V and lower V/Ni, Sc/Cr and Sc/Ni ratios compared to Andean type mudrocks.

7.11 ROBERTSON BAY GROUP: COMPOSITION AND TECTONIC SETTING

The Robertson Bay Group is a 10,000m thick Late Precambrian-Lower Cambrian turbidite sequence in the Northern Victorialand of Antarctica. Sedimentary rocks of this group have been suggested to form the source rocks of the Ordovician quartz-rich graywackes of Australia and New Zealand (Nathan, 1976; Wyborn, 1977; Chapter 6). The Robertson Bay Group sedimentary rocks have also been suggested as the protoliths of the S-type granitoids of the Lachlan Fold Belt (Wyborn and Chappell, 1979). Thus the nature of the Robertson Bay Group has an important bearing on the understanding of the Phanerozoic evolution of the Lachlan Fold Belt.

Unfortunately, the data on the mineralogy and geochemistry are too meagre to make a definite statement about these rocks. Although a study by B.W. Chappell and D. Wyborn on the chemistry of these rocks is underway at A.N.U., certain observations are worth mentioning here. Wyborn (1977) noted that the Robertson Bay Group graywackes are quartz-rich, and similar to the Ordovician quartz-rich graywackes of the Tasman Geosyncline, except that they have slightly more feldspar and less clay matrix. However, on examination of the arenite thin sections, it was found that the graywackes show large mineralogical variation, but

Table 7.19 Geochemical Comparison of Robertson Bay Group Graywackes with Arenites from Various Tectonic Settings[1)2)]

	Oceanic Island Arc	Continental Island Arc	Robertson Bay Group[3)]	Andean Type
$Fe_2O_3^*+MgO$ (%)	11.73	6.79	6.77	4.63
TiO_2 (%)	1.06	0.84	0.57	0.46
Th	2.3	11	16.1	19
Zr	96	229	112	179
Hf	2.1	6.3	2.6	6.8
La	9	24	35	33
Yb	2.14	2.8	1.62	2.97
Sc	20	15	16.3	8
K/Th	4055	1296	2938	1252
La/Sc	0.55	1.8	2.17	4.55
Ti/Zr	57	19.7	30.4	15.3
La/Th	4.3	2.4	2.2	1.77
Hf/Yb	0.98	2.2	1.6	2.28
Th/Sc	0.15	0.85	0.99	2.59
Zr/Hf	46	36	43	26

Notes:

* Total Fe as Fe_2O_3

1) All abundances in ppm unless otherwise indicated.

2) Data for various tectonic setting from Tables 7.11 and 7.15.

3) Robertson Bay Group data from Table 6.12
(after Harrington et al. 1967; Nathan, 1976).

they are dominantly quartz-intermediate and contain common to abundant penecontemporaneously derived volcanic lithic grains and chloritic fragments.

A comparison of the chemical composition of the Robertson Bay Group with the characteristics of graywackes representing various tectonic settings can help in constraining the provenance type and tectonic setting of the Robertson Bay Group. A comparison of the two most discriminating major element parameters, $Fe_20_3{}^t$+Mg0 and $Ti0_2$, shows that the Robertson Bay Group graywackes lie between oceanic island arc and Andean type graywackes and are comparable to continental island arc type graywackes (Table 7.19). On the discrimination plot of $Fe_20_3{}^t$+Mg0 vs. $Ti0_2$ the Robertson Bay Group graywackes fall in the continental island arc field.

The immobile trace elements and element ratios of the Robertson Bay Group graywackes also exhibit characteristics between those of the oceanic island arc and Andean type settings (Table 7.19). Zr, Hf, Yb, La/Sc are too low and Sc, K/Th, Ti/Zr, Zr/Hf and Th/Sc are too high in the Antarctican graywackes to be assigned to the Andean type setting. A large difference is also noted between the Robertson Bay graywackes and those of the ocean island arc, particularly in the Th, La Sc, La/Sc and La/Th values, but the Zr, Hf and Zr/Hf ratios between the two groups are quite comparable. On the other hand, a remarkable similarity is noted particularly in the Th, Sc, La/Sc, La/Th and Th/Sc values between the average Robertson Bay Group graywacke and continental island arc type graywackes. On the discrimination plot of Ti/Zr versus La/Sc, the Robertson Bay Group falls close to the continental island arc field.

Thus the geochemical evidences suggest that the Robertson Bay Group can be related to the island arc occurring on a well developed continental crust or on a thin continental margin, rather than a thick continental margin. If the Robertson Bay Group sedimentary rocks form the basement of the Paleozoic Tasman Geosyncline sequence, their nature does not support the presence of a thick continental crust (of the Andean type) below the Tasman Geosyncline as envisaged by White et al. (1976).

CHAPTER 8
RARE EARTH ELEMENT GEOCHEMISTRY AND TECTONIC SETTING OF SEDIMENTARY ROCKS

8.1 INTRODUCTION

In recent years, the contribution of rare earth element (REE) geochemistry to the understanding of the processes of crustal evolution has been widely recognized. The general uniformity of REE patterns in Post-Archean fine-grained sedimentary rocks and their fundamental distinction from those of Archean sedimentary rocks has been noted by many authors (e.g. Haskin et al., 1968; Nance and Taylor, 1976; Taylor, 1979; Taylor and McLennan, 1981a). The difference between Archean and Post-Archean sedimentary rocks has been correlated with the mafic crust during Archean and a granodioritic crust during Post-Archean times (Wildeman and Condie, 1973; Wildeman and Haskin, 1973; Nance and Taylor, 1976; 1977; Taylor and McLennan, 1981a).

The REE are generally considered to be immobile elements exhibiting only minor changes during sedimentary processes. Their abundance in source rocks, and the weathering conditions in the provenance region, have been considered as the major factors controlling the REE in sediments. Syn- and post-depositional processes such as exchange reactions during transportation, deposition and diagenesis are insignificant in altering the REE content of sediments (Cullers et al. 1975, 1979; Chaudhuri and Cullers, 1979; Roaldset, 1978). Although slight enrichment of REE has been noted in the extensively weathered profiles of platform sediments (Ronov et al. 1967; Cullers et al. 1979; Duddy, 1981); REE differentiation is less pronounced in geosynclinal sediments due to general low weathering conditions in this regime (Ronov et al. 1967). Thus, the REE signatures of source rocks are faithfully preserved in flysch sediments. Many studies have documented insignificant REE mobility up to the granulite facies of metamorphism (Cullers et al. 1974; Muecke et al. 1979). The REE distribution in sediments is generally unaffected by the marine environment as total REE in seawater is very small (equal to the upper 0.2 mm of the ocean floor sediments) and these elements have very short residence times in seawater (Haskin and Paster, 1979).

Due to their relatively immobile nature the REE are widely used to discriminate the tectonic settings of volcanic rocks. However, no attempt has yet been made to relate rare earth element chemistry to the tectonic settings of sedimentary basins. In view of this, a separate investigation of rare earth element geochemistry was undertaken during the present work. Selected samples of graywackes and mudrocks representing the Tamworth, Hill End, Hodgkinson, Bendigo and Cookman suites were analysed by Spark Source Mass Spectrograph for REE, Th, U, and Hf (see Appendix A for technique). A part of this investigation has already been published (Bhatia and Taylor, 1981; Appendix F) and other results are presented in this chapter.

The purposes of the present investigation are:

(1) to study the relationship between rare earth element parameters, and mineralogical and geochemical characteristics of sedimentary rocks.

(2) to decipher provenance and tectonic setting on the basis of REE characteristics.

(3) Comparison of REE characteristics of tektites with those of sedimentary rocks.

8.2 REE PARAMETERS

Elements of Group III B, having atomic numbers between 57 and 71, are called the Rare Earth or Lanthanide Elements. Yttrium (atomic number 39) geochemically behaves similar to Er-Ho and is generally included with the rare earth elements. Rare earth elements comprise a uniquely coherent group of elements. As the 4f orbital in lanthanides is filled, the electron configuration remains the same and this is the reason for their chemical similarity. The coherent behaviour is caused by the +3 oxidation state of these elements in most geological environments. However, Eu and Ce can also occur in +2 and +4 oxidation states, respectively. When reduced to the +2 state, Eu resembles Sr^{+2} in its behaviour, due to the same ionic size.

Elements from La to Sm have large ionic radii and are generally concentrated in the last phase of crystallisation. They are called the "light rare earth elements" (LREE). The elements from Gd to Lu have smaller ionic radii and occupy lattice sites in some major minerals. They are called the "heavy rare earth elements" (HREE).

Table 8.1 Rare Earth Element Abundance in Chondrites and Post-Archean Average Australian Shale (in ppm)

	Chondrites+	PAAS#
La	0.367	38
Ce	0.957	80
Pr	0.137	8.9
Nd	0.711	32
Sm	0.231	5.6
Eu	0.087	1.1
Gd	0.306	4.7
Tb	0.058	0.77
Dy	0.381	4.4
Ho	0.0851	1.0
Er	0.249	2.9
Tm	0.0356	0.4
Yb	0.248	2.8
Lu	0.0381	0.43
ΣREE	3.89	183.0
Eu/Eu^*	-	0.66
La_N/Yb_N	-	9.2

\+ From Taylor and McLennan (1981).

\# From Nance and Taylor (1976).

Table 8.2 RARE EARTH ELEMENT PARAMETERS

$$\Sigma REE = La + Ce + Pr + Nd + Sm + Eu + Gd + Tb + Dy + Ho + Er + Yb$$

$$\Sigma LREE/\Sigma HREE = \frac{La + Ce + Pr + Nd + Sm}{Gd + Tb + Dy + Ho + Er + Yb}$$

$$La_N/Yb_N = \frac{\text{La (Chondrite normalised)}}{\text{Yb (Chondrite normalised)}}$$

$$Eu/Eu^* = \frac{\text{Eu (actual chondrite normalised)}}{\text{Eu (interpolated normalised for no enrichment or depletion)}}$$

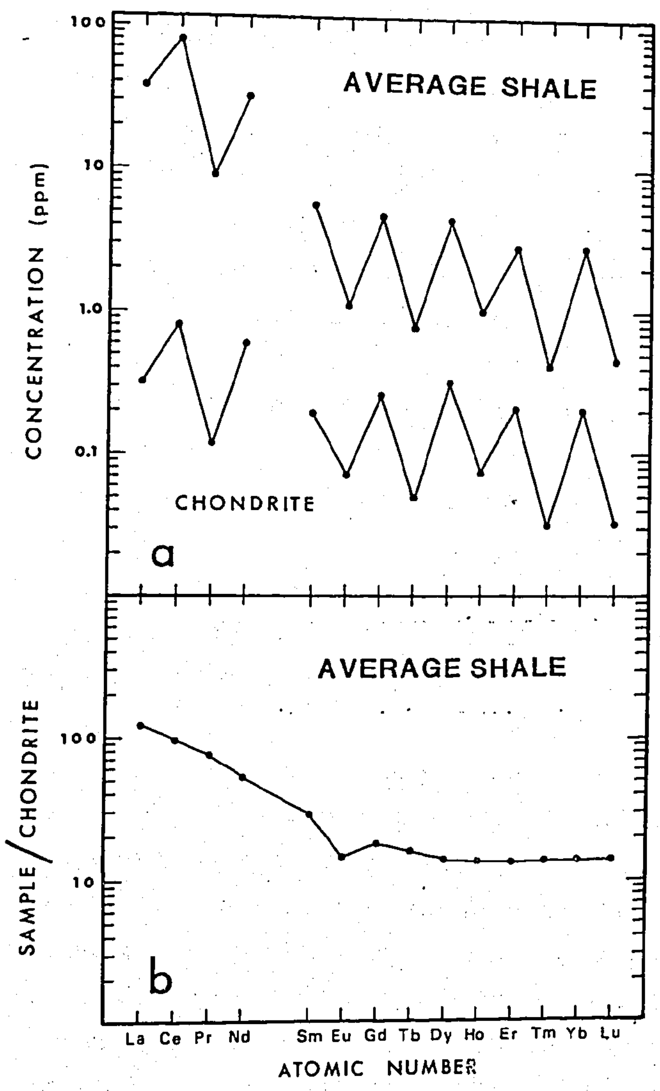


Figure 8.1 (a) Rare earth element abundance in chondrite and average shale (PAAS)
(b) Chondrite normalised rare earth element pattern of average shale (PAAS)

In Figure 8.1a, the distribution of rare earth elements in chondrite and in average shale (average of 35 shales, Nance and Taylor, 1976) is shown. The elements are arranged with increasing atomic numbers. The diagram shows that the elements with even atomic numbers are more abundant than those of odd atomic numbers on either side. This regularity is known as the Oddo-Harkins rule. This zig-zag effect makes it very difficult to interpret the REE distribution in rocks. To avoid this, it is common practice to present REE data on plots of normalised abundances versus atomic numbers. Coryell et al. (1963) suggested to normalise the REE abundances to chondritic meteorites, because the chondrite composition may represent the cosmic abundance, and the bulk composition of the earth may also be close to the chondritic abundance. Thus, the average shale normalised to chondrite (Figure 8.1b) is much easier to interpret than the simple abundance plot. Another plot commonly used is shale-normalised. The two sets of values commonly employed are NASC (North American Shale Composite - Haskin and Paster, 1979) and PAAS (Post-Archean Average Australian Shale - Nance and Taylor, 1976). In the present work, chondrite and PAAS normalised plots are used and the values employed are presented in Table 8.1.

Besides the normalised plots, four parameters are used to characterise the REE abundance in rocks (Table 8.2). The sum of all rare earth elements determined (La-Yb) represents ΣREE. The ΣLREE/ΣHREE is the ratio of the sum of light rare earth elements (La-Sm) to the sum of heavy rare earth elements (Gd-Yb). The La/Yb ratio is an index of the enrichment of light rare earth elements over heavy rare earth elements and when expressed as the chondrite normalised ratio it is called La_N/Yb_N. The anomalous behaviour of Eu can be seen on the chondrite normalised plot of average shale in Figure 8.1b. The value of Eu/Eu^* represents the ratio of actual normalised Eu to interpolated normalised Eu for no depletion or enrichment. For the chondrite normalised, this value is calculated by the following equation:

$$Eu/Eu^* = (Eu/.087)/[([Sm/.231] + [Gd/.306])/2]$$

8.3 REE PATTERNS AND SOURCE ROCKS

8.3.1 Tamworth Suite

The REE geochemistry of the Baldwin Formation graywackes was studied by Nance and Taylor (1977). Four additional Tamworth Trough samples, showing extreme variation of texture and mineralogy, were analysed in the present work (Table 8.3). On chondrite normalised plots, these samples exhibit only slight LREE enrichment compared to the HREE and in general have smooth patterns with the absence of a negative Eu anomaly (Figures 8.2 & 8.3). Few samples exhibit a positive Eu anomaly. Petrographic examination reveals that sample MK 14 contains ∿ 69% modal plagioclase. Thus the sporadic occurrence of a positive Eu anomaly can be attributed to the local enrichment of plagioclase grains from volcanic sources, in proximity to the source terrain. On the PAAS normalised plots, these samples are characterised by high depletion of LREE and the presence of a positive Eu anomaly (Figure 8.3). The chondrite normalised REE patterns, characterised by the absence of a negative Eu anomaly and slight LREE enrichment, are similar to the REE patterns of calc-alkaline andesitic rocks of island arcs (Taylor, 1979) and confirm the petrographic and geochemical evidences that those sediments are derived from an andesitic source. The Crow Mountain Creek bed sample (MK 46) shows significant enrichment of LREE over HREE and a negative Eu anomaly on the chondrite normalised plot and suggests a felsic volcanic source terrain. The REE patterns of the Tamworth suite graywackes, are in general similar to those of Archean sedimentary rocks from various regions (Wildeman and Condie, 1973; Wildeman and Haskin, 1973; Nance and Taylor, 1977; Bavinton and Taylor, 1980; Taylor and McLennan, 1981a,b). However, the Archean samples are slightly more enriched in LREE compared to Tamworth suite graywackes (see also Chapter 9, Section 9.5.3g).

The only mudrock sample (MK43) of the Tamworth suite contains abundant radiolarians. The chondrite-normalised REE pattern of this sample is characterised by the enrichment of LREE over HREE. The PAAS normalised plot exhibits the presence of a significant positive Eu anomaly (Figure 8.3). However, the significant feature of this rock is the presence of a high Ce anomaly on both the chondrite-normalised plot, the PAAS-normalised plot. The exact reason for the Ce anomaly in sedimentary rocks is not completely understood. Shimizu and Masuda

Table 8.3 Rare Earth Elements (in ppm), Mineralogical and Geochemical Maturity Indices in the Tamworth Suite Sedimentary Rocks[1)]

	B216	M277	M282	M283	M284	M285	B10	MK14	MK16	MK46[3)]	MK43
Lithology[2)]	G	G	G	G	G	G	G	G	G	G	M
La	11	10	8.0	6.3	5.4	6.8	7.2	7.9	11.3	26	26
Ce	26	18	19	16	15	15	18	19	29	61	24
Pr	3.5	2.2	3.2	2.0	1.9	2.0	2.5	2.6	4.3	7.3	7.5
Nd	12	10	13	8.6	8.5	8.2	11	10.0	19.1	31	28
Sm	2.9	2.8	3.6	2.5	2.7	2.2	3.1	2.5	5.1	6.8	6.1
Eu	0.89	0.97	1.2	0.85	1.4	1.1	1.0	0.92	1.3	1.3	1.6
Gd	3.2	3.4	4.3	3.0	3.3	2.6	3.5	1.8	4.5	5.6	4.9
Tb	0.43	0.52	0.62	0.47	0.48	0.39	0.52	0.29	0.77	0.82	0.73
Dy	2.6	3.1	3.9	3.0	3.1	2.7	3.3	1.9	5.0	4.7	4.3
Ho	0.53	0.79	0.95	0.70	0.79	0.59	0.81	0.38	1.06	1.0	0.96
Er	1.5	2.2	2.8	2.0	2.3	1.9	2.4	1.0	2.8	2.9	2.6
Yb	1.4	2.3	2.8	2.2	2.3	1.8	2.3	1.3	2.8	2.8	2.5
ΣREE	66	56	63	48	47	45	56	50	88	152	110
Eu/Eu^*	0.98	1.06	1.00	1.05	1.53	1.55	1.04	1.33	0.84	0.66	0.90
ΣLREE/ΣHREE	5.6	3.5	3.2	2.9	2.7	3.5	3.2	5.9	3.9	7.1	6.4
La/Yb	7.9	4.3	2.9	3.2	2.3	3.8	3.1	6.0	4.1	9.1	10.2
La_N/Yb_N	5.4	2.9	1.9	2.2	1.6	2.6	2.1	4.1	2.8	6.2	6.9
SiO_2/Al_2O_3	3.7	3.5	3.3	3.5	3.5	3.5	3.4	2.8	3.7	18.7	4.4
K_2O/Na_2O	0.18	0.12	0.19	0.06	0.11	0.12	0.21	0.23	0.15	0.15	1.9
Maturity[4)]	0	0	0	0	0	7	0	2	4	15	13
Prov. Index	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.74	0.99	0.60	-

1) Data for samples B216-B10 from Chappell (1968) and Nance and Taylor (1976).
2) Lithology : G = Graywacke; M = Mudrock.
3) Crow Mountain Creek Beds.
4) Maturity : for graywackes - mineralogical maturity index
for mudrocks - clay maturity index.

Table 8.4 Rare Earth Elements (in ppm), Mineralogical and Geochemical Maturity Indices in the Hill End Suite Sedimentary Rocks

	MK26	MK29	MK57	MK58	MK59	MK66	MK65	MK64	MK73	MK4	MK49	MK51
Lithology[1)]	G	G	G	M	G	G	M	G	M	G	G	M
La	29	22	28	37	32	21	45	25	31	22	36	25
Ce	60	48	64	90	70	48	92	53	69	59	75	55
Pr	8.9	4.8	8.5	10.2	8.9	6.5	10	5.8	8	5.7	6.8	6.8
Nd	35	19	35	43	39	31	37	22	36	22	23	27
Sm	6.8	3.4	6.8	8.3	7.2	7.8	6.7	4.5	6.8	4.8	4.2	4.9
Eu	1.8	1.1	1.5	1.95	1.8	1.5	1.3	0.9	1.4	0.9	1.2	1.1
Gd	6.6	2.9	6.5	7.1	5.5	6.2	5.3	3.5	5.7	4.7	3.3	3.9
Tb	1.0	0.46	1.0	1.2	0.86	0.9	0.9	0.6	0.9	0.8	0.6	0.7
Dy	5.9	2.7	6.0	7.3	5.0	6.2	5.5	3.6	5.6	5.1	3.7	4.0
Ho	1.2	0.57	1.2	1.5	1.1	1.3	1.2	0.8	1.2	1.0	0.8	0.8
Er	3.5	1.5	3.4	3.9	3.1	3.6	3.3	2.2	3.6	2.8	2.2	2.3
Yb	3.5	1.4	3.3	4.0	3.1	3.6	2.6	2.0	3.5	2.6	1.9	2.4
ΣREE	165	108	166	217	178	137	212	124	174	133	159	134
Eu/Eu^*	0.83	1.03	0.69	0.77	0.89	0.64	0.64	0.72	0.70	0.59	0.95	0.75
ΣLREE/ΣHREE	6.2	9.8	6.3	7.2	8.5	5.0	9.7	8.3	7.0	6.4	11.0	8.1
La/Yb	8.4	16.1	8.4	9.2	10.3	5.8	17.3	12.3	9.0	8.5	18.9	10.6
La_N/Yb_N	5.7	10.9	5.7	6.2	6.9	3.9	11.7	8.3	6.1	5.8	12.8	7.2
SiO_2/Al_2O_3	4.4	6.2	5.5	4.1	5.6	7.8	4.3	5.3	5.3	9.4	4.4	5.2
K_2O/Na_2O	0.5	0.85	0.88	3.0	1.4	0.83	0.83	0.28	0.28	4.4	0.35	2.7
Maturity[2)]	22	45	11	39	30	56	58	26	58	74	35	32
Prov. Index	0.94	0.39	0.35	-	0.77	0.54	-	0.54	-	0.15	0.51	-

1) Lithology : G = Graywacke; M = Mudrock.

2) Maturity : for graywackes - mineralogical maturity index
for mudrocks - clay maturity index.

Table 8.5 Rare Earth Elements (in ppm), Mineralogical and Geochemical Maturity Indices in Hodgkinson, Bendigo and Cookman Suite Sedimentary Rocks

	Hodgkinson			Bendigo		Cookman	
	MK84	MK86	MK92	MK97	MK101	MK54	MK55
Lithology[1)]	G	G	M	G	M	G	M
La	39	35	38	43	52	34	73
Ce	82	75	79	83	81	87	144
Pr	9.7	9	10	12	12	11	18
Nd	37	35	35	42	50	42	67
Sm	7.3	6.2	7.4	7.1	9.3	10.3	12.2
Eu	1.2	0.99	1.4	1.0	1.9	2.0	2.0
Gd	5.6	3.8	5.4	5.6	7.0	9.7	9.0
Tb	0.95	0.64	0.97	0.88	1.1	1.5	1.5
Dy	5.5	4.4	5.8	4.7	6.5	7.8	7.4
Ho	1.2	0.94	1.3	1.0	1.4	1.3	1.5
Er	3.6	2.8	3.7	2.9	4.0	3.1	4.1
Yb	3.2	2.8	3.7	2.9	4.0	2.0	4.6
ΣREE	197	177	192	207	230	212	347
Eu/Eu^*	0.57	0.63	0.65	0.51	0.73	0.61	0.59
ΣLREE/ΣHREE	8.3	9.9	7.7	10.0	8.1	7.1	10.7
La/Yb	12.3	12.8	10.3	15.1	12.9	16.7	15.8
La_N/Yb_N	8.3	8.7	7.0	10.2	8.7	11.3	10.7
SiO_2/Al_2O_3	5.8	6.7	3.6	8.1	2.9	11.1	2.8
K_2O/Na_2O	1.1	0.91	3.2	1.1	11.4	75	63
Maturity[2)]	54	64	70	85	89	98[3)]	85
Prov. Index	0.14	0.32	-	0.0	-	0.03	-

1) Lithology : G = Graywacke; M = Mudrock.

2) Maturity : for graywackes = mineralogical maturity index.
for mudrocks = clay maturity index.

3) Contains 40% siltstone lithic grains, which are included with quartzose grains to determine maturity.

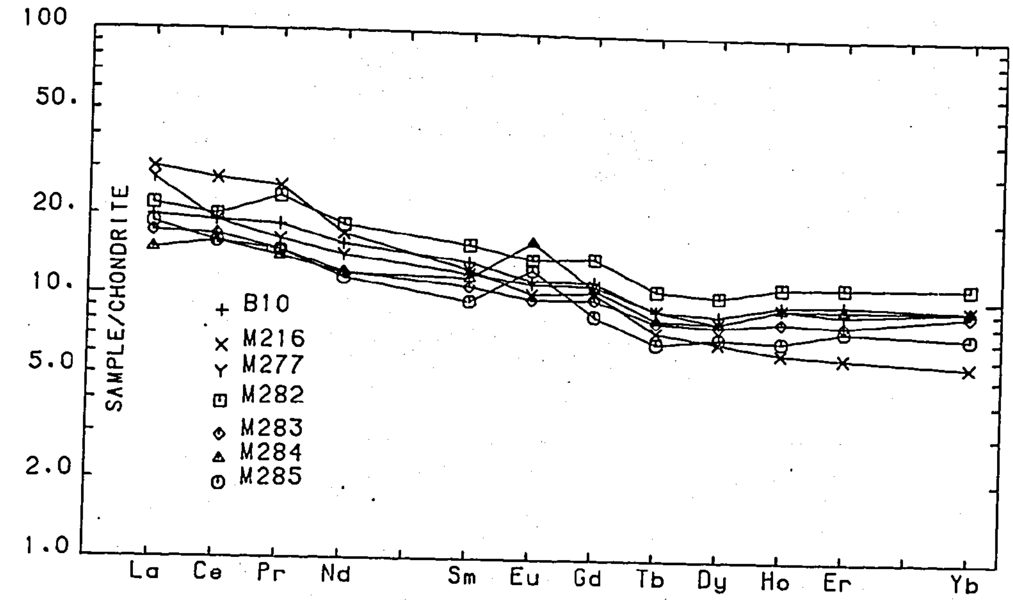


Figure 8.2 Chondrite normalised REE plots of the Baldwin Formation graywackes, Tamworth Trough (data from Nance and Taylor, 1977).

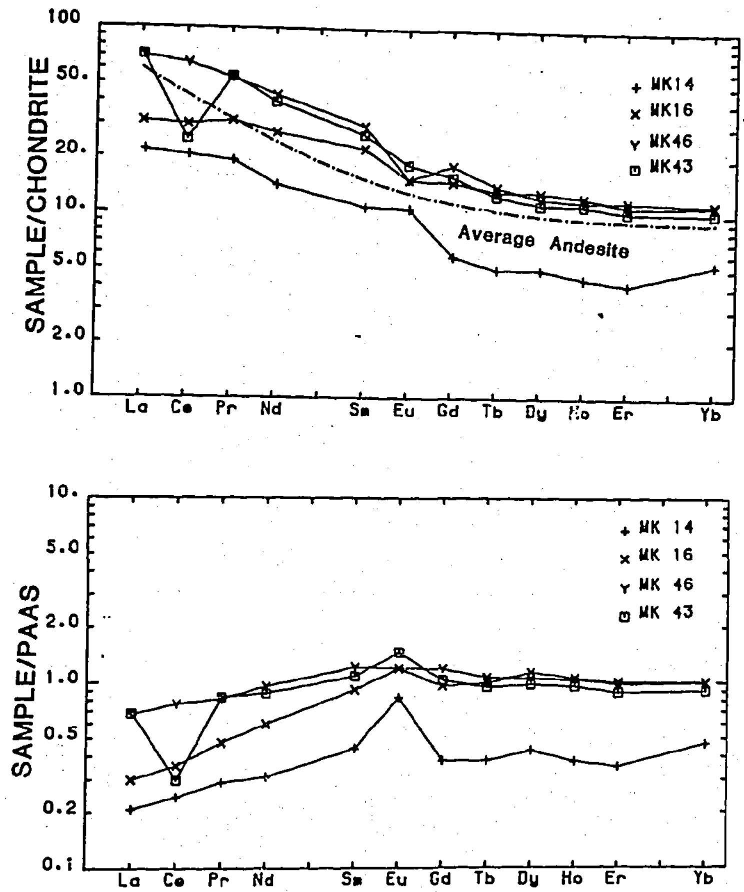


Figure 8.3 Chondrite and PAAS normalised REE plots of the Tamworth suite sedimentary rocks. REE data of average andesite from Taylor (1979).

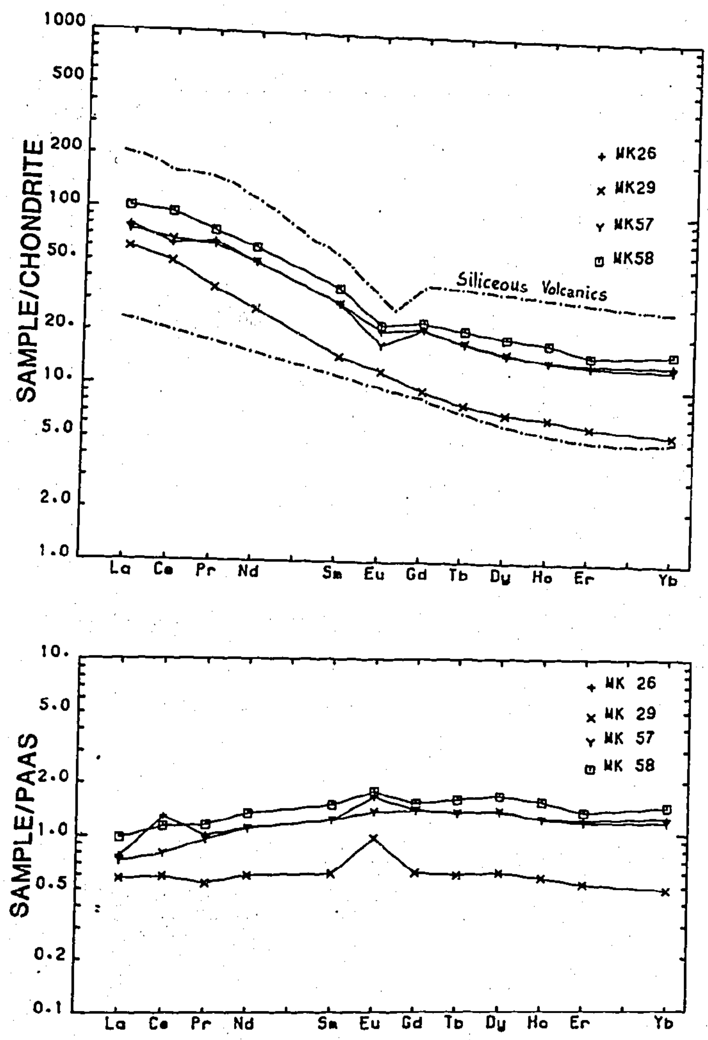


Figure 8.4 Chondrite and PAAS normalised REE plots of the Hill End suite sedimentary rocks (Turondale Formation). The field for siliceous volcanics adopted from Condie (1976).

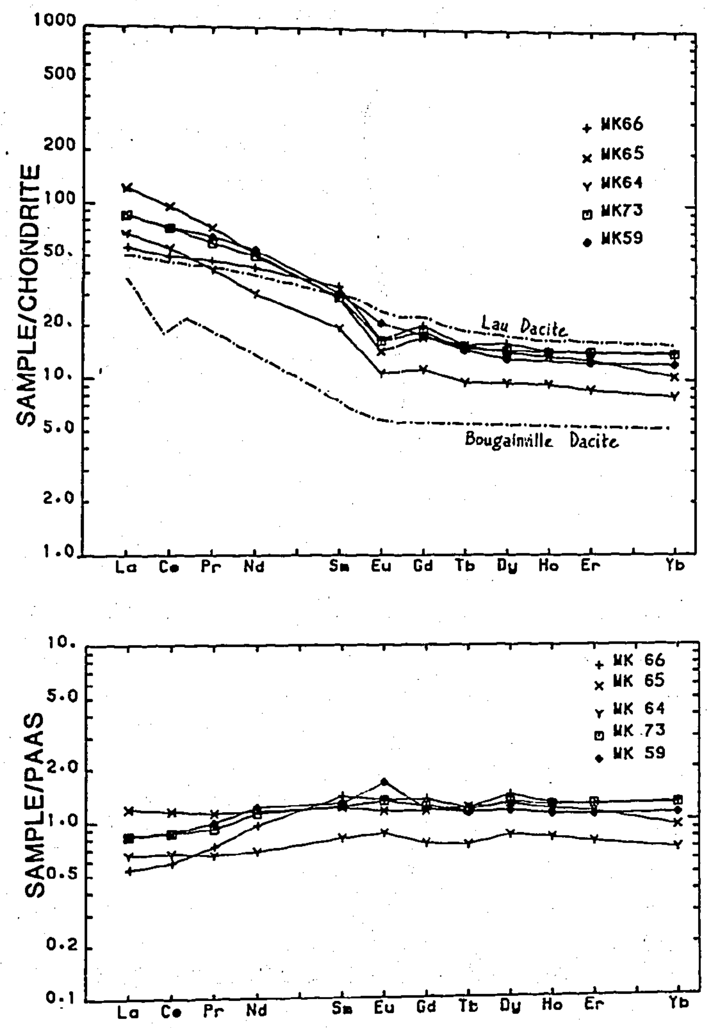


Figure 8.5 Chondrite and PAAS normalised REE plots of the Hill End suite sedimentary rocks (Waterbeach, Merrions Tuff and Cunningham Formation). REE plots of Lau and Bougainville dacites are adopted from Taylor et al. (1969) and Gill (1976), respectively.

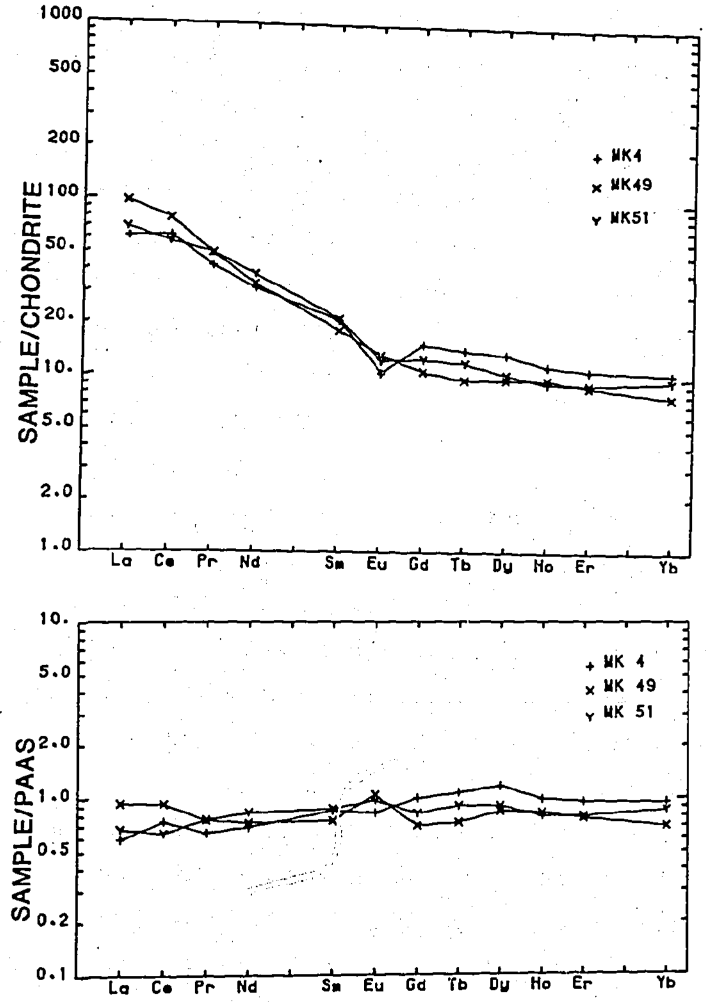


Figure 8.6 Chondrite and PAAS normalised REE plots of the Hill End suite sedimentary rocks (Chesleigh Formation).

(1977) have noted that a significant Ce anomaly is characteristic of radiolarians of the open sea environment of the Pacific, and is absent in radiolarians of the continental shelf and marginal basins. A decrease in the magnitude of the negative Ce anomaly towards the coastline, due to the increasing abundance of detrital material from the continent, has also been noted in recent sediments of the south-eastern Pacific sea floor (Courtois and Hoffert, 1977). Thus, the presence of a negative Ce anomaly in the siliceous mudrocks of the Tamworth suite suggests an open sea environment, in front of a magmatic arc, rather than a marginal basin close to the continent.

8.3.2 Hill End Suite

The sedimentary rocks of the Hill End suite show a large variation from smooth chondrite-normalised REE patterns with no Eu anomaly, to LREE enriched patterns having a significant negative Eu anomaly (Figures 8.4 to 8.6; Tables 8.4). This is due to the differential mixing of volcanic and sedimentary detritus in various proportions. The samples with smooth patterns and no Eu anomaly contain common plagioclase and volcanic rock fragments (e.g. MK 29, MK 49; MK 59). With the increase in sedimentary detritus, there is an increase in LREE enrichment over HREE and an increase in the Eu anomaly on the chondrite normalised plots. The chondrite-normalised REE patterns of volcanic detritus rich Hill End suite graywackes are, in general, similar to the Lau and Bougainville dacites of the Pacific region (Taylor et al. 1969; Gill, 1976). The REE patterns of the sediments also plot within the field of modern siliceous volcanics (Condie, 1976). Thus the REE characteristics of the Hill End suite sedimentary rocks are consistent with their derivation from felsic volcanic and sedimentary rocks.

The PAAS-normalised REE patterns of the Hill End suite sedimentary rocks also show a variation from LREE-depleted with positive Eu anomaly, to flat patterns with no Eu anomaly.

8.3.3 Hodgkinson Suite

The chondrite-normalised REE patterns of the Hodgkinson suite sedimentary rocks are characterised by the high enrichment of LREE over HREE and the presence of a negative Eu anomaly (Figure 8.7; Tables 8.5). On PAAS-normalised plots, these sediments exhibit a flat pattern. The REE characteristics of the Hodgkinson suite sedimentary rocks are similar to those of Paleozoic granites, gneisses and migmatites

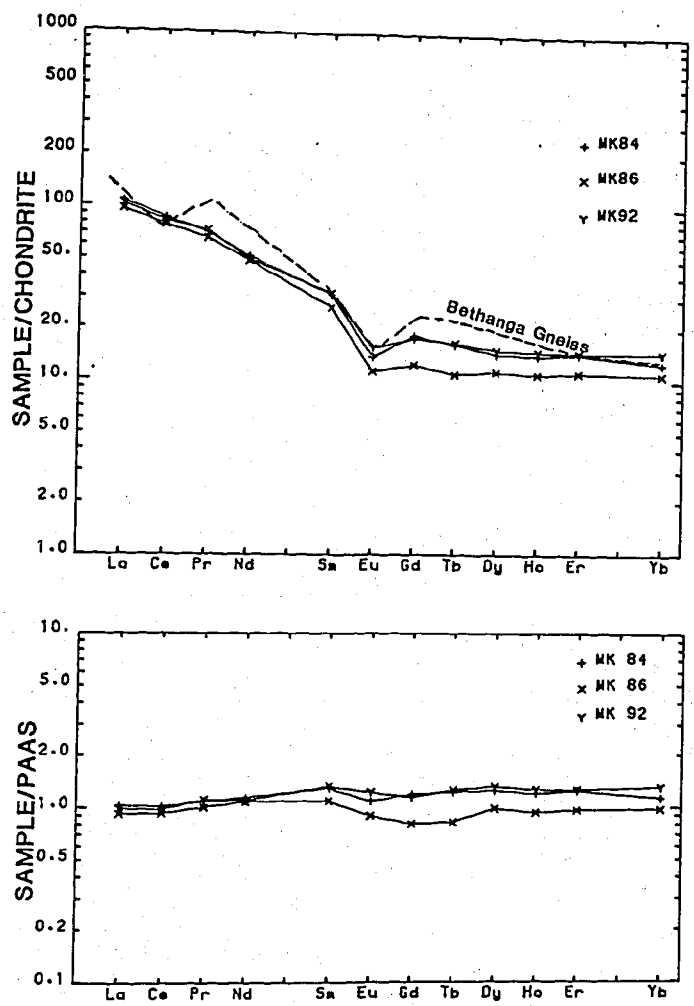
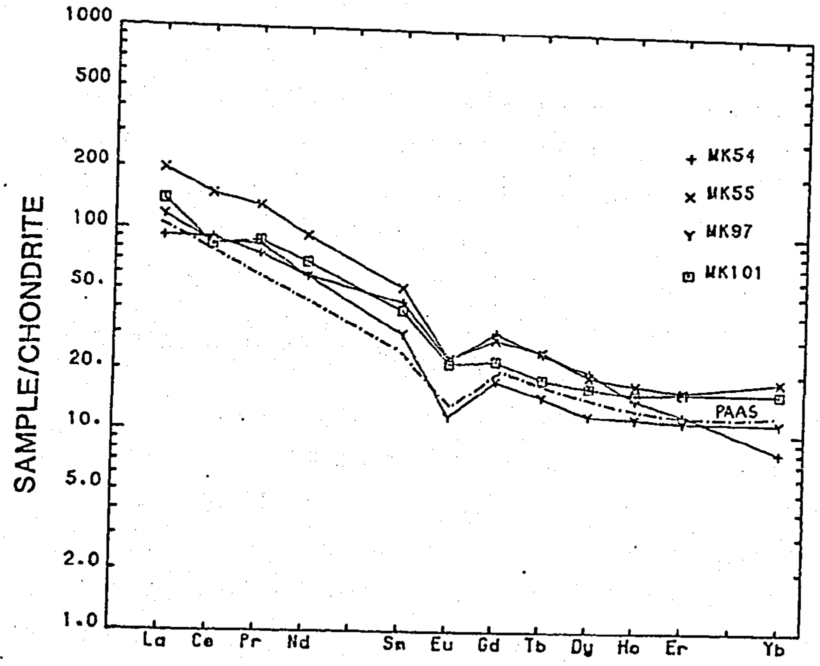


Figure 8.7 Chondrite and PAAS normalised REE plots of the Hodgkinson suite sedimentary rocks. Data for Bethanga gneiss adopted from Price and Taylor (1977).



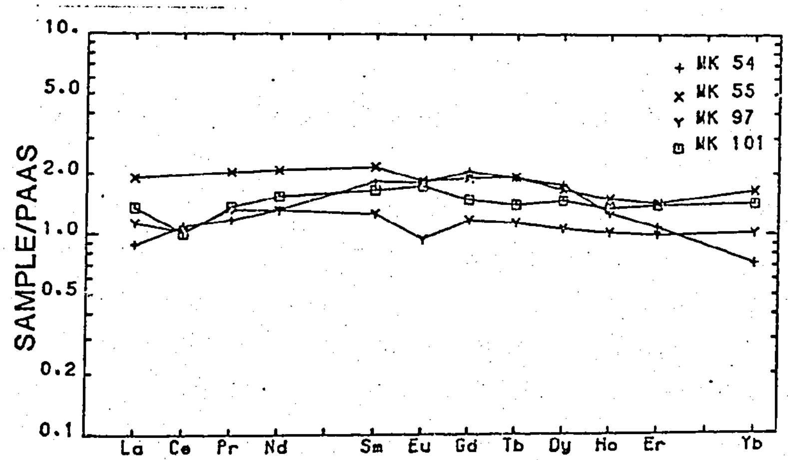


Figure 8.8 Chondrite and PAAS normalised REE plots of the Bendigo and Cookman suite sedimentary rocks. Data for PAAS adopted from Nance and Taylor (1976) (Table 8.1).

of southeastern Australia (e.g. Bethanga gneiss - Price and Taylor, 1977), substantiating the petrographic evidence that crystalline rocks constituted the source terrain for these sediments.

8.3.4 Bendigo and Cookman Suites

The chondrite-normalised REE patterns of the Bendigo and Cookman suite sedimentary rocks are characterised by the high enrichment of LREE compared to HREE and the presence of a negative Eu anomaly (Figure 8.8; Table 8.5). These features are typical of the Post-Archean sedimentary rocks of Australia (Nance and Taylor, 1976). On PAAS-normalised plots, these sediments exhibit a generally flat pattern with REE enrichment up to a factor of 2. The REE features are compatible with the highly matured nature of the sediments, suggesting their derivation from older sedimentary rocks. The slight negative Eu anomaly in a few samples, (MK 55, MK 97), on PAAS-normalized plots may be due to the loss of feldspar during recycling.

8.4 REE PARAMETERS AND COMPOSITIONAL CHARACTERISTICS

8.4.1 Grain Size

Grain size is an important attribute of clastic sedimentary rocks. The medium grained rocks (graywackes/sandstones) are enriched in framework grains whereas the fine-grained sedimentary rocks (mudrocks) are enriched in phyllosilicate and clay-sized material. A plot of mean grain size against ΣREE, shows the effect of textural variation on the REE (Figure 8.9). No significant difference can be deciphered if all graywackes and all mudrocks are grouped together. However, when mudrocks of each suite were compared with the corresponding graywackes, it was noted that most mudrocks are enriched in ΣREE by ≅ 20-30%. Culler et al. (1979) have also shown that the REE abundance is high in the clay-size fraction. Thus, not all fine grained clastics are rich in ΣREE, rather the finer fraction is only enriched compared to coarser size fraction, within each suite.

8.4.2 Detrital Mineralogy

The maturity index [MI = 100 x Quartz/(Quartz + Feldspar + Rock Fragments)] and provenance index (PI = Volcanic Lithic Grains (Lv)/Total Lithic Grains (L)) are two parameters of detrital framework grains, which reflect the nature of the source rocks. (Note that the PI used here is different from the PI used in Chapter 3). The REE

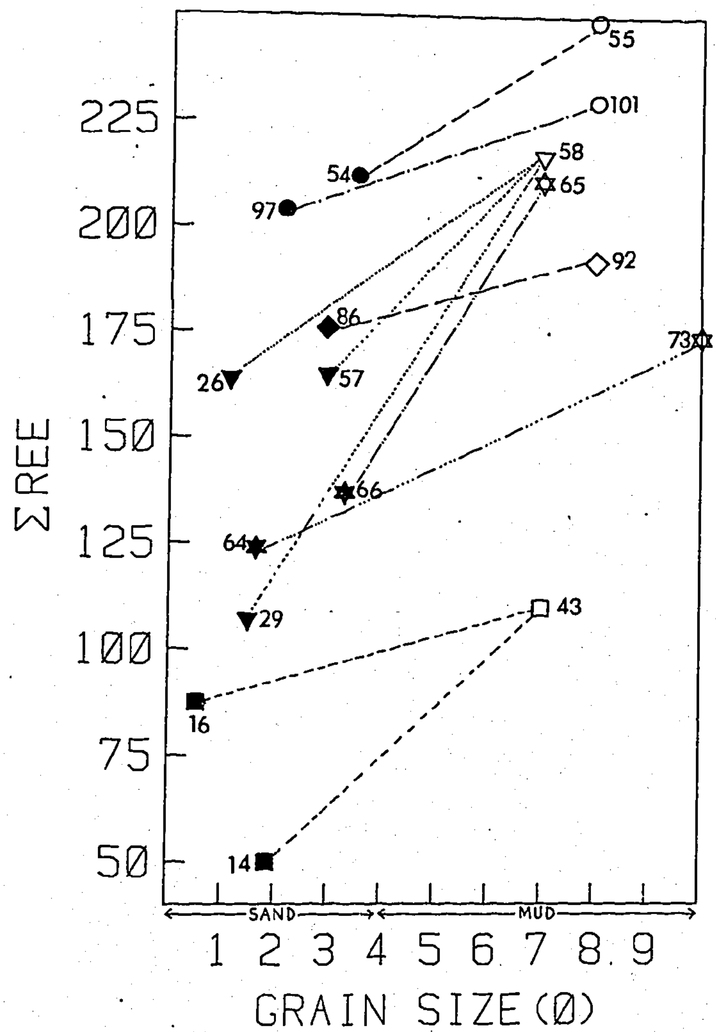


Figure 8.9 Plot of mean grain size (Ø) versus ΣREE. Note that the mudrocks are enriched in ΣREE compared to the graywackes in each suite. The numbers (e.g. 14, 16) refer to the sample numbers in Tables 8.2-8.4 (prefix MK omitted in Figure 8.9).

Note that Sample 55 has total REE 347ppm but is plotted at 250ppm for convenience.

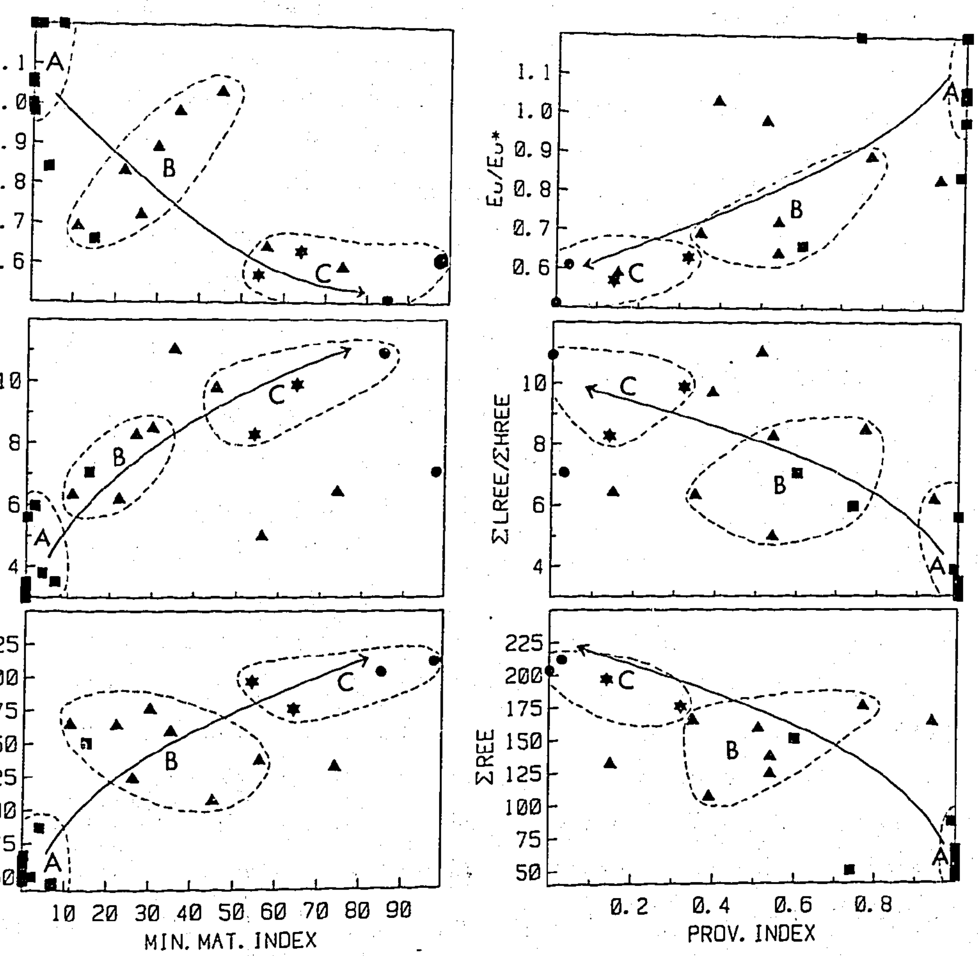


Figure 8.10 Plots of mineralogical maturity and provenance indices versus the REE parameters of graywackes. The arrow indicates increasing maturity. The dotted lines mark various source rocks : A - Andesite; B - Dacite; C - granite-gneiss and sedimentary rocks. Symbols are:

■ Tamworth suite
▲ Hill End suite
✱ Hodgkinson suite
● Bendigo & Cookman suites

parameters (ΣREE; ΣLREE/ΣHREE; Eu/Eu*) are plotted against MI and PI (Figure 8.10). La_N/Yb_N ratio shows variation similar to that of ΣLREE/ΣHREE and hence is not plotted. Though there is a large variation, the graywacke suites characterising various provenance types occupy quite distinct fields. In general, there is an increase in ΣREE, ΣLREE/ΣHREE and a decrease in Eu/Eu* with the increase in MI and decrease in PI, corresponding to the change in dominant source rocks from andesite to dacite to granite-gneisses and sedimentary rocks.

Graywackes derived from granite-gneisses (e.g. Hodgkinson suite) are difficult to distinguish from recycled graywackes (e.g. Bendigo and Cookman suites) on the basis of REE characteristics, except probably the latter are slightly more enriched in ΣREE.

8.4.3 Clay Mineralogy

Is there any definite relationship between the mineralogical and REE characteristics of mudrocks? The mudrocks analysed in the present work are mainly composed of illite, chlorite, quartz, feldspar and minor kaolinite (Chapter 5). A characteristic of the mudrocks can be expressed by the clay maturity index [CMI = 100 x Clay minerals/(Clay minerals + Quartz)]. This has been correlated with the Th, U, and Th/U ratio of mudrocks (Bhatia and Taylor, 1981). Although, the present data set is very small, an excellent correlation was observed between ΣREE, Eu/Eu*, and CMI (Figure 8.11). In general, there is an increase in ΣREE and a decrease in Eu/Eu*, with the increase in CMI in mudrocks due to change in the dominant provenance from andesite to dacite to granite-gneisses and sedimentary rocks. The relationship with ΣLREE/ΣHREE and La_N/Yb_N is less well defined, but in mudrocks signatures of source rocks can be identified in ΣREE and the Eu/Eu*.

8.4.4 Chemical Maturity

The relationship between REE parameters and major element chemistry can be used to decipher the nature of the parent material, especially if framework grains are obliterated due to post-depositional modifications. SiO_2/Al_2O_3 and K_2O/Na_2O ratios have been used as indices of chemical maturity and their relations with the REE parameters are shown in Figure 8.12. Graywacke suites representing various provenance types occupy quite distinct fields. In general, there is an increase in ΣREE and ΣLREE/ΣHREE, and a decrease in Eu/Eu* corresponding to the increase in SiO_2/Al_2O_3 and K_2O/Na_2O ratios in

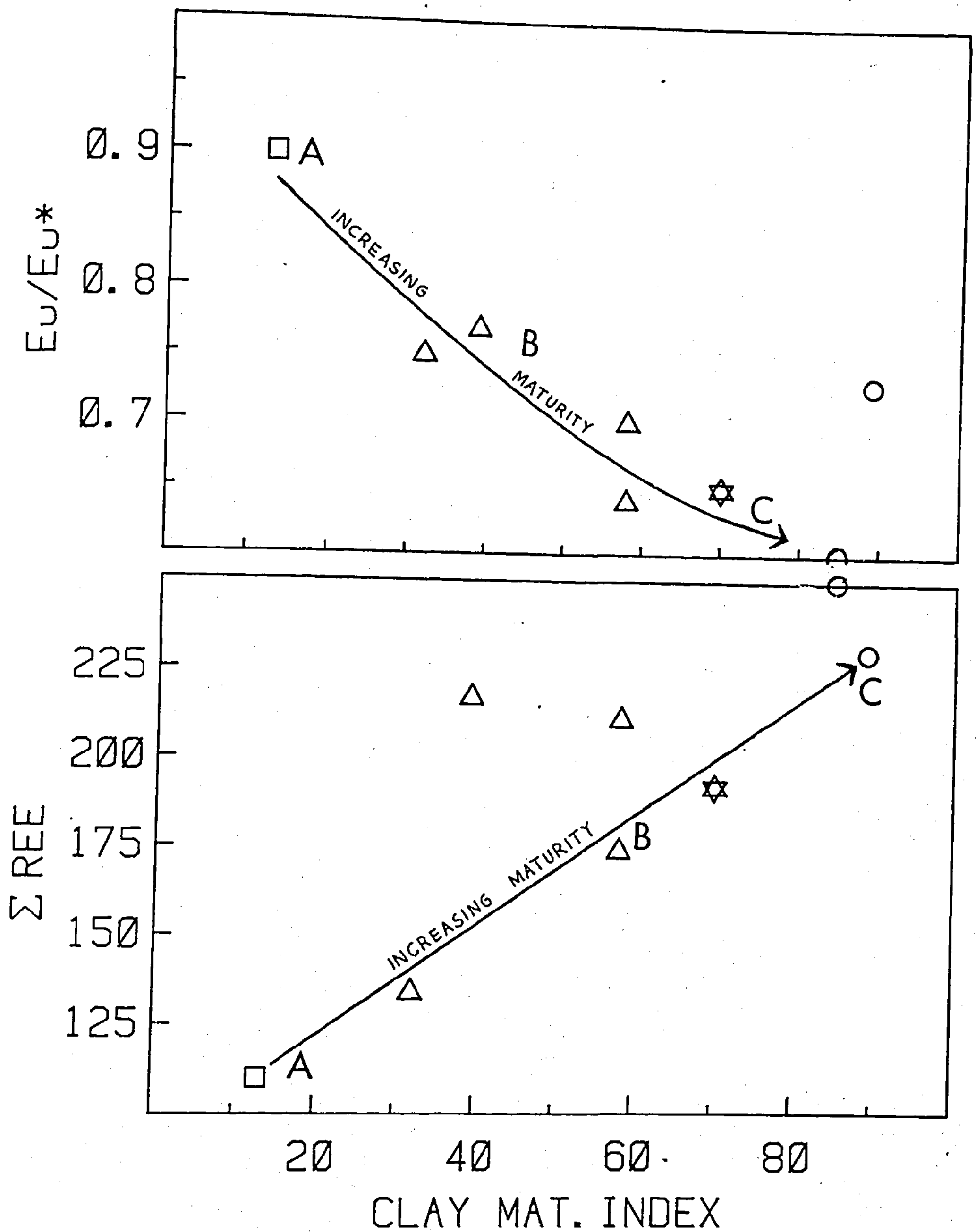


Figure 8.11 Plot of clay maturity index versus ΣREE and Eu/Eu*. The arrow indicates increasing maturity from andesitic (A), through dacite (B) to granite gneiss and sedimentary (C) source rocks. The Cookman suite sample has ΣREE 347 ppm but is plotted at 250 ppm here for convenience. The symbols are:

□ Tamworth suite

△ Hill End suite

✡ Hodgkinson suite

○ Bendigo & Cookman suites

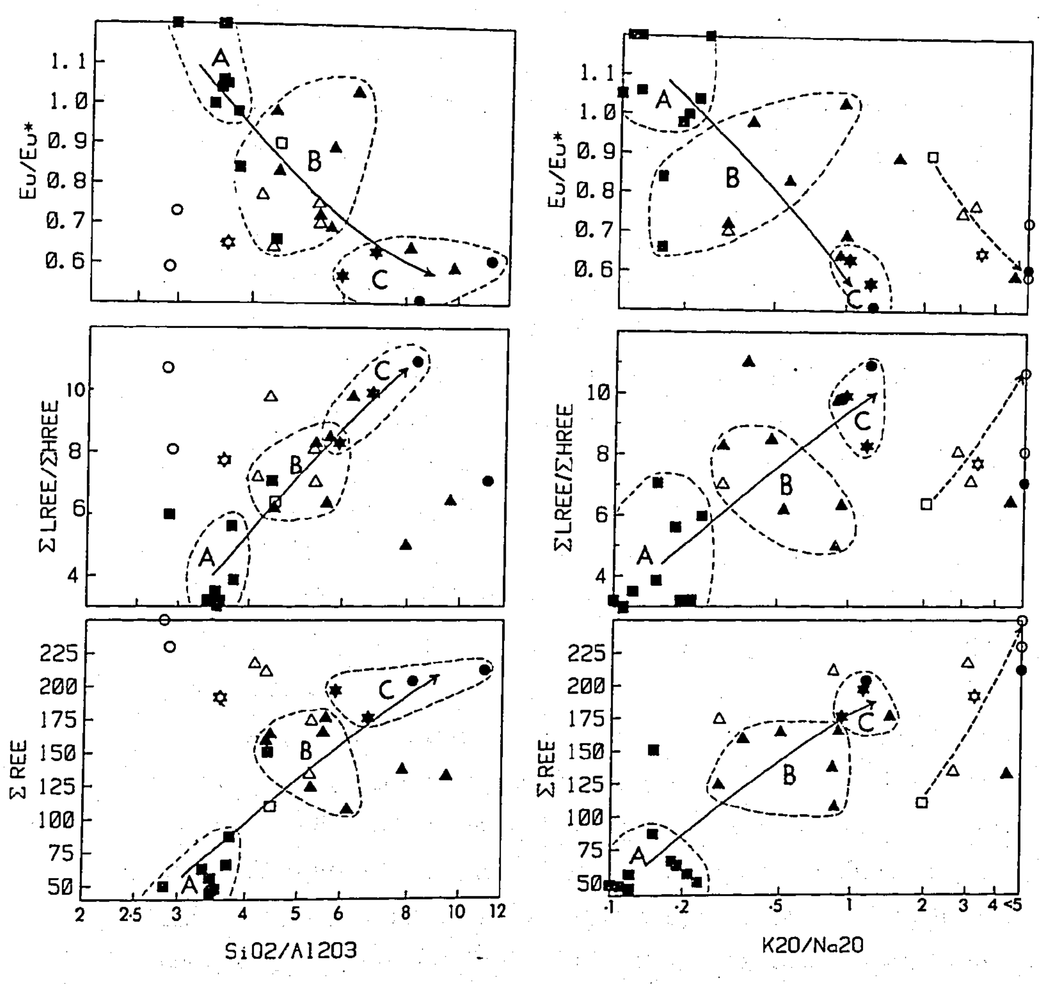


Figure 8.12 Plots of SiO_2/Al_2O_3 and K_2O/Na_2O versus REE parameters for graywackes and mudrocks. The arrow indicates increasing maturity from andesitic (A) through dacitic (B) to granite-gneiss and sedimentary (C) source rocks. Note the log scale along the X-axis. The Cookman suite mudrock has ΣREE 347 ppm but is plotted at 250 ppm for convenience. Solid symbols are for graywackes (as in Figure 8.10), and open symbols are for mudrocks (as in Figure 8.11).

graywackes, due to the change of dominant source rocks from andesite to dacite to granite-gneiss and sedimentary rocks.

The variation in the chemical maturity indices is not very clear in mudrocks. Mudrocks are significantly enriched in K_20 and Al_20_3 due to the enrichment of phyllosilicates, and thus show higher K_20/Na_20 and probably lower $Si0_2/Al_20_3$ ratios compared to the corresponding graywackes. Although there is a large variation, in general ΣREE increases and Eu/Eu^* decreases in mudrocks, with the increase in K_20/Na_20 and probably decrease in $Si0_2/Al_20_3$, as the dominant source rock changes from andesite to dacite to granite-gneiss and sedimentary rocks (Figure 8.12).

8.5 TECTONIC SETTINGS AND REE CHARACTERISTICS

REE characteristics are related to the mineralogical and geochemical composition of clastic sedimentary rocks, suggesting that the signatures of the provenance types are faithfully preserved in rare earth element geochemistry. However, tectonic setting governs the relationship between the provenance type, the source rocks and the detrital composition of arenites (Crook, 1974; Schwab, 1975; Dickinson and Suczek, 1979; Dickinson and Valloni, 1980; Valloni and Maynard, 1981; Chapter 8). Hence the influence of tectonic setting will also be reflected in the REE geochemistry of clastic sedimentary rocks.

The geochemical composition of volcanic rocks of orogenic belts has been widely used to characterise the tectonic settings, and the nature of the crust. Bailey (1981) has compiled REE parameters which can be used to discriminate the tectonic setting of andesites. The sedimentary rocks studied in the present work are from the orogenic zone (flysch types) and the direct comparison of their REE characteristics with those of orogenic andesites can provide evidence on the tectonic setting of sedimentary basins (Table 8.6; Figure 8.13).

8.5.1 Tamworth Suite

The Tamworth suite graywackes exhibit smooth chondrite-normalised REE patterns, with slight LREE enrichment (upto ≅ 25 x chondritic La) and the absence of a negative Eu anomaly. These REE characteristics of the graywackes are similar to those of the oceanic island arc type andesites (Figure 8.13; Jakes and Gill, 1970; Kay, 1978; Bailey, 1981). These sediments are significantly less fractionated and

Table 8.6 Rare Earth Element Comparison of Graywacke Suites with Andesites from Various Tectonic Settings (Abundances in ppm).

	Oceanic Island Arc[1)]		Tamworth Suite[2)]	Continental Island Arc[1)]	Hill End Suite[2)]	Andean Type[1)]	Hodgkinson Suite[2)]
	Low K	Others					
La	3.0	11.7	8.2	17	27	28.5	37
Ce	6.9	23.5	19.4	37	59	60.7	78
Pr	1.27	2.9	2.68	4.7	6.97	7.3	9.3
Nd	7.8	17	11.16	18.3	28.3	30.	35.8
Sm	2.6	4.15	3.05	3.87	5.68	4.9	6.7
Eu	1.0	1.37	1.07	1.11	1.33	1.29	1.1
Gd	2.4	3.4	3.29	3.1	4.89	4.3	4.72
Tb	0.52	0.70	0.50	0.57	0.78	0.65	0.8
Dy	3.0	3.5	3.18	3.15	4.77	3.55	4.95
Ho	0.9	0.86	0.73	0.76	1.10	0.60	1.08
Er	2.5	2.6	2.11	2.2	2.78	1.7	3.23
Yb	2.55	1.86	2.14	2.04	2.66	1.5	2.97
ΣREE	34.4	73.46	58	93.79	145	146	165
La/Yb	1.2	6.4	3.8	8.9	10.15	16.5	12.4
La/Sm	1.2	4.0	2.69	4.3	4.7	5.3	5.5
Eu/Eu*	1.00	0.98	1.03	0.87	0.75	0.83	0.64
Hf	1.55	2.43	2.1	3.44	6.3	5.75	6.8
Hf/Yb	0.61	1.3	0.98	1.7	2.37	3.4	2.29
Th	0.72	1.95	1.4	5.36	10	6.0	15.9
U	0.37	0.62	0.52	1.6	2.2	1.25	3.8
Th/U	1.7	2.8	2.8	3.6	4.6	3.3	4.22
Sc/Ni	3.4	2.0	2.3	1.1	1.4	0.55	0.77

1) Andesites of various tectonic settings, from Bailey (1981).

2) Mean element abundance in graywacke suite. Element ratios are calculated from individual ratios. Data for Th, U, Th/U and Hf from Bhatia and Taylor (1981). Data for Sc/Ni from Table 7.15.

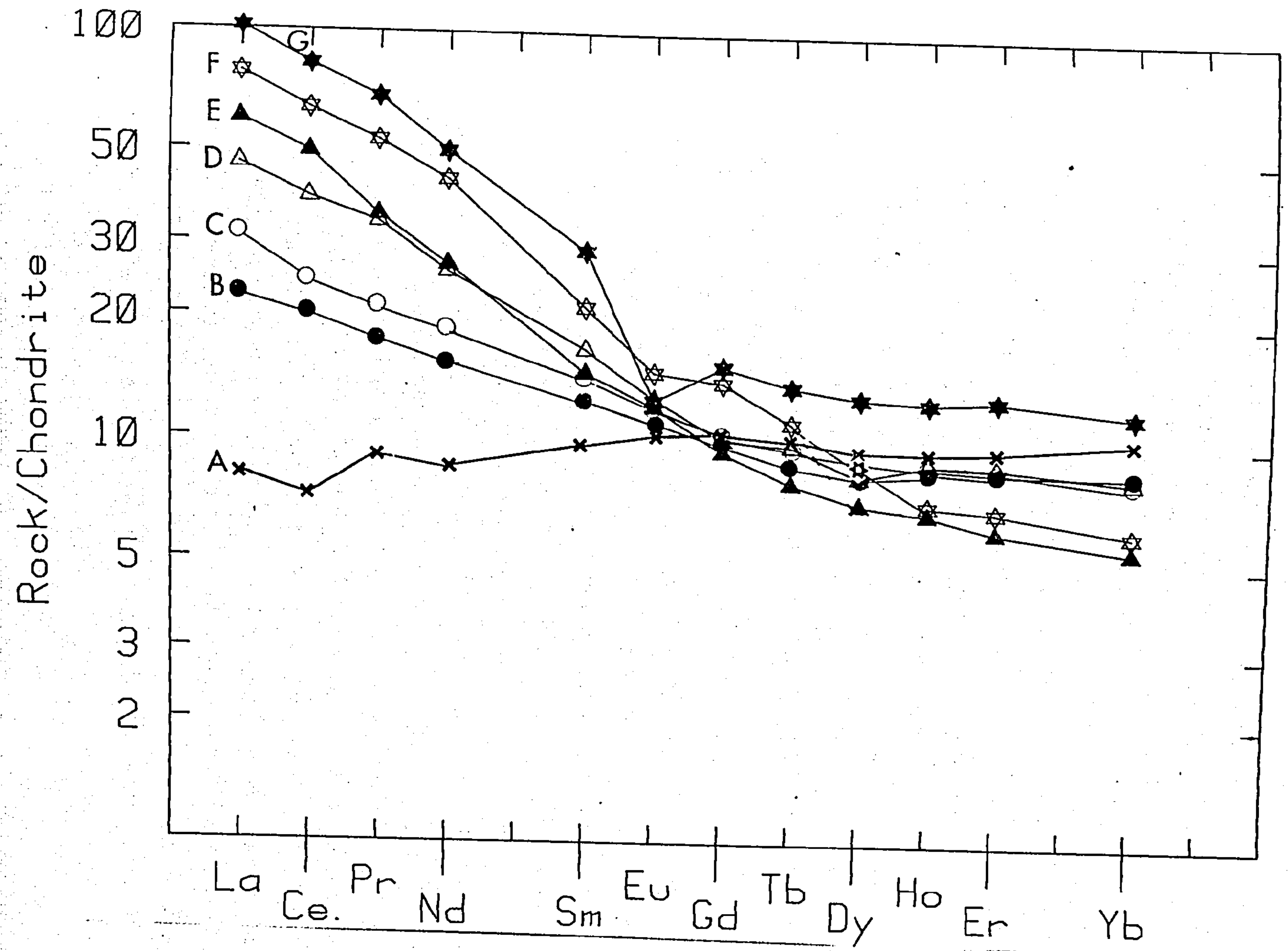


Figure 8.13 Comparison of chondrite normalised REE patterns of various graywacke suites (present work) and orogenic andesites (after Bailey,1981). A- Low K Oceanic island arc andesite; B- other Oceanic island arc andesites; C- average Tamworth suite; D - Continental island arc andesite; E- Hill End suite (Sample MK29) ; F- Andean type andesite; G- average Hodgkinson suite. Note similarities between B & C: D & E; F & G.

are low in ΣLREE compared to "continental" or "quasi-continental" calc-alkaline rocks (e.g. Thorpe et al. 1976; Johnson et al. 1978; Bailey, 1981). The abundance of La, Ce, ΣREE, and the La/Yb, Eu/Eu*, Hf/Yb and Th/U ratios of the Tamworth suite graywackes also resemble the values of oceanic island arc andesites and differ significantly from continental island or Andean type andesites (Table 8.6).

Bailey (1981) proposed plots of Th versus La/Yb, and Sc/Ni versus La/Yb to discriminate oceanic island arc, continental island arc and Andean type andesites. On the Th vs La/Yb plot, most Tamworth suite graywackes fall close to the oceanic island arc fields (Figure 8.14). Similarly, on the Sc/Ni vs La/Yb plot, the average Tamworth suite graywacke plots in the high K - oceanic island arc field (Figure 8.15, "other" variety of Bailey, 1981). Thus on the basis of REE characteristics, a dominant andesitic source, an undissected magmatic provenance and an oceanic island arc tectonic setting can be assigned to the Tamworth Trough.

8.5.2 Hill End Suite

Large variation is seen in the REE patterns of the Hill End suite graywackes, due to the mixing of detritus from felsic volcanic and sedimentary sources. However, graywackes with dominant volcanic detritus (e.g. MK 29) exhibit a smooth chondrite-normalised REE pattern with no Eu anomaly and a low La_N/Yb_N ratio. These patterns are similar to those of continental island arc andesites (Figure 8.13). A large difference in the REE parameters between the Hill End and the Tamworth suite and oceanic island arc andesites preclude an intra-oceanic character for the Hill End Trough. A close similarity is observed in the La/Yb, La/Sm and Hf/Yb ratios of the average Hill End suite graywacke and continental island arc andesite (Table 8.6). The continental island arc type tectonic setting for the Hill End Trough is further confirmed by the plot of Sc/Ni vs La/Yb, in which the average Hill End suite graywacke plots in the field of the andesites of this tectonic setting (Figure 8.15).

8.5.3 Hodgkinson Suite

The chondrite normalised REE patterns of the Hodgkinson suite graywackes, characterised by the presence of a pronounced negative Eu anomaly and the significant enrichment of LREE over HREE, are similar to those of Andean type andesites (Figure 8.13). Other trace element

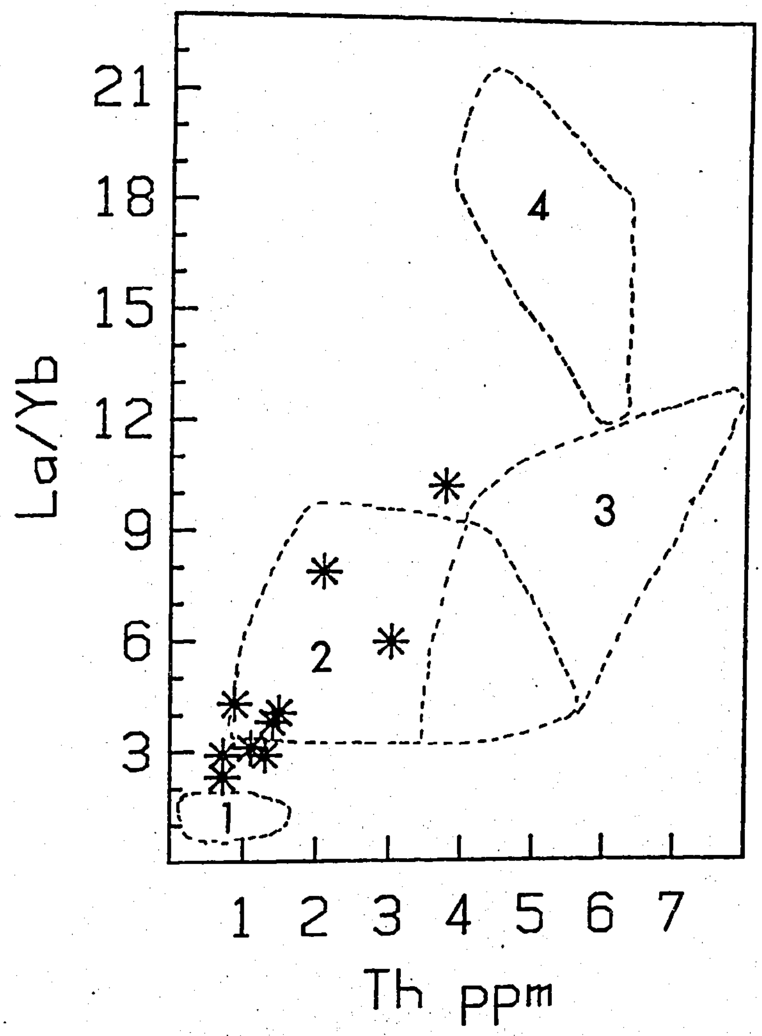


Figure 8.14 Th versus La/Yb plot of the Tamworth suite graywackes (✱). The dotted fields are for the andesites of various tectonic settings (after Bailey, 1981):
1 - "low K" Oceanic Island Arc
2 - "other" Oceanic Island Arc
3 - continental Island Arc
4 - Andean type
Note that the Tamworth suite samples plot close to the oceanic island arc fields.

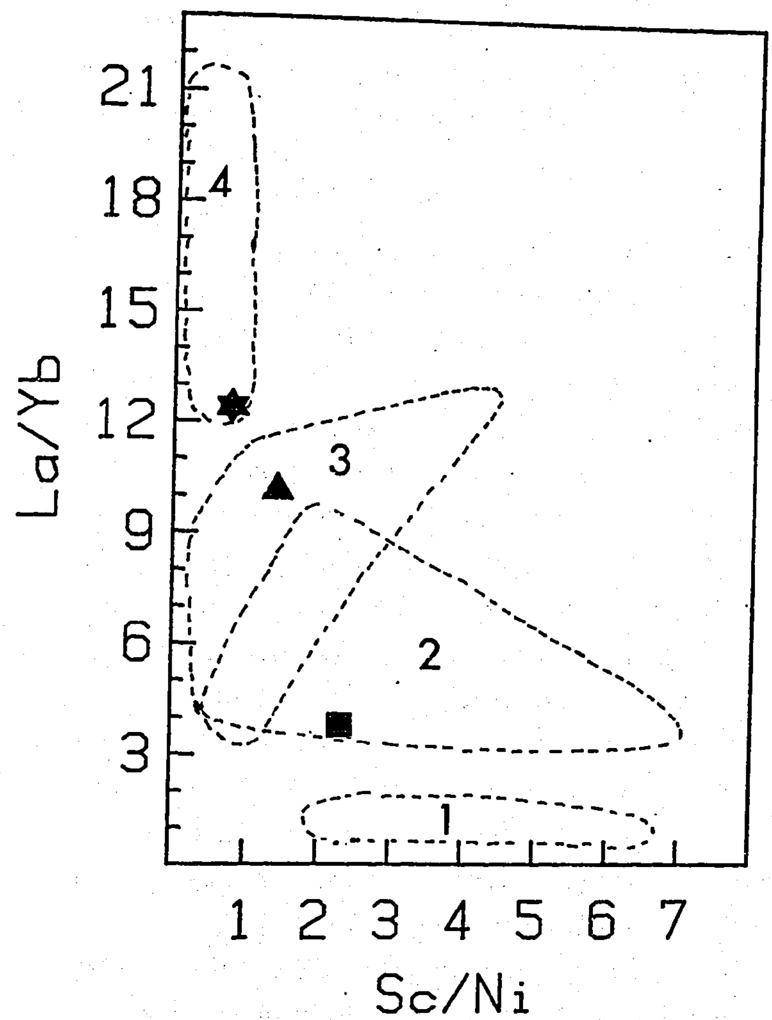


Figure 8.15 Sc/Ni versus La/Yb plot of average graywacke suites. The dotted fields are for the andesites of various tectonic settings after Bailey (1981) (Defined in Figure 8.14). Graywacke symbols are as follows:

■ Tamworth suite
▲ Hill End suite
✡ Hodgkinson suite

parameters like La, Ce, Hf and the La/Yb, La/Sm and Hf/Yb ratios are quite close between these sediments and Andean type andesites. On the discrimant plot of Sc/Ni vs La/Yb, the average Hodgkinson suite graywacke plots in the field of andesites of the Andean type tectonic setting (Figure 8.15).

8.5.4 Bendigo and Cookman Suites

The chondrite-normalised REE patterns of the Bendigo and Cookman suites are similar to PAAS, characterised by the presence of a significant negative Eu anomaly and the high enrichment of LREE over HREE (Figure 8.8). These features are similar to the REE characteristics of modern deep sea turbidites of the northwest Atlantic Ocean (Addy, 1979), suggesting a recycled nature and a passive margin type of tectonic setting for the Bendigo and Cookman suites.

8.5.5 Tectonic Setting Discrimination

Various sedimentary suites of eastern Australia are assigned to the following tectonic settings on the basis of REE geochemistry : Oceanic island arc (Tamworth suite); Continental island arc (Hill End suite); Andean type (Hodgkinson suite); and passive margins (Bendigo and Cookman suites). These tectonic settings correspond to the undissected magmatic arc (andesites); dissected magmatic arc (dacites); uplifted basement (crystalline rocks); and recycled orogen-craton interior (sedimentary rocks) types of provenance (and source rocks), respectively. Thus, REE characteristics can be used to discriminate the various tectonic settings of sedimentary basins. The discriminating REE parameters for each tectonic setting are outlined in Table 8.7 and the characteristic chondrite- and PAAS-normalised plots are given in Figure 8.16.

Oceanic island arc type graywackes are discriminated by the low abundance of La, Ce, ΣREE, the low La_N/Yb_N ratio, and the absence of a negative Eu anomaly on chondrite-normalised plots. On PAAS normalised plots, these sediments are distinguished by the high depletion of LREE compared to PAAS and the presence of a Eu anomaly (Figure 8.16). Continental island arc type graywackes show a large variation in their REE characteristics, due to the mixing of volcanic and sedimentary detritus in various proportions, but they are discriminated from the oceanic island arc type by their higher La, Ce and ΣREE, and higher La_N/Yb_N and ΣLREE/ΣHREE ratios (Table 8.7). The graywackes of this

Table 8.7 Most Discriminating Rare Earth Element Characteristics of Tectonic Settings of Sedimentary Basins[1)]

	Oceanic Island Arc[3)]	Continental Island Arc[3)]	Andean Type[3)]	Passive Margin[3)]
N[2)]	9	8	2	2
La (ppm)	8 ± 1.7	27 ± 4.5	38	38
Ce (ppm)	19.4 ± 3.7	59 ± 8.2	78	85
ΣREE	60 ± 10	146 ± 20	187	219
La/Yb	4.2 ± 1.3	11.0 ± 3.6	12.5	15.9
La_N/Yb_N	2.8 ± 0.9	7.5 ± 2.5	8.5	10.8
$\frac{\Sigma REE}{\Sigma HREE}$	3.8 ± 0.9	7.7 ± 1.7	9.1	8.5
Eu/Eu^*	1.04 ± 0.11	0.79 ± 0.13	0.60	0.56

1) Based on graywacke data.

2) Number of samples.

3) Mean values. Mean element ratios calculated from individual ratios. Uncertainties represent 95% confidence limits on the means. Uncertainties not given for Andean type and passive margin because of small data set.

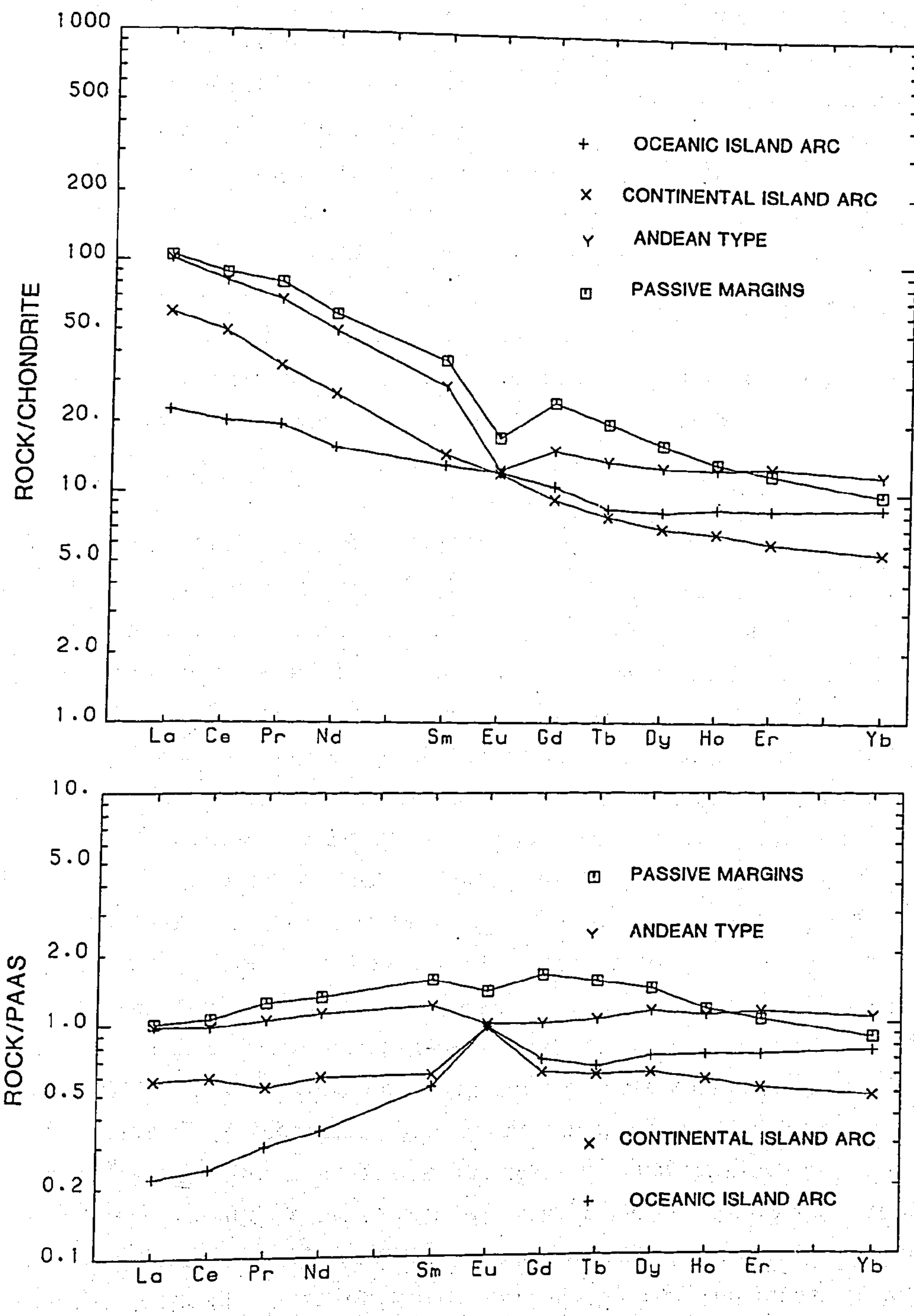


Figure 8.16 Chondrite and PAAS normalised discriminatory plots for graywackes of various tectonic settings. Data are from average graywacke for all tectonic settings (Table 8.7), except for the continental island arc. Sample MK29 represents the characteristic of the continental island arc tectonic setting (Table 8.4).

tectonic setting, containing abundant volcanic detritus, (e.g. MK 29) are characterised by the slight depletion of LREE and the presence of a positive Eu anomaly on PAAS normalised plots. Andean type graywackes are characterised by the high abundance of La, Ce, ΣREE, the high La_N/Yb_N and ΣLREE/ΣHREE ratios and the presence of a significant negative Eu anomaly on chondrite-normalised plots. These graywackes are very similar to PAAS as evidenced by the flat pattern on PAAS-normalised plots (Figure 8.16). Passive margin type graywackes are similar to those of the Andean type but probably can be distinguished by their higher La_N/Yb_N ratio on chondrite-normalised plots and slightly higher ΣREE, due to recycling.

Mudrocks associated with graywackes in each tectonic setting also show discrimination, especially in their ΣREE and Eu/Eu^* (Figure 8.11), but more data are needed to formulate discrimination criteria.

8.6 RARE EARTH ELEMENTS IN TEKTITES AND SEDIMENTARY ROCKS

The origin and source of tektites has been debated for a long time. Before the return of lunar material, tektites were thought to be of lunar origin. However, a lunar origin has been discounted due to the large geochemical differences observed between tektites and lunar samples (e.g. Taylor, 1973, 1975). All Australasian tektites exhibit chondrite-normalised REE patterns similar to those of PAAS, characterized by the presence of a negative Eu anomaly and significant enrichment of LREE over HREE. In view of this similarity a terrestial origin and formation due to the meteoritic or cometary impact on sediments and soils has been favoured (e.g. Nance and Taylor, 1976; Taylor and McLennan, 1979).

Sedimentary rocks show a large variation in their REE patterns, depending upon provenance types and tectonic settings. Thus a comparison of tektite REE and sedimentary patterns can constrain the parent material of tektites. The chondrite-normalised REE patterns of Australasian tektites are similar to those of sedimentary rocks of the Andean or passive margin types, suggesting that these tektites originated from a well developed continental crust or fractionated sedimentary rocks. The chondrite-normalised REE patterns of silica-poor Zhamanshinite and Irghizite, are characterised by the slight enrichment of LREE over HREE and the absence of a negative Eu anomaly (Taylor and McLennan, 1979). These features are similar to those of the oceanic island arc type rocks and indicate derivation from andesitic source material.

CHAPTER 9
GEOCHEMICAL EVOLUTION OF SEDIMENTARY ROCKS AND CRUSTAL GROWTH

9.1 INTRODUCTION

The geochemical composition, evolution and growth of the crust have always been fascinating subjects in earth science. The continental crust makes up only ≅ 0.3 percent of the earth's total mass but is strongly enriched in many elements (e.g. K, U, Th, Rb, Ba). An understanding of the nature and composition of the continental crust helps to constrain models of the evolution of the earth.

Various models of the evolution and growth of the crust have been proposed (see reviews by Taylor, 1977, 1979; Windley, 1977; Hanson, 1980; Shaw, 1980; Kröner, 1981). The models are generally of two types. The first type favours the formation of the whole mass of the continental crust very early in the earth's history, whereas the second type favours the progressive growth of the crust during the earth's history.

9.1.1 Upper Continental Crust

Many geochemical and geophysical studies have indicated that the abundances of K, Th, U and Ba, observed in the upper 10-15 km of the crust, cannot extend to the base of the continental crust (Gast, 1960; Taylor, 1977; Heier, 1978). This part of the continental crust, which is highly enriched in incompatible elements is called the upper continental crust (UCC) and comprises about one-third of the total continental crust.

Rocks of the upper crust are exposed on the surface of the earth. The composition of the UCC can be directly calculated if the proportion and composition of each rock type is known. Such studies have been carried out in the Canadian Shield and have indicated that the UCC in shield areas is of granodioritic composition (Eade and Fahrig, 1971, 1973; Shaw et al. 1967; 1976) (Table 9.1). Data on various types of sedimentary rocks have generally confirmed a granodioritic upper crust (Goldschmidt, 1954; Ronov, 1972; Ronov and Migdisov, 1971).

9.1.2 Total Crust

The bulk composition of the total crust is more difficult to estimate and is modal dependent. The granodioritic upper crust formed as a result of fractionation of the total crust. According to Taylor (1967, 1977, 1979), island-arc volcanism provides the only suitable source from which the granodioritic upper crust can be extracted. Thus, the average andesite of the island arc has been suggested to represent the bulk composition of the total crust (Table 9.1). This composition is similar to the estimate of the total crustal composition suggested by Ronov and Yaroshevsky (1969).

The composition of the lower crust has been calculated by subtracting the weighted upper crustal composition from the total crustal composition (Taylor, 1979; Taylor and McLennan, 1981a).

9.1.3 Aim

Due to their ubiquitous occurrence sedimentary rocks provide an excellent opportunity to understand the evolution and composition of the crust with time. Based on studies of sedimentary rocks, significant contributions have been made in deciphering the crustal growth (e.g. Garrels and Mackenzie, 1971; Garrels et al. 1972; Ronov and Migdisov, 1971; Veizer and Compston, 1974, 1976). As is evident, the present data set is too small to be able to propose an unequivocal model of crustal evolution. However, it is hoped that the assemblage of such complete data sets will lead to new approaches and help constrain the models (Veizer, 1979; Hanson, 1980). In the present chapter, the following aspects of crustal evolution are treated : tectonic model of the geochemical evolution of sedimentary rocks; average compositions of clastic sedimentary rocks in various tectonic settings and their comparison with crustal compositions; constraints on the provenance of Archean sedimentary rocks; secular variations and crustal growth.

9.2 TECTONIC MODEL OF GEOCHEMICAL DIFFERENTIATION OF SEDIMENTARY ROCKS

Clastic sedimentary rocks form due to the decomposition of igneous, metamorphic and sedimentary rocks. The evolution of clastic assemblages is a function of the transformation of source rock minerals and in general, has been documented as the reverse of the Bowen Series of mineral formation in igneous rocks (Garrels and Mackenzie, 1971; Sharma, 1979). Sedimentary rocks are formed by the degradation of felsic minerals in a series of Ca plagioclase-Na plagioclase-K feldspar-muscovite-quartz, and mafic minerals are degraded in a sequence of iron oxide-olivine-pyroxene-amphibole and biotite. The reconstitution of original source minerals takes place during sedimentary cycles, and the elements are redistributed depending upon source rocks, weathering, cation exchange and adsorption conditions.

However, it has been shown that the tectonic setting of the sedimentary basin governs the compositional variables (Chapter 7) and thus has an over-riding effect on the geochemical evolution and differentiation of clastic sedimentary rocks. The source rocks, which form the most important attribute of the composition of sedimentary rocks, vary from andesite to dacite to granite-gneiss to sedimentary rocks as a result of change in tectonic setting from oceanic island arc to continental island arc to Andean type to the passive margin, respectively. Thus based on observations in Chapter 6 and 7, a tectonic model of geochemical differentiation of sedimentary rocks is formulated.

The quartz and phyllosilicate content express the maturity of graywackes and mudrocks, respectively. "Immature" sediments are deficient in quartz and phyllosilicates, and rich in feldspar and lithic grains. Quartz is resistant to physical weathering and its chemical breakdown during marine transport is minimal. Feldspars, lithic fragments and other labile grains are degraded during sedimentary cycles, and therefore the sand-size fraction enriches in quartz grains, and the finer fraction enriches in phyllosilicates, with increasing maturity. This transformation is expressed chemically, in the form of enrichment of SiO_2 in graywackes and Al_2O_3 in mudrocks with the change of tectonic setting from oceanic island arc to continental island arc to Andean type to passive margins in clastic sequences of eastern Australia (Figure 9.1).

The differentiation of clastic sedimentary rocks is shown on a triangular diagram using SiO_2, Al_2O_3 + K_2O, and Rest (combined percentage of FeO^t+MgO+CaO+Na_2O+TiO_2) as end members (Figure 9.2; scaling factors have been used to bring the points near the middle of the plot without altering the relative positions). Estimate of the total crust (Taylor and McLennan, 1981a) is also plotted on this diagram. The graywackes and mudrocks follow paths in almost opposite directions during the sedimentary cycle. Oceanic island arc sediments are similar to the total crust and thus are least differentiated. Increasing differentiation is observed from continental island arc to Andean type to

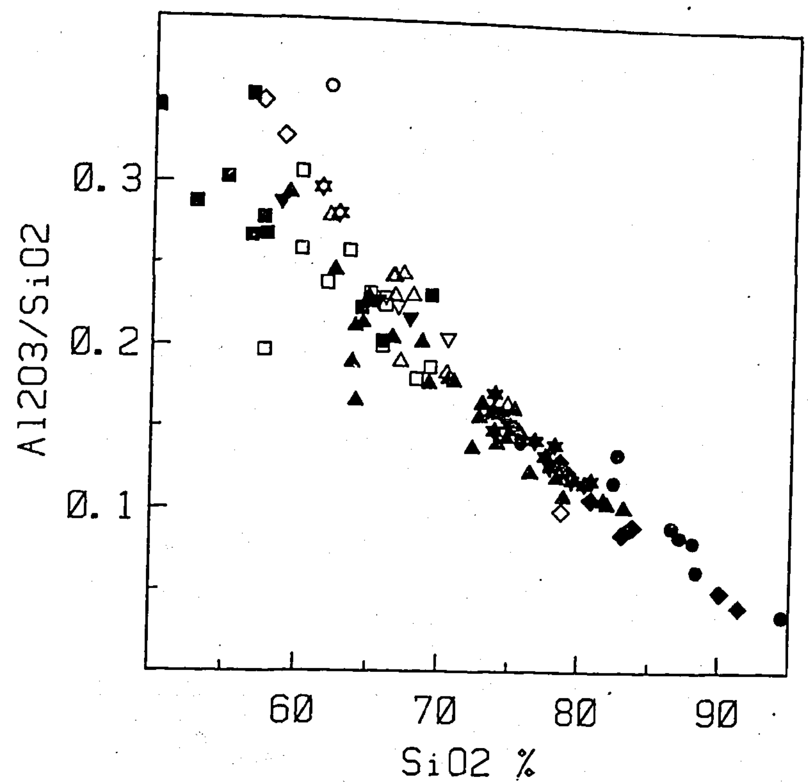


Figure 9.1 Plot of SiO_2 versus Al_2O_3/SiO_2 for graywackes and mudrocks of eastern Australia. Note the almost opposite trend of fractionation with increasing maturity from the Tamworth to the Bendigo-Cookman suites. Solid symbols are for graywackes, and open symbols are for mudrocks.

Tamworth suite	Tamworth suite
Crow Mountain Creek Beds	Crow Mountain Creek Beds
Hill End suite	Hill End suite
Hodgkinson suite	Hodgkinson suite
Bendigo suite	Bendigo suite
Cookman suite	Cookman suite

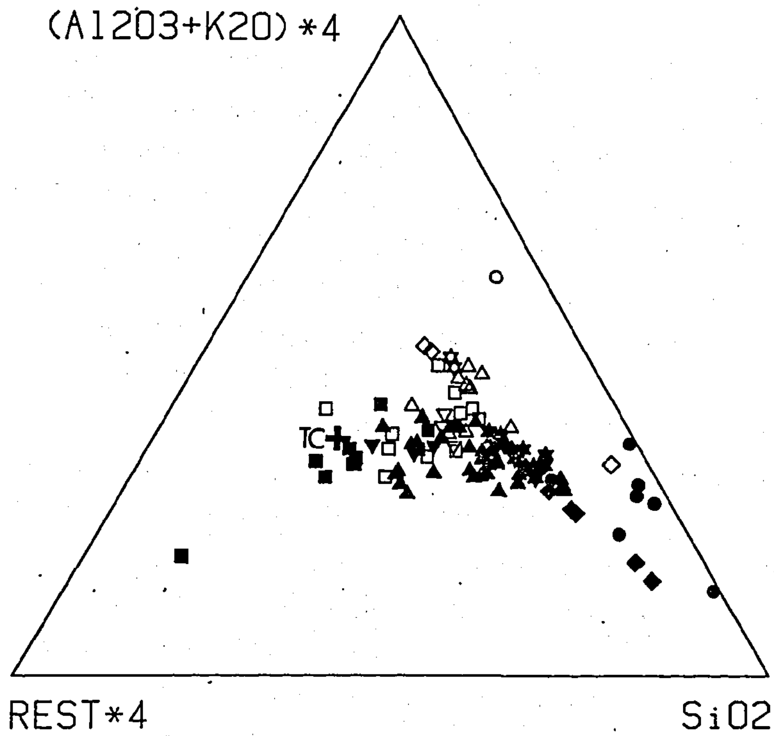


Figure 9.2 Plot of SiO_2-Al_2O_3+K_2O - Rest, to show the geochemical fractionation in sedimentary rocks. The trend in graywackes is towards an increase in the SiO_2 content, and in mudrocks towards an increase in Al_2O_3+K_2O. TC represents the estimate of the total crustal composition (after Taylor, 1979). Scaling factors are used to being the points towards the centre of the diagram without altering their relative positions. Symbols are as in Figure 9.1.

passive margin type sediments. The graywackes become enriched in SiO_2 on weathering, transportation and change of source rocks, leading to quartz-rich arenites as the end member because of the chemical and mechanical breakdown of unstable grains. The mudrocks follow a trend towards enrichment of Al_2O_3+K_2O due to the accumulation of phyllosilicates. Tectonic controls on evolutionary trends in the composition of clastic sedimentary rocks are summarized in Figure 9.3. There is an increase in the geochemical differentiation of the bulk composition of clastic sediments with change in tectonic setting from oceanic island arc through continental island arc, Andean type to the passive margins. The increase in geochemical differentiation is reflected in the enrichment of Si, Th, U, Zr, Nb and rare earth elements, and the decrease in small cations (Ca, Na, Sr) and ferromagnesian elements (Fe, Mg, Ti, V, Sc, Co, Zn) in graywackes. In mudrocks, the increase in differentiation with change in tectonic setting is reflected by the increase in large cations (K, Rb, Ba), Th, Nb and rare earth elements. Transition elements Cr and Ni also increase in mudrocks with increasing geochemical differentiation, because of the increase of adsorption processes acting during sedimentation.

Coarse-medium grained (graywacke) and fine-grained (mudrock) beds are formed by different depositional energies. Moderate-high energy environments yield graywackes and low-energy environments yield mudrocks. Within each tectonic setting, geochemical differentiation takes place with decreasing energy. Because of this, large cations (K, Rb, Ba), Al-group (Al, Ga) and some ferromagnesian elements (Cr, Ni, Zn) are enriched in mudrocks, and small cations (Na, Ca, Sr), Zr and Si are retained in graywackes. The geochemical differentiation between graywackes and mudrocks is minimal in the oceanic island arc tectonic setting and increases with the change of tectonic setting from continental island arc to Andean type to passive margins.

Elements Ca, Na and Sr are lost in solution during sedimentary processes. The loss of these elements increases with the tectonic stability of the basin. However, complex diagenetic reactions, by which Na is added to graywackes, mainly take place in the oceanic and continental island arc tectonic settings. Such reactions are probably absent or very minor in tectonically stable regions. Sea water is also rich in K, Rb and Ba. The addition of these elements in sediments due to sea-water interaction, is very poorly understood.

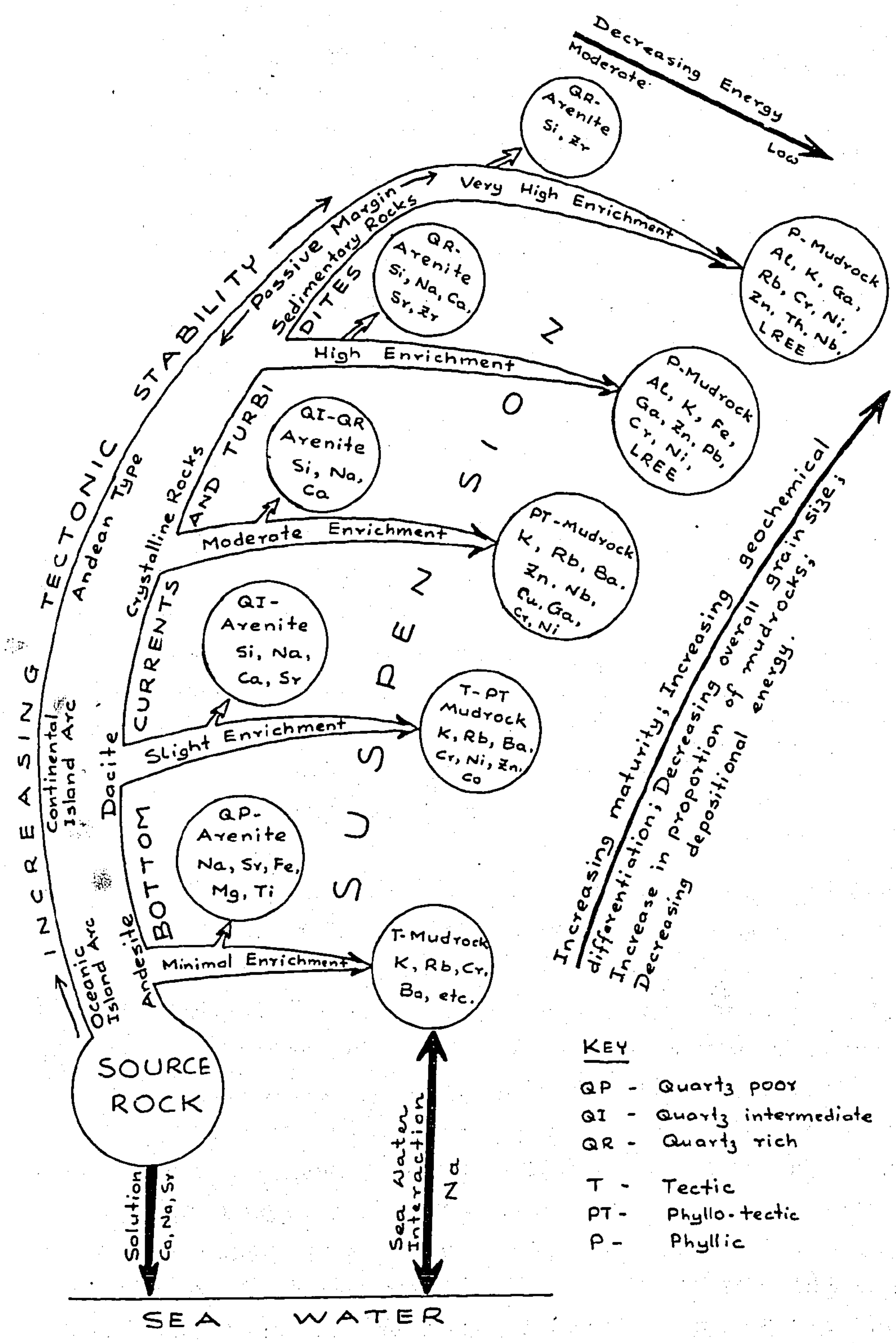


Figure 9.3 Tectonic model of the geochemical evolution of sedimentary rocks.

The increasing geochemical differentiation of clastic sedimentary rocks is also reflected in the overall texture and facies of the depositional basin. In general, chemical maturity is always accompanied by textural maturity (Sharma, 1979). In tectonically active settings, such as oceanic and continental island arcs, the depositional energy is moderate to high and results in the formation of common conglomerates and coarse to medium grained graywackes. However, with increasing tectonic stability, the energy of the depositional processes decreases and there is a dominance of mudrocks over medium to coarse grained beds. Similarly, chemical differentiation is also related to the facies development in the basin. In tectonically active regions, there is a common development of upper and mid fan facies, but in tectonically stable settings, e.g. passive margins, lower fan facies sequences predominate.

9.3 AVERAGE COMPOSITIONS OF SEDIMENTARY BASINS

The average compositions of the sequences representing various tectonic settings are useful in understanding the geochemical evolution of sedimentary rocks and the continental crust. Such averages have also been used to calculate the chemical mass balance of the Earth's crust (Sibley and Wilband, 1977). The estimation of average compositions is always fraught with problems, the most serious being that of obtaining representative samples.

Estimates of the composition of sedimentary rocks representing various segments of the sedimentary shell are not well constrained, as they are based either on composite samples or on the average composition of various lithologies (Poldervaart, 1955; Ronov and Yaroshevsky, 1969; Schwab, 1971). Schwab (1978) has estimated the average major element Phanerozoic sedimentary composition from various averages of geosynclines and platform cover rocks. McLennan (1981a) has refined this estimate by recalculating it on a volatile free basis and by deleting many incomplete analyses. The exact significance of this estimate is not clear as it groups together sedimentary rocks of various tectonic settings. However, this estimate of the average Phanerozoic sedimentary composition has been suggested to be close to that of the upper continental crust (Schwab, 1978; McLennan, 1981a). This estimate has been adopted here for comparison with the average compositions of

Table 9.1 Average Major Element Composition of Clastic Sedimentary Rocks of Various Tectonic Settings, and other Crustal Estimates#

	Oceanic Island Arc[1]		Archean Sedimentary Rocks[3]		Total Crust[4]	Total Crust[5]	Continental-Island Arc[1]		Geosyncline[5]	Sub-Continental[5]
	$\bar{X}$	S.D	$\bar{X}$	S.D			$\bar{X}$	S.D		
SiO_2	62.00	2.5	65.6	2.6	58.0	59.50	68.48	2.6	64.4	69.0
TiO_2	0.93	0.1	0.7	0.2	0.8	0.83	0.69	0.07	0.9	0.7
Al_2O_3	16.87	0.7	16.3	2.7	18.0	15.80	16.02	1.2	16.8	14.8
FeO^*	6.89	1.0	6.1	0.5	7.5	6.77	4.72	0.7	7.1	6.48
MnO	0.11	0.03	-	-	-	0.21	0.07	-	0.1	0.1
MgO	2.92	0.7	3.3	0.7	3.5	4.03	2.05	0.3	4.0	3.0
CaO	4.84	1.4	2.5	1.0	7.5	7.23	2.54	1.4	1.5	1.4
Na_2O	3.32	0.4	3.1	0.5	3.5	3.00	2.39	0.3	2.0	2.1
K_2O	1.82	0.3	2.4	0.5	1.5	2.38	2.56	0.4	2.6	2.1
P_2O_5	0.25	0.03	-	-	-	-	0.16	0.1	0.2	0.1

	Andean Type[2]		Passive Margin[2]		Phanerozoic Sedimentary Rock[3]		Fractionated Sedimentary Comp.[6]		Upper Continental Crust[4]
	$\bar{X}$	S.D	$\bar{X}$	S.D	$\bar{X}$	S.D	$\bar{X}$	S.D	
SiO_2	67.83	1.8	69.68	1.8	70.9	4.0	68.76	1.3	66.0
TiO_2	0.71	0.1	0.72	0.1	0.8	0.1	0.71	0.1	0.6
Al_2O_3	17.47	0.9	15.95	1.3	13.6	2.2	16.71	0.8	16.0
FeO^*	5.01	0.7	5.05	0.7	5.5	0.8	5.03	0.2	4.5
MnO	0.07	-	0.03	-	-	-	0.05	-	-
MgO	1.68	0.2	2.52	0.4	2.5	0.8	2.10	0.2	2.3
CaO	1.16	0.3	0.86	0.7	2.3	1.1	0.01	0.4	3.5
Na_2O	1.72	0.2	0.87	0.3	1.6	0.6	1.30	0.2	3.8
K_2O	3.69	0.2	3.95	0.2	2.7	0.6	3.82	0.2	3.3
P_2O_5	0.12	-	0.15	-	-	-	0.14	-	-

Notes:

* Total Fe as FeO.
\# Recalculated on volatile free basis.
1) Present work 1:1 - Graywacke : Mudrock (Averages from Tables 7.11-7.14).
2) Present work 1:2 - Graywacke : Mudrock (Averages from Tables 7.11-7.14).
3) After Schwab (1978) - refined by McLennan (1981a).
4) From Taylor and McLennan (1981a).
5) From Ronov and Yaroshevsky (1969).
6) Mean of average Andean and passive margin compositions.
$\bar{X}$ Mean
S.D Standard Deviations calculated by the formula (after Anderson, 1977).
$S.D = \frac{1}{2}\sqrt{a^2 + b^2}$ where a and b are standard deviations of mean graywacke and mudrock compositions, respectively.

Table 9.2 Average Trace Element Compositions of Clastic Sedimentary Rocks of Various Tectonic Settings, and Crustal Compositions*

	Oceanic Island Arc 1)	Total Crust 3)	Continental-Island Arc 1)	Andean Type 2)	Passive Margin 2)	Fractionated Sedimentary Comp. 4)	Upper Continental Crust 3)
Ba	531	350	578	608	602	605	700
Rb	43	42	103	181	175	178	110
Sr	462	400	222	99	65	82	350
Pb	7.5	7	17	24	19	21	15
Th	3.89	4.8	14	25	20	22	10.5
U	1.8	1.25	2.9	5.2	3.4	4.3	2.5
Zr	113	100	207	185	217	201	240
Nb	2.8	4	9	14	13.1	13.5	25
Y	21	22	25	30	29	30	22
La	14	19	24	39	33	36	30
Ce	30	38	52	82	72	77	64
Nd	15	16	21	30	28	29	26
Sc	19	30	14	14	13	14	10
V	145	175	87	82	76	79	60
Cr	38	55	53	47	79	63	35
Co	17	25	12	14	11	12	10
Ni	13	20	16	20	26	23	13
Cu	34	60	16	31	22	27	25
Zn	97	-	80	90	71	81	52
Ga	18	18	15	21	18	20	-

Notes:

* All abundances in ppm.

1) Present work 1:1 - Arenite : Mudrock (Averages from Tables 7.15 and 7.17).

2) Present work 1:2 - Arenite : Mudrock (Averages from Tables 7.15 and 7.17).

3) From Taylor and McLennan (1981a).

4) Average of Andean type and passive margin.

sedimentary sequences representing various tectonic settings (Table 9.1).

9.3.1 Procedure

The average major and trace element compositions of sedimentary sequences representing oceanic island arc, continental island arc, Andean type and passive margin tectonic settings have been calculated separately (Tables 9.1 and 9.2). Only arenites and mudrocks, which form the most dominant lithologies of these sequences, have been considered. Thus, the averages are estimates of the "clastic residue" only (Schwab, 1971). The average major element compositions of arenites and mudrocks of each tectonic setting are adopted from Tables 7.11 and 7.14 to calculate the bulk sedimentary composition of each tectonic setting.

Calculations of the average compositions of the sequences are hindered by the difficulty in estimating the proportions of arenites and mudrocks in each tectonic setting. The sedimentary sequences of oceanic and continental island arcs, are in general immature, and arenites and mudrocks are present in almost equal proportions (e.g. Hill End Trough - sections measured by Packham, 1968). Thus the average compositions of these basins have been estimated by taking arenites and mudrocks in a 1:1 proportion. In the Andean type and passive margin tectonic zones (e.g. Hodgkinson and Bendigo suites), mudrocks are twice as abundant as arenites and hence their average compositions have been estimated by taking arenites and mudrocks in a 1:2 proportion.

The present approach of estimating average compositions based on geotectonics is more realistic than taking the average of composite samples or on the basis of age. All the major element averages are calculated on a volatile free basis (Table 9.1). Standard deviations are only meaningful in denoting the uncertainties in determining mean from various averages. Average trace element abundances are calculated in the same way as major element compositions (Table 9.2). However, the estimates are less well founded because the data base is only the present work on eastern Australian sedimentary rocks. Log-log scale diagrams have been used to compare the various average compositions. On these plots, a difference of up to $\pm$ 20% is probably not significant.

9.3.2 Oceanic Island Arc Basin

The average composition of mudrocks of oceanic island arc basins is not well established because of the small data set and the presence of abundant biogenic silica in these mudrocks. Arenites may give the best estimate of the oceanic island arc composition, but a 1:1 average of arenite and mudrock compositions still signifies the character of this sequence.

Large differences are observed between the average oceanic island arc and Phanerozoic sedimentary compositions (Figure 9.4), in spite of large uncertainties on the means. The average oceanic island arc sedimentary composition is higher in CaO, Na_2O, FeO^t and Al_2O_3 by a factor of more than 1.2 and depleted in SiO_2 and K_2O by a magnitude of the same factor. Thus the average oceanic island arc sedimentary composition is significantly more mafic than the average Phanerozoic sedimentary composition and also average upper continental crust.

9.3.3 Continental Island Arc Basin

The average composition of the continental island arc basin is comparable with the estimates of average geosynclinal and subcontinental sedimentary compositions of Ronov and Yaroshevsky (1969), particularly in Al_2O_3, K_2O and Na_2O (Table 9.1). However, significant differences are seen in FeO^t and MgO. Compared to the average Phanerozoic sedimentary composition, the average continental island arc composition is higher in Al_2O_3 and Na_2O by a factor of more than 1.2 and lower in FeO^t and MgO by a magnitude of the same factor (Figure 9.5). The abundances of SiO_2, K_2O and CaO in the two averages are quite comparable. Large uncertainties on the means of many elements make it difficult to highlight the similarities or differences between the two averages (see Section 9.4).

9.3.4 Andean Type Basin

The average Andean type sedimentary composition is comparable to that of the average Phanerozoic sedimentary composition in SiO_2, FeO^t, Na_2O and TiO_2 (Figure 9.6). The data shows large uncertainties, however, the average Andean type composition is higher in Al_2O_3 and K_2O and depleted in MgO and CaO by a factor of more than 1.2. These differences can be explained by the enrichment of phyllosilicates, the non-inclusion of carbonates or the redistribution of elements in the Andean type sedimentary composition.

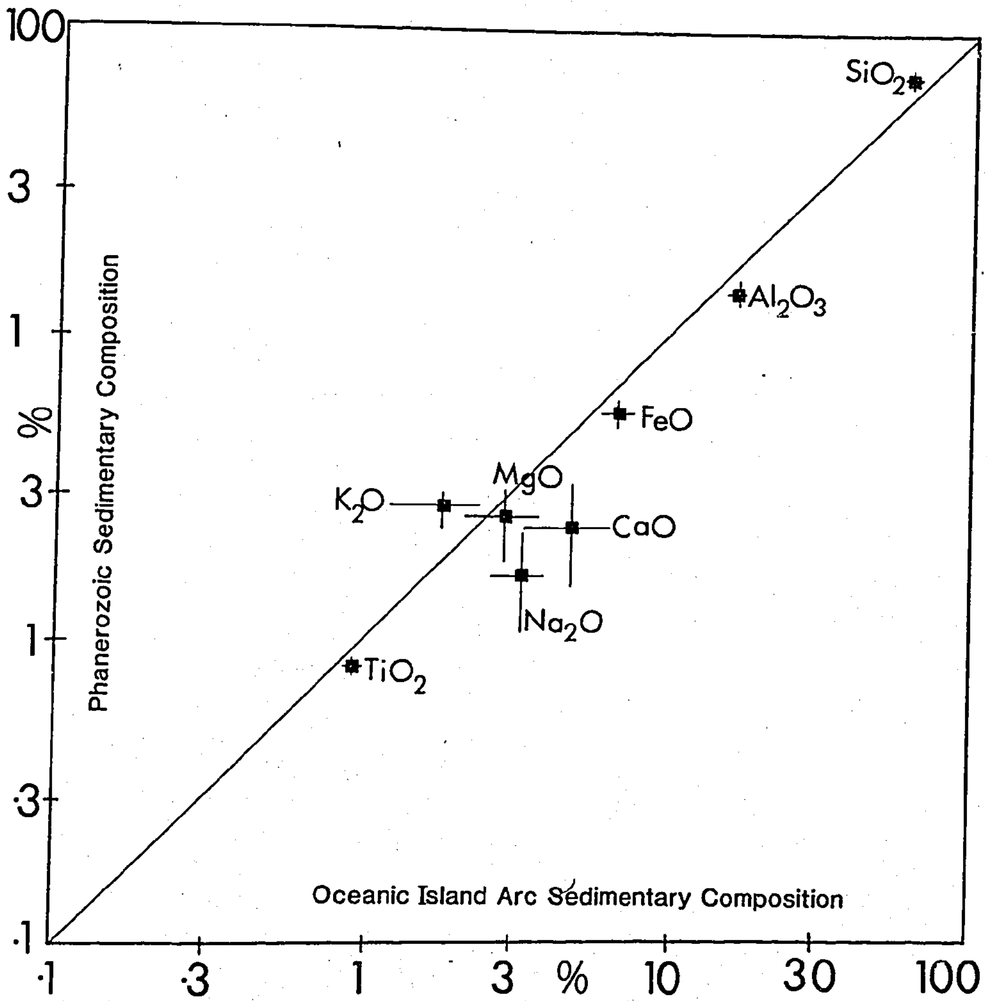


Figure 9.4 Comparison diagram of average oceanic island arc and Phanerozoic sedimentary compositions. Note the higher CaO, Na_2O, Al_2O_3 and FeO (total Fe) content in the oceanic island arc composition and the higher SiO_2 and K_2O content in the Phanerozoic sedimentary composition. In all comparison diagrams, the scale is log-log, the diagonal line represents equal compositions and the bars represent the standard deviations.

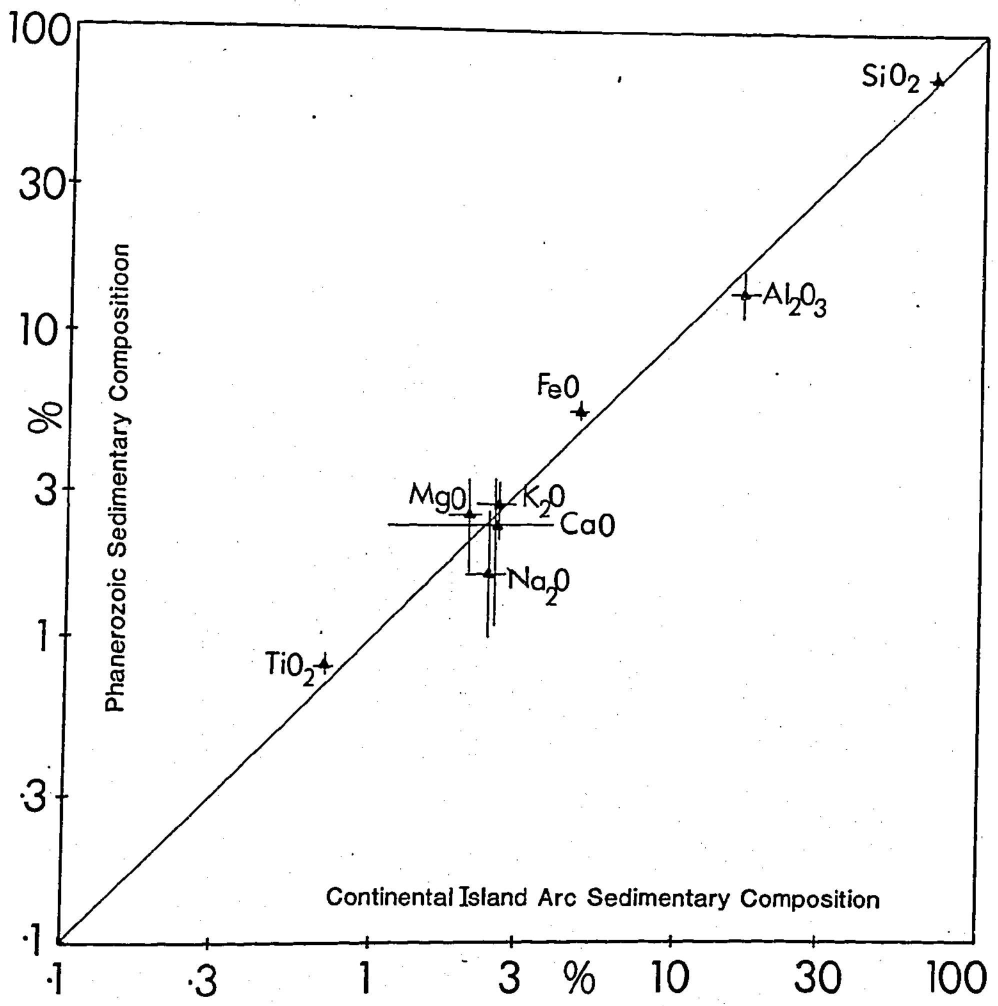


Figure 9.5 Comparison diagram of average continental island arc and Phanerozoic sedimentary compositions.

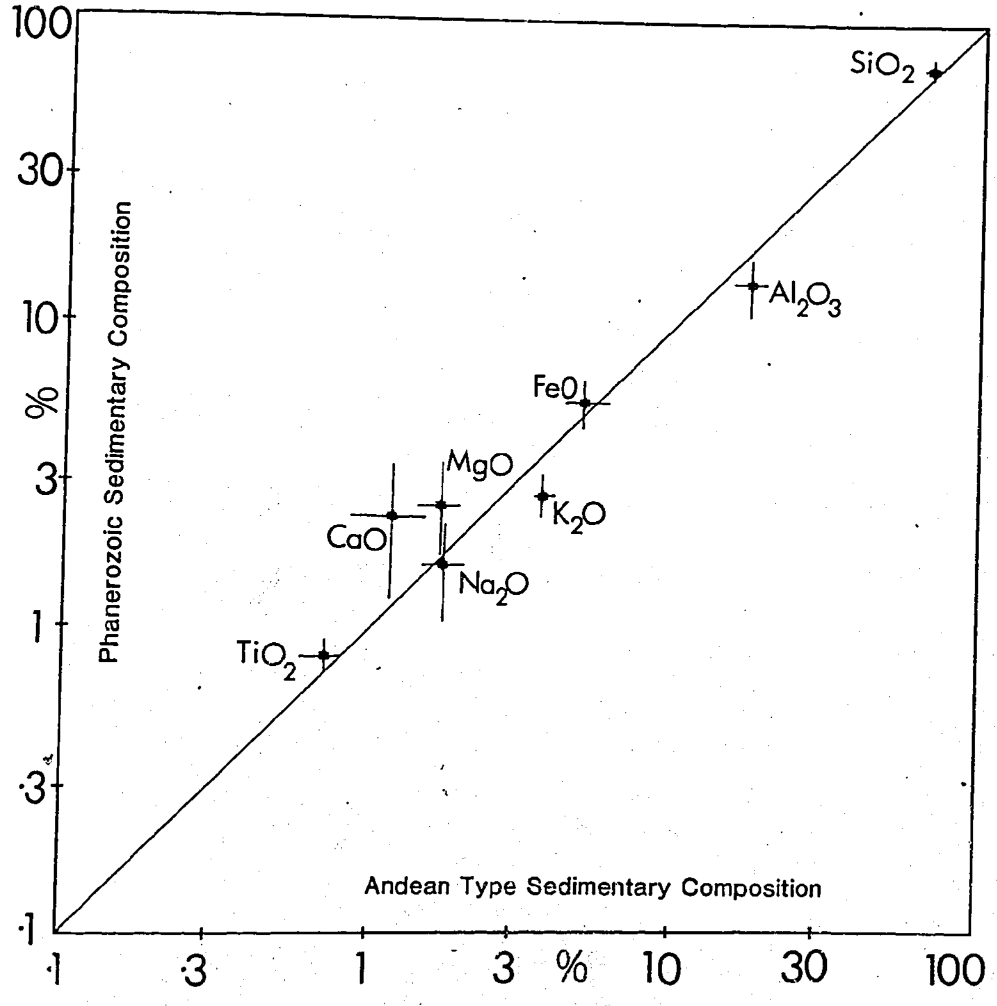


Figure 9.6 Comparison diagram of average Andean and Phanerozoic sedimentary compositions. Note the higher abundances of K_2O and Al_2O_3 in the Andean composition and of CaO and MgO in the Phanerozoic composition. Note also the close similarity between the two in the SiO_2, FeO, Na_2O and TiO_2 content.

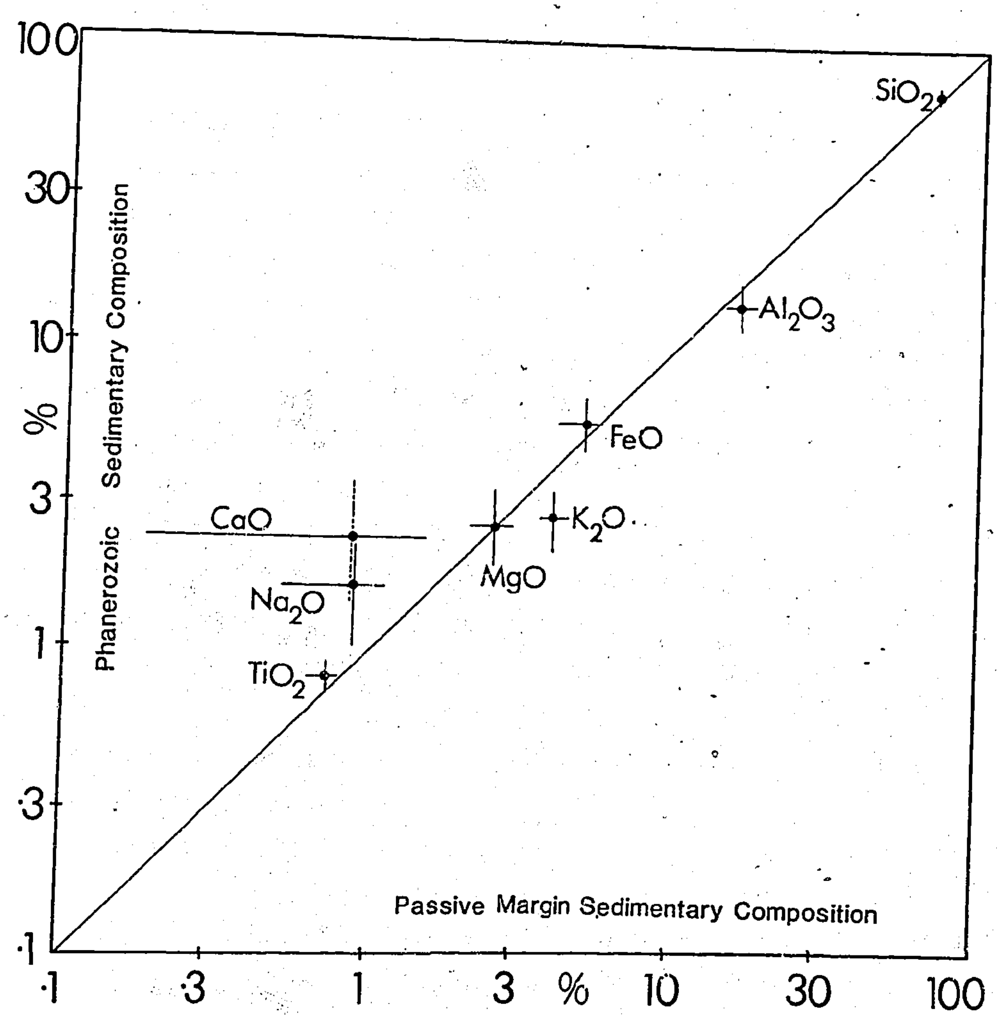


Figure 9.7 Comparison diagram of average passive margin and Phanerozoic sedimentary compositions. Note the general agreement between the two compositions, except for the higher abundances of CaO and Na_2O in the Phanerozoic and of K_2O and Al_2O_3 in the Passive margin sedimentary compositions.

9.3.5 Passive Margin Type Basins

The average passive margin sedimentary composition is quite similar to the average Phanerozoic sedimentary composition, especially in SiO_2, FeO^t, MgO and TiO_2 (Figure 9.7). However, K_2O and to some extent Al_2O_3 are significantly enriched, and CaO and Na_2O are depleted in the average passive margin rocks. These differences can be explained by the highly recycled nature of passive margin sediments.

9.4 SEDIMENTARY ROCK AND CRUSTAL COMPOSITIONS

How do the average compositions of sedimentary rocks of various tectonic settings compare with the crustal compositions? This aspect has been investigated by Ronov (1968, 1972), Veizer (1973, 1979), Schwab (1978), and McLennan (1981a). Veizer and Jansen (1979) have cautioned against using average sedimentary rock compositions, particularly from mobile belts, as estimates of upper crust. However, such a comparison provides insights into secular variations as documented by Schwab (1978) and McLennan (1981a).

The average oceanic island arc composition is significantly more mafic than the average Phanerozoic composition and thus represents the Unfractionated Sedimentary Composition (USC). A broad similarity is seen between the average Andean type and passive margin sedimentary composition and the average Phanerozic composition. Thus the Andean type-passive margin average composition can be called Fractionated Sedimentary Composition (FSC).

The average continental island arc sedimentary composition is lower in Al_2O_3, TiO, FeO^t, MgO and Na_2O and less mafic compared to the average oceanic island arc composition. However, the differences (or similarities) in the major element chemistry of the continental island arc and average Phanerozoic sedimentary rocks are not clearly established. Rare earth elements provide evidence of the less fractionated nature of continental island arc sedimentary rocks compared to average Phanerozoic sedimentary rocks. The chondrite normalised REE patterns show a large variation in the continental island arc rocks (e.g. in the Hill End Suite), due to the mixing of volcanic and sedimentary detritus in various proportions (Chapter 8). However, some samples (e.g. MK29, MK59) clearly exhibit the absence of a negative Eu anomaly on chondrite normalised plots and are lower in the La_N/Yb_N ratio compared to the

PAAS or upper continental crust. The presence of a negative Eu anomaly has been considered as the most important characteristic of upper continental crustal rocks and has been widely recognized in recycled Post-Archean sedimentary rocks (e.g. Nance and Taylor, 1976; Taylor and McLennan, 1981a). The absence of a negative Eu anomaly in some continental island arc clastic rocks suggests that they differ to some extent from the upper crustal and Phanerozoic sedimentary rocks. The average continental island arc composition represents the Intermediate Sedimentary Composition (ISC).

A comparison between the two shows that the USC is higher in CaO, Na_2O, MgO, FeO^t, TiO_2 and P_2O_5, whereas the FSC is higher in SiO_2 and K_2O (Table 9.1). The FSC is significantly enriched in light-ion lithophile elements (Th, U, Zr, Nb, Rb, Pb, Ba, Y & REE) (Table 9.2). On the other hand, compared to the FSC, the USC is significantly enriched in Sr, and ferromagnesian elements (V, Co, Sc, Cu, Zn), clearly suggesting a more mafic nature for the USC. However, Ni and Cr are enriched in the FSC by a factor of more than 1.5. This can be explained as due to enrichment of Cr and Ni in phyllosilicates with recycling. Trace element characteristics of the ISC fall between that of the USC and FSC (Table 9.2).

A remarkable similarity is seen in all major elements, except CaO, between the estimate of total crust and the oceanic island arc composition (Figure 9.8). CaO shows large variation in the latter and may have been leached out during burial metamorphic changes. A large similarity is also seen in the trace element abundances (except Nb) of the oceanic island arc (represented by the Tamworth suite data only) and total crust (represented by average andesite) in Figure 6.18.

The FSC is compared with the estimate of the upper continental crust (Figure 9.9 and 9.10). Except for CaO and Na_2O, the two compositions are very similar in major elements. The depletion of CaO and Na_2O in the FSC is due to the loss of these elements during weathering and their subsequent enrichment in carbonates and evaporites. Compared to the upper continental crust estimate, the FSC is also enriched in most trace elements except Sr, Nb, Zr and Ba (Figure 9.10). The depletion of Sr in the FSC can be explained as due to the loss of Sr during weathering and sedimentation, similar to a mechanism envisaged for the loss of Na_2O and CaO. La, Nd, Y, Sc, Ga, Co and V

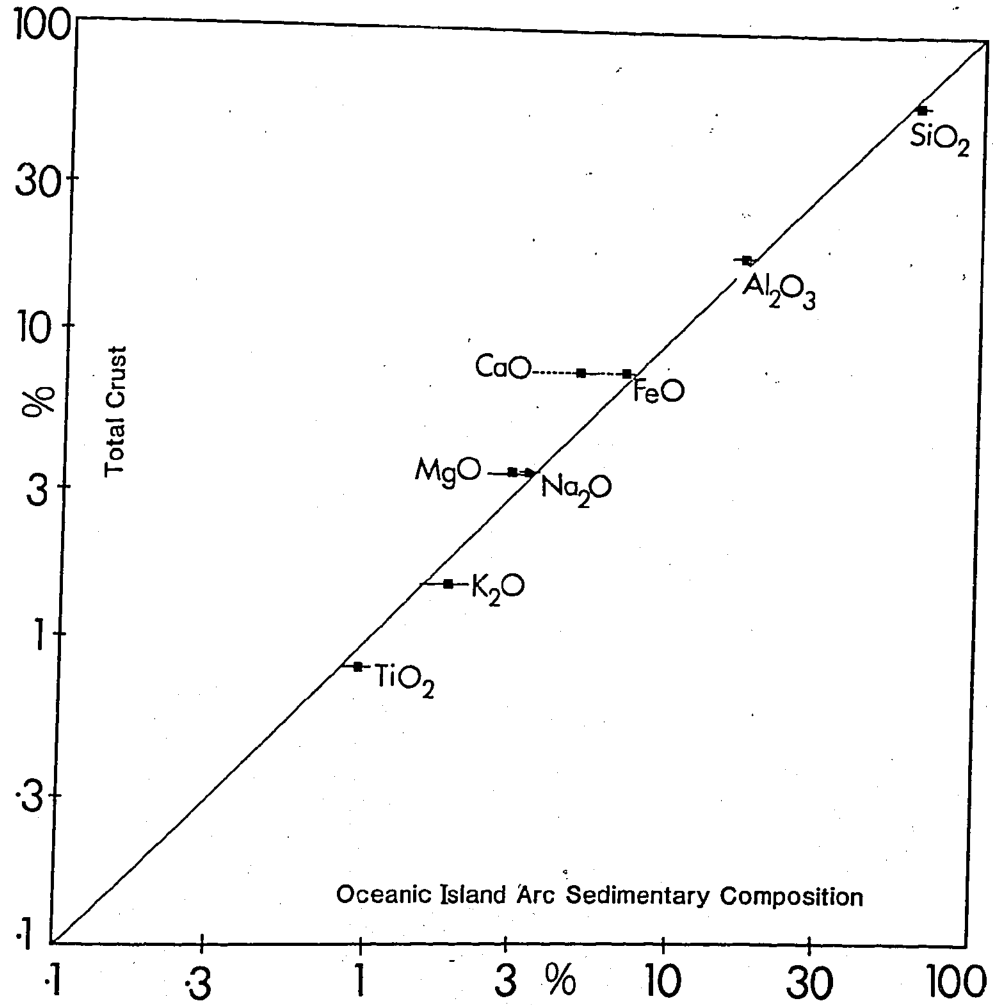


Figure 9.8 Comparison diagram of average oceanic island arc sedimentary and total crustal compositions. Note the excellent agreement between the two, except for the higher Ca0 content in the total crust.

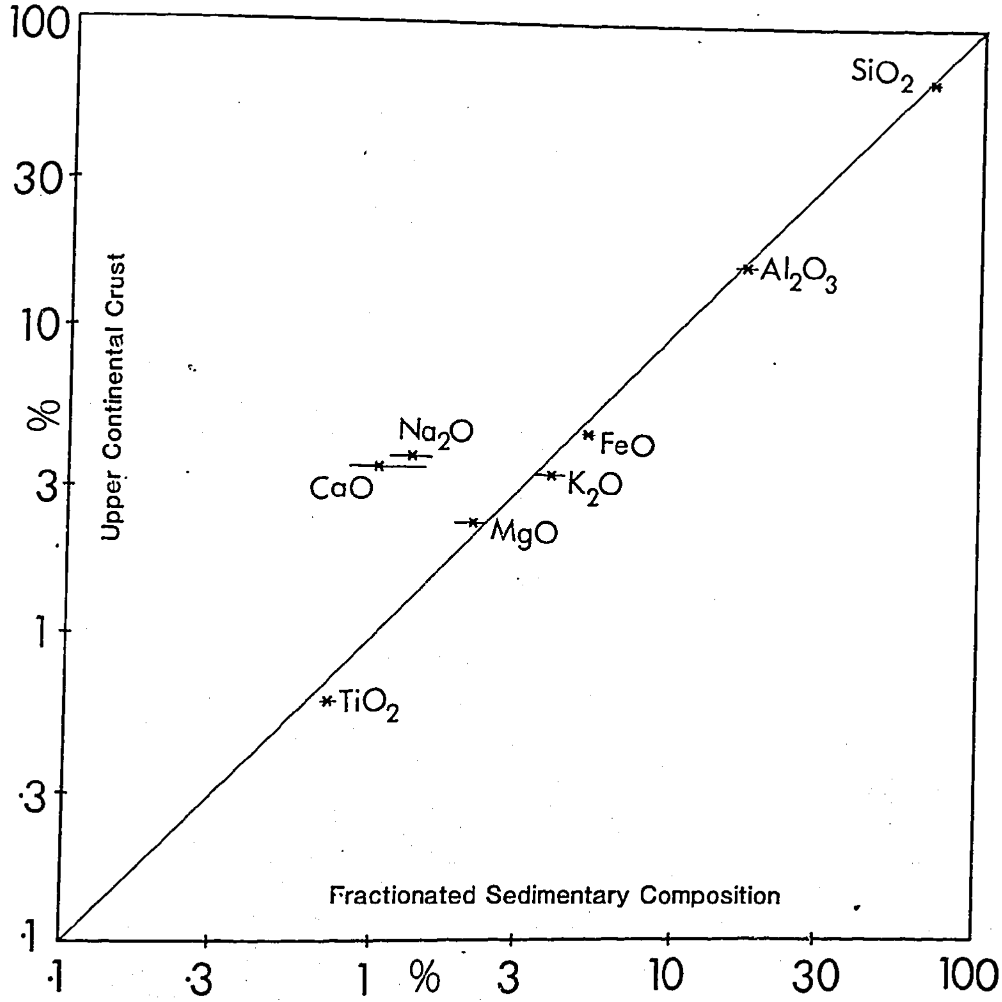


Figure 9.9 Comparison of average Fractionated (Andean and Passive margin types) sedimentary composition and upper continental crustal composition. Note the general agreement between the two, but the fractionated sedimentary rocks are depleted in CaO and Na_2O compared to the upper crust.

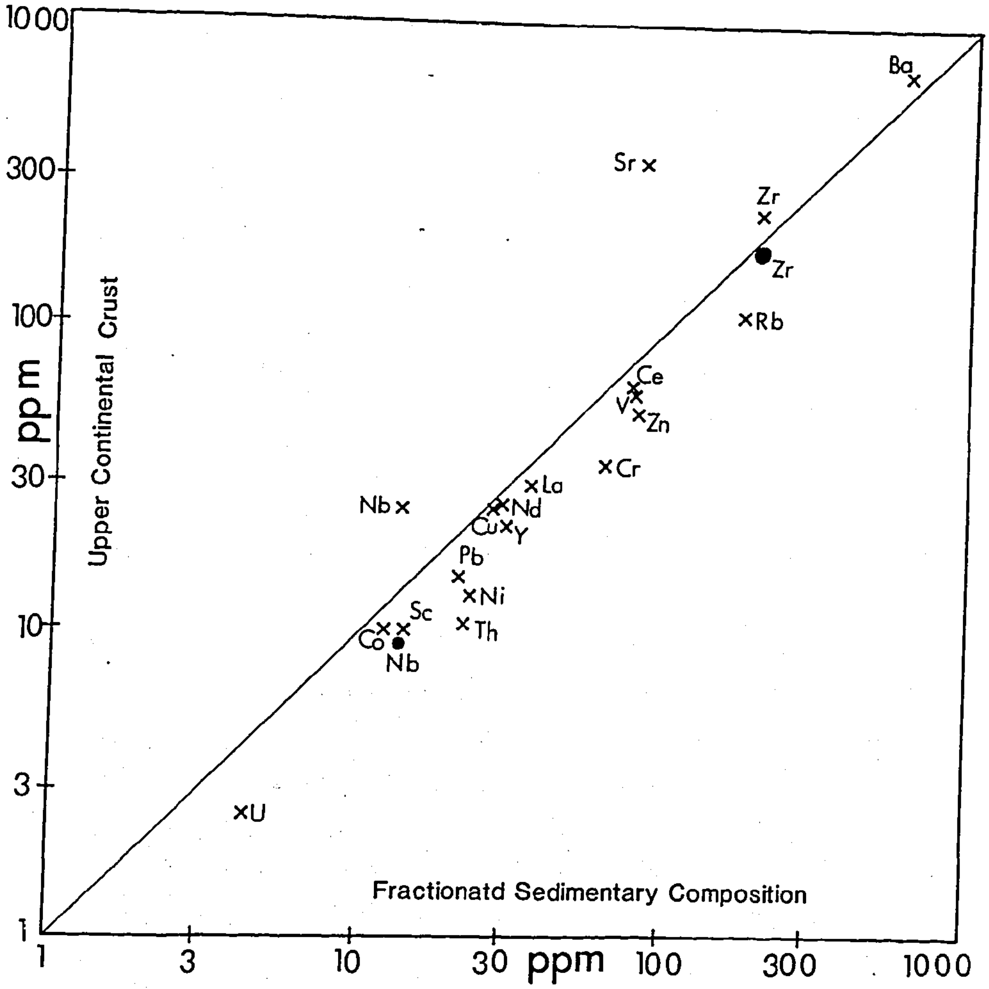


Figure 9.10 Comparison diagram of trace elements of the Fractionated sedimentary and upper continental crustal compositions. (● for revised values of Nb and Zr in the upper continental crust).

are only slightly enriched in the FSC compared to the UCC, thus indicating a close similarity between the two compositions. The heat producing elements like Th, U, Rb and Pb are enriched in the FSC compared to the UCC by a factor of more than 1.3. Cr and Ni are also significantly enriched in the FSC and can be explained as due to adsorption and enrichment of these elements with phyllosilicates during recycling.

The depletion of Nb and Zr in the FSC compared to the upper crustal estimate is surprising, as these elements form part of the lithophile elements and are relatively immobile. Nb has been estimated to be 25 ppm in the upper continental crust, by adopting data from the Precambrian Canadian Shield (Taylor and McLennan, 1981a). However, this estimate is not well constrained, as Nb shows large regional variation ranging in abundance from 4 to 51 ppm in various segments of the Canandian Shield rocks (Shaw et al. 1976). The average Nb abundance in I- and S-type granitoids of southeastern Australia is 9 and 11 ppm respectively (Table 6.11). As the upper crust is of granodioritic composition, an estimate of 10 ppm Nb in the upper contiental crust is more realistic. This is in agreement with the 12 ppm Nb in the FSC. A similar abundance of 12 ppm Nb has also been reported in the Andean type andesites (Bailey, 1981). Nb has been estimated to be 11 ppm in the total crust (Taylor and McLennan, 1981a). This estimate also seems to be high. Nb also shows large variation in magmatic rocks. A low value of 4 ppm Nb has been reported in the Bagana andesites of Papua New Guinea, which have been suggested to be the reference andesite (Bultitude et al. 1978). Bailey (1981) has estimated a median 5 ppm Nb value in the oceanic island arc high K-andesites. 4 ppm Nb for the total crust seems to be more reasonable and is in agreement with oceanic island arc volcanic and sedimentary data. Thus, if a value of 10 ppm Nb for the upper continental crust and 4 ppm for the whole crust is accepted, the value of 1 ppm Nb for the lower crust is extrapolated by considering that the upper crust forms one-third of the total crust (Taylor, 1979).

Zr also exhibits a large variation in its abundance in the Canadian Shield (Shaw et al. 1976), and an estimate of 240 ppm Zr for the upper continental crust seems to be slightly high. Eade and Fahrig (1971, 1973) have estimated an average 190 ppm Zr in the Precambrian continental shield of Canada. The Zr content in I- and S-type granitoids is 142 and 167 ppm, respectively. Median Zr content in Andean type andesites is 181 ppm (Bailey, 1981) and this seems to be a more reasonable estimate of the upper continental crust. This is also in remarkable agreement with the average 181 ppm Zr observed in the average Andean type sedimentary compositions. The high Zr in the passive margins is due to enrichment of Zr during sedimentation. The slight enrichment of Ba in the upper continental crust is probably within the uncertainty of the data.

9.5 ARCHEAN SEDIMENTARY ROCKS : GEOCHEMICAL COMPOSITION AND CONSTRAINTS ON PROVENANCE

9.5.1 Introduction

Rocks older than 2.5 billion years are generally known as Archean rocks. The study of these rocks has acquired a significant dimension in recent years as they provide excellent evidence on the origin and development of the early crust.

The geochemistry of Archean clastic sedimentary rocks has been investigated by many workers. However, till this chapter, a deliberate attempt had been made not to take into account Archean sedimentary rocks for tectonic setting discrimination purposes, despite many new and reliable analyses available in literature. This has been done because of debate as to whether or not the modern plate tectonic regimes were valid during the Archean.

In Chapter 7, geochemical parameters and criteria to decipher the provenance and tectonic setting of clastic sedimentary rocks were proposed. A geochemical comparison of Archean sedimentary rocks with sedimentary rocks of the various tectonic settings can constrain the provenance of Archean rocks.

Graywackes and mudrocks showing turbidite structures are common in Archean clastic sequences. The graywackes are mainly quartz-poor to quartz-intermediate in nature with common felspar and lithic grains. The lithic grains are mainly of felsic and intermediate volcanics with minor contribution from granite and sedimentary rocks (Condie et al. 1970; Ojankangas, 1972; Henderson, 1972).

Table 9.3 Average Major Element Compositions of Archean Graywackes and Mudrocks#

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
SiO_2	66.25	70.43	65.69	64.31	60.00	62.49	61.88	60.08	61.99
TiO_2	0.59	0.55	0.63	0.57	0.73	0.76	0.55	0.72	0.83
Al_2O_3	15.50	10.85	15.81	13.51	19.10	18.20	13.48	23.50	19.60
$Fe_2O_3^*$	5.41	6.89	5.60	5.50	7.53	7.12	11.43	6.16	7.99
MnO	0.11	0.11	-	0.10	0.09	0.10	0.07	0.04	0.09
MgO	3.11	4.79	3.18	3.76	4.08	3.42	2.54	3.58	2.35
CaO	2.74	2.10	2.26	3.45	1.96	1.61	3.76	0.20	0.83
Na_2O	3.27	1.92	3.81	2.95	2.27	2.68	2.65	0.69	1.02
K_2O	2.50	1.68	2.49	2.13	3.38	3.10	2.43	4.32	4.70
P_2O_5	0.15	0.09	-	0.15	0.20	0.16	0.11	-	0.14
$Fe_2O_3^*$+MgO	8.52	11.68	8.78	9.26	-	-	-	-	-
Al_2O_3/SiO_2	0.23	0.15	0.24	0.21	-	-	-	-	-
K_2O/Na_2O	0.76	0.88	0.65	0.72	1.49	1.16	0.91	6.26	4.6
$Al_2O_3/(Na_2O+CaO)$	2.58	2.70	2.60	2.11	4.51	4.24	2.10	26.4	10.6

Notes:

* Total Fe as Fe_2O_3

\# Recalculated on volatile free basis.

(1) Archean graywacke, Yellowknife, Canada (Henderson, 1972) - 20 samples.

(2) Sheba Formation graywacke, South Africa (Condie et al. 1970) - 17 samples.

(3) Archean graywacke, Wyoming (Condie, 1967) - 23 samples.

(4) Composite Archean graywacke (Condie, 1976).

(5) Archean slate, Yellowknife, Canada (Henderson, 1972) - 20 samples.

(6) Archean Mudrock, Superior Province, Canada (Cameron and Garrels, 1980) - 8 samples.

(7) Archean Mudrocks, Yilgarn Block, Australia (McLennan, 1981b) - 19 samples.

(8) Archean Mudrocks, Pilbara Block, Australia (McLennan, 1981b) - 12 samples.

(9) Precambrian mudrocks (Nanz, 1953).

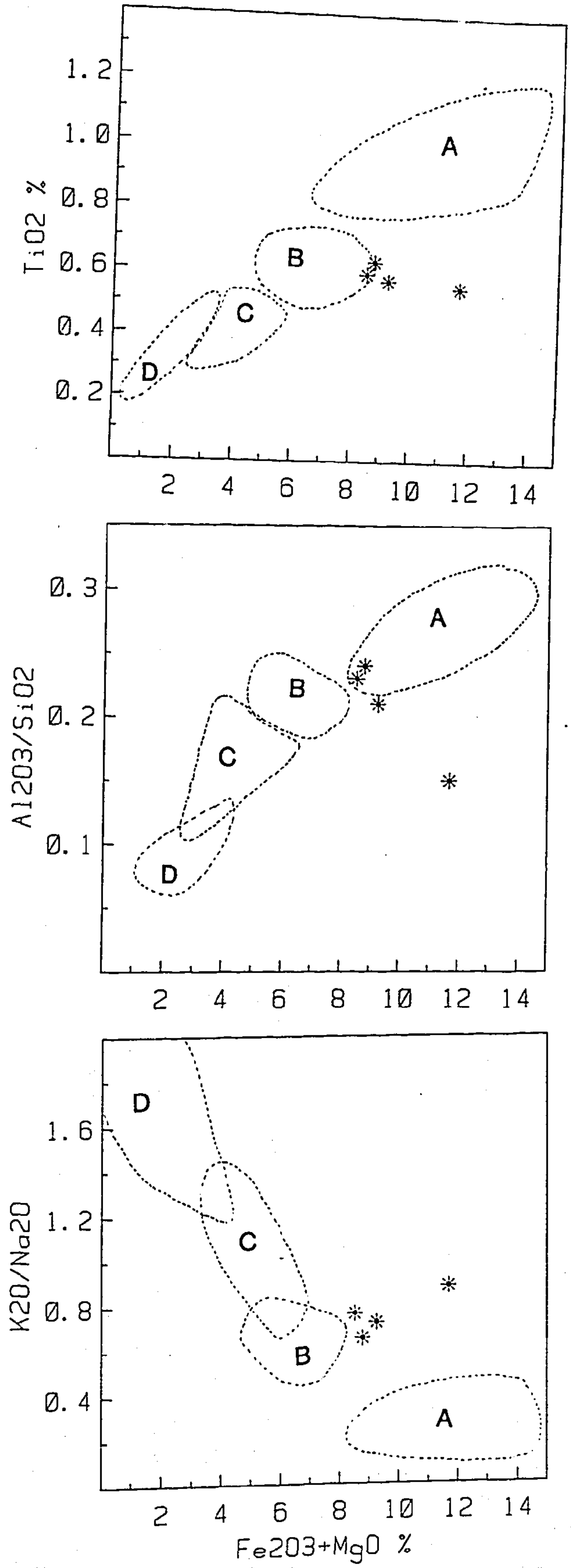


Figure 9.11 Plot of Archean graywackes (*) on the major element discriminatory diagrams of arenites. The fields represent the various tectonic settings (adopted from Figure 7.6): A - oceanic island arc; B - continental island arc; C - Andean type; D - passive margins.

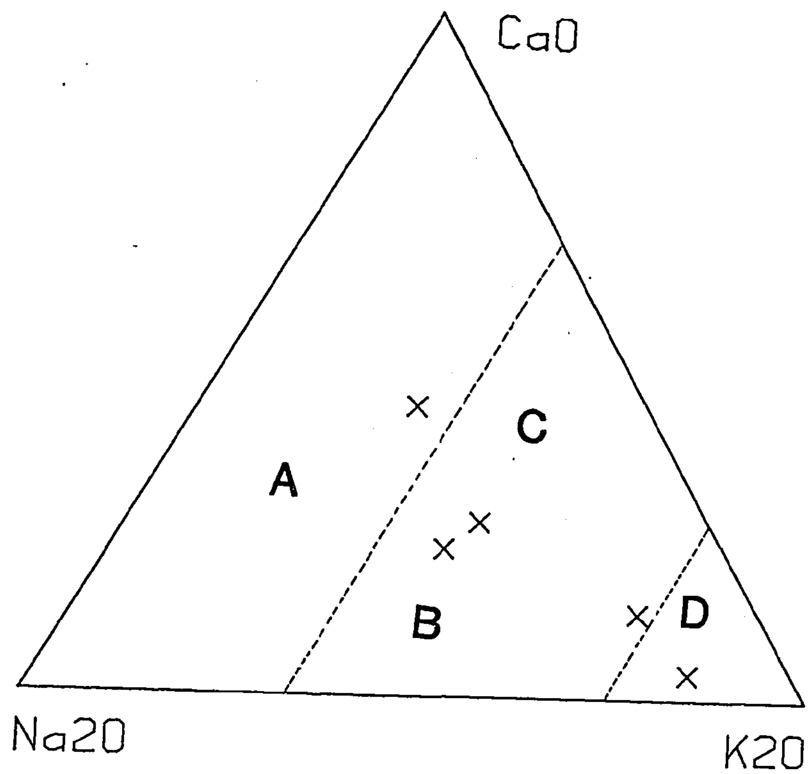


Figure 9.12 Plot of Archean mudrocks (x) on the CaO-Na_2O-K_2O discriminatory diagram. The fields represent the various tectonic settings (adopted from Figure 7.8) : A - oceanic island arc; B - continental island arc; C - Andean type; D - passive margins.

9.5.2 Major Element Geochemistry

Various averages of Archean graywackes and mudrocks from different regions are given in Table 9.3. The plot of graywackes on major element discriminatory diagrams, shows they differ significantly from oceanic island arc type arenites, mainly in their lower $Fe_2O_3^t$+MgO, TiO_2 and Al_2O_3/SiO_2 and higher K_2O/Na_2O ratios (Figure 9.11). The Archean averages also differ significantly from Andean type arenites in having higher $Fe_2O_3^t$+MgO, TiO_2, Al_2O_3/SiO_2 and lower K_2O/Na_2O ratios. However, Archean averages plot close to the continental island arc field indicating a dominantly felsic or mixed felsic-mafic source terrain.

The Archean mudrocks show a large variation in their major element characteristics, as shown by the CaO-Na_2O-K_2O plot (Figure 9.12). The Yilgarn block mudrocks (Australia), are significantly mafic and similar to oceanic island arc mudrocks; whereas those of Canadian provinces are mainly felsic in nature and similar to continental island arc mudrocks. Mudrocks of the Pilbara block (Australia) and of Arizona (USA) show a higher K_2O/Na_2O ratio indicating a more matured nature. The large variation in characteristics probably suggests a mixed and varied provenance, in different regions.

9.5.3 Trace Element Geochemistry

The trace element geochemistry of Archean clastic sedimentary rocks has been studied by many workers (e.g. Condie et al. 1970; Wildeman and Condie, 1973; Nance and Taylor, 1977; Bavinton and Taylor, 1980; Cameron and Garrels, 1980; Taylor and McLennan, 1981a,b). McLennan (1981b) has carried out a detailed investigation of the trace element geochemistry of Archean fine-grained clastic sedimentary and metasedimentary rocks, of Australia, Greenland and South Africa. Some of the data used in the present discussion are adopted from his unpublished work (McLennan, 1981b). Trace element characteristics of the average Archean shale are compared with the average oceanic and continental island arc mudrocks, representing dominantly andesitic and dacitic source rocks, respectively (Table 9.4).

9.5.3a Ba-Rb-Sr-Pb

The average 575 ppm Ba and 60 ppm Rb in the Archean shale is comparable to 654 ppm Ba and 67 ppm Rb in the average oceanic island arc mudrock. However, the Sr and Pb abundances of Archean rocks are more comparable to continental island arc mudrocks (Table 9.4). The high K/Rb and low Rb/Sr ratios indicate significant mafic-intermediate volcanic contributions in the Archean sediments. The Ba/Rb and Ba/Sr ratio fall intermediate between oceanic and continental island arc mudrocks, suggesting mafic to felsic source rocks.

9.5.3b La-Th-Sc

The La/Th and La/Sc ratios in the average Archean shale are 3.1 and 1.0, respectively and are in excellent agreement with the 3.9 La/Th and 1.0 La/Sc ratios of the average oceanic island arc mudrock.

The Archean mudrock samples from various regions (data from McLennan, 1981b) are plotted on the La-Th-Sc discriminatory plot (Figure 9.13). The Archean samples occupy a large field. The Greenland and Yilgarn block mudrocks plot mainly in the oceanic island arc field, implying a dominant andesitic source, whereas the mudrocks of Pilbara and South Africa plot in the continental island arc field indicating a dominant felsic volcanic source terrain.

9.5.3c Th-Sc-Zr

The average abundances of Sc and V, and the Th/Sc ratio are very similar between the Archean and oceanic island arc mudrocks (Table 9.4). On the Th-Sc-Zr/10 plot, the Archean samples show a large variation, but mudrocks from Pilbara, South Africa and some samples from the Yilgarn block plot in the oceanic island arc field (Figure 9.13). The samples from Greenland and some samples from the Yilgarn block plot in the continental island arc field, suggesting a mafic to felsic volcanic source terrain for Archean sedimentary rocks.

9.5.3d Th-U

The Archean sedimentary rocks are characterised by low Th and U abundances (Rogers et al. 1969; Nance and Taylor, 1977; Bavinton and Taylor, 1980; McLennan and Taylor, 1980). Average Th and U abundances in Archean shales are 6.3 ppm and 1.6 ppm respectively (McLennan, 1981b). These values are comparable with the 5.5 ppm Th and 2.3 ppm U in the average oceanic island arc mudrocks (Table 9.4). The Th/U ratio varies from 3.5 to 5.7 in Archean sedimentary rocks of various regions (Rogers et al. 1969; McLennan and Taylor, 1980). The average Th/U ratio in the Archean shales is 3.9 and is comparable with the 2.8 Th/U ratio of the oceanic island arc mudrocks. Continental island arc mudrocks are characterised by average 16.2 ppm Th, 3.17

Table 9.4 Comparison of Average Archean Shale with Oceanic Island Arc and Continental Island Arc Mudrocks*

	Oceanic Island Arc Mudrock[1)]	Archean Shale[2)]	Continental Island Arc Mudrock[1)]
Ba	692	575	713
Rb	67	60	139
Sr	287	180	194
Pb	8.1	20	18.8
K/Rb	339	318	199
Rb/Sr	0.29	0.33	1.31
Ba/Rb	11.7	9.6	5.2
Ba/Sr	2.4	3.2	6.28
Th	5.5	6.3	16.2
U	2.36	1.6	3.17
Zr	130	120	185
Hf	3.5	3.5	6.6
Nb	3.7	9	9.0
Y	22	18.3	26.5
Th/U	2.81	3.9	5.15
Zr/Hf	37.7	34.3	28.0
Zr/Th	27.7	19.1	11.6
La/Th	3.9	3.1	1.58
La	18	19.8	24.4
Ce	37	41.7	53
Nd	19	14.5	21.4
La/Y	0.92	1.08	0.93
La/Sc	1.0	1.0	1.78
Th/Sc	0.29	0.32	1.17
Sc	20	20	14.1
V	159	135	84
Cr	39	350	55
Co	15	40	11
Ni	15	200	18
Cu	44	150	20
Zr	104	-	85
Ga	19	15	17
Ni/Co	1.08	5.0	1.74
Sc/Ni	1.70	1.0	0.96

Notes:

* All abundances in ppm.

1) From Table 7.17.

2) From McLennan (1981b).

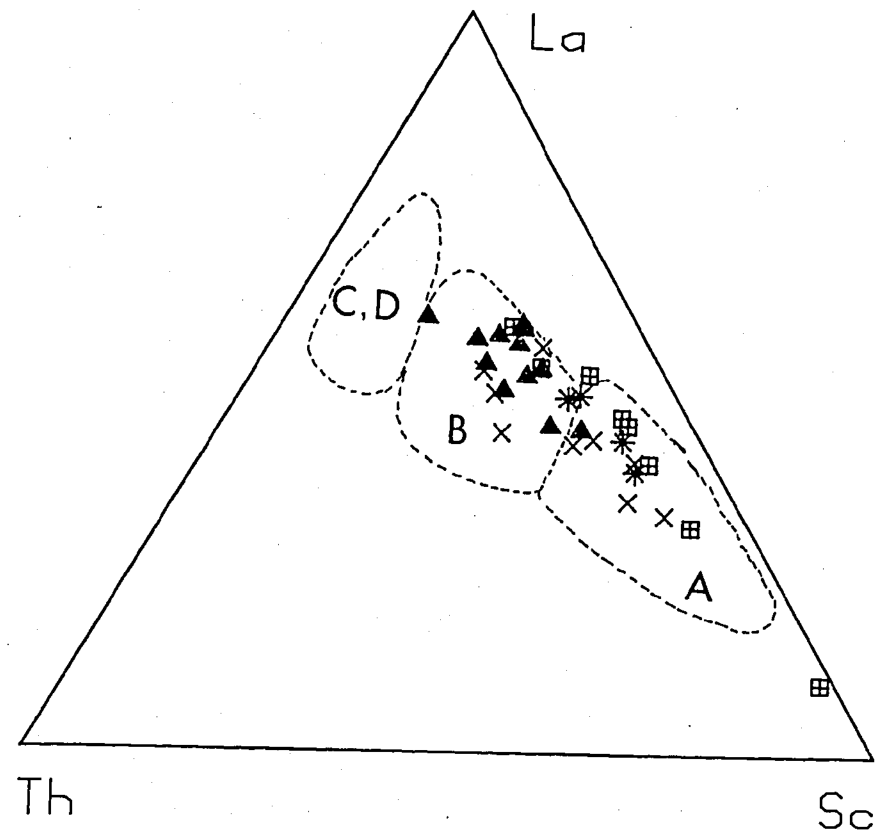
Figure 9.13 La-Th-Sc and Th-Sc-Zr/10 discriminatory plots of Archean samples. The fields represent various tectonic settings (Figures 7.11 and 7.14) : A - Oceanic island arc; B - Continental island arc; C - Andean type; D - passive margins. Note that the Archean samples mainly plot in the oceanic and continental island arc fields. Symbols for Archean samples are (data from McLennan, 1981b):

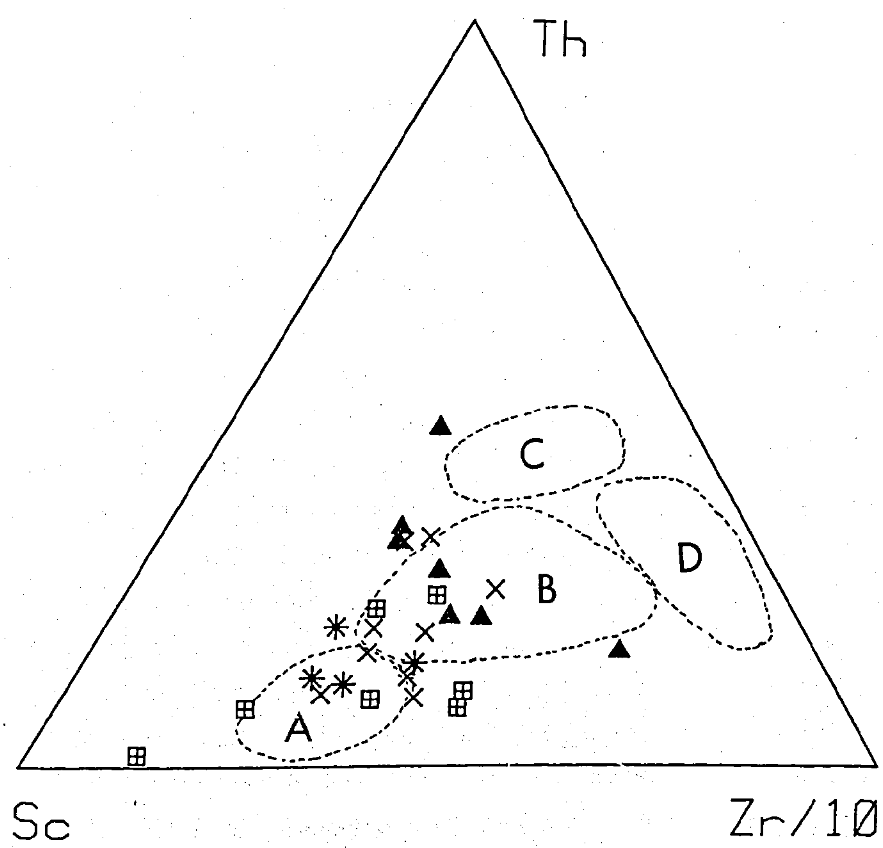
▲ Pilbara

× Yilgarn

✳ South Africa

⊞ Greenland


La
C,D
B
A
Th
Sc


Th
C
B
D
A
Sc
Zr/10

ppm U and 5.15 Th/U ratio. The Th-U characteristics of Archean mudrocks are significantly low compared to continental island arc mudrocks, and suggest a significant mafic-intermediate volcanic component in the Archean source regions.

9.5.3e Zr-Hf-Nb

Zr and Hf abundances in the average Archean shale are 120 ppm and 3.5 ppm, respectively (McLennan, 1981b). These values are in remarkable agreement with the 130 ppm Zr and 3.5 ppm Hf recorded in the average oceanic island arc mudrocks (Table 9.4). Significantly higher Zr (185 ppm) and Hf (6.6 ppm) abundances are observed in the continental island arc rocks. However, Nb is 9 ppm in the average Archean shale and is similar to the Nb abundance in continental island arc rocks (Table 9.4). The Zr/Hf and Zr/Th values for the average Archean shale are intermediate between oceanic and continental island arc mudrocks and suggest a mixed mafic-felsic source terrain.

9.5.3f Cr-Ni

The abundances of Cr and Ni in Archean sedimentary rocks have been a matter of discussion for some time. The 350 ppm Cr and 200 ppm Ni values in the average Archean shale are significantly higher than those of oceanic and continental island arc mudrocks (Table 9.4). Danchin (1967) recorded average 860 ppm Cr and 495 ppm Ni in the Archean shales of South Africa. Similar high Cr and Ni abundances have also been reported in the Archean metapetites of India (Naqvi and Hussain, 1972). This feature of Archean sedimentary rocks has been explained by presuming an ultramafic source terrain (Danchin, 1967; Condie et al. 1970). However, McLennan (1981b) pointed out that if ultramafic rocks are assumed to constitute the source region, they should yield 9% MgO content in the clastic sediments. The mean MgO content of Archean shales is only ≅ 7%.

Data on sedimentary rocks of eastern Australia show that, in general, the Cr and Ni content increases in mudrocks with increasing maturity and fractionation (Figure 6.5). High Cr and Ni abundances were noted in passive margin type mudrocks compared to mudrocks of other tectonic settings and has been explained as due to the enrichment of these elements with phyllosilicates (See Section 6.9). The extremely high Cr and Ni content in Archean sedimentary rocks may also be due to the enrichment of these elements with mudrocks during the weathering of volcanic source rocks.

9.5.3g Rare Earth Elements

Many studies have shown that the chondrite normalised REE patterns of Archean sedimentary rocks are characterised by the absence of a detectable negative Eu anomaly, and low La_N/Yb_N ratios (Wildeman and Condie, 1973; Nance and Taylor, 1977; Bavinton and Taylor, 1980; Taylor and McLennan, 1981a,b). Two separate REE estimates, from Taylor and McLennan (1981a,b) and McLennan (1981b), of average Archean shale are given in Table 9.5. The chondrite normalised plots of these averages are compared with those of oceanic island arc and continental island graywackes (Figure 9.14). The differences in ΣREE and in the La_N/Yb_N ratio between the two averages are apparent. Both the averages are higher in ΣREE and La_N/Yb_N compared to oceanic island arc graywackes. However, the average Archean shale of Taylor and McLennan (1981a) is more comparable with oceanic island arc graywackes, whereas the average Archean shale of McLennan (1981b) is more comparable with typical continental island arc graywackes. In general, the Archean mudrocks plot between the oceanic and continental island arc sediments, indicating mixed mafic-felsic source rocks. Archean type REE patterns can be produced by the mixture of tonalite-trondhjemite and mafic volcanics, which are so common in Archean terrains (Nance and Taylor, 1977; Taylor, 1977; Taylor and McLennan, 1981a,b).

9.5.4 Provenance

The major element composition of Archean sedimentary rocks suggests that they can not be derived only from andesitic sources. The composition of these sediments is more compatible with a mixture of mafic-felsic volcanic sources. Some trace element characteristics, such as Th, U, Th/U, Ba, Rb, Rb/Sr, Zr and Hf definitely indicate that mafic-intermediate volcanic rocks constituted part of the source regions. The trace element discriminatory plots (e.g. La-Th-Sc; Th-Sc-Zr/10) also exhibit that the Archean sediments overlap on oceanic and continental island arc fields, suggesting a derivation from a mixture of mafic and felsic volcanic rocks and an almost negligible contribution from Andean type (K-rich granites) source rocks. The chondrite normalized REE patterns are also intermediate between the typical patterns of oceanic and continental island arc sedimentary rocks and can be best modelled by a mixture of mafic and felsic source rocks. The

Table 9.5 Comparison of Rare Earth Element Characteristics of Archean Shales with Oceanic Island Arc and Continental Island Arc Graywackes*

	Oceanic Island Arc[1)]	AAS[3)]	Archean Shale[4)]	Continental Island Arc[2)]
La	8.23	12.6	19.8	21.86
Ce	19.43	26.8	41.7	47.57
Pr	2.68	3.13	4.88	4.83
Nd	11.16	13.0	19.5	19.04
Sm	3.05	2.78	3.97	3.40
Eu	1.07	0.92	1.16	1.06
Gd	3.29	2.85	3.43	2.89
Tb	0.50	0.48	0.57	0.46
Dy	3.18	2.93	3.40	2.69
Ho	0.73	0.63	0.74	0.57
Er	2.11	1.81	2.12	1.51
Yb	2.14	1.79	2.03	1.36
ΣREE	57.6	70.3	103.9	107.2
La_N/Yb_N	2.6	4.8	6.6	10.8
Eu/Eu^*	0.97	1.0	0.96	0.99

Notes:

* All abundances in ppm.

1) Average oceanic island arc graywacke (Table 8.6).

2) Continental island arc graywacke (Sample MK29; Table 8.4).

3) Average Archean Shale (Taylor and McLennan, 1981a).

4) Average Archean Shale (McLennan, 1981b).

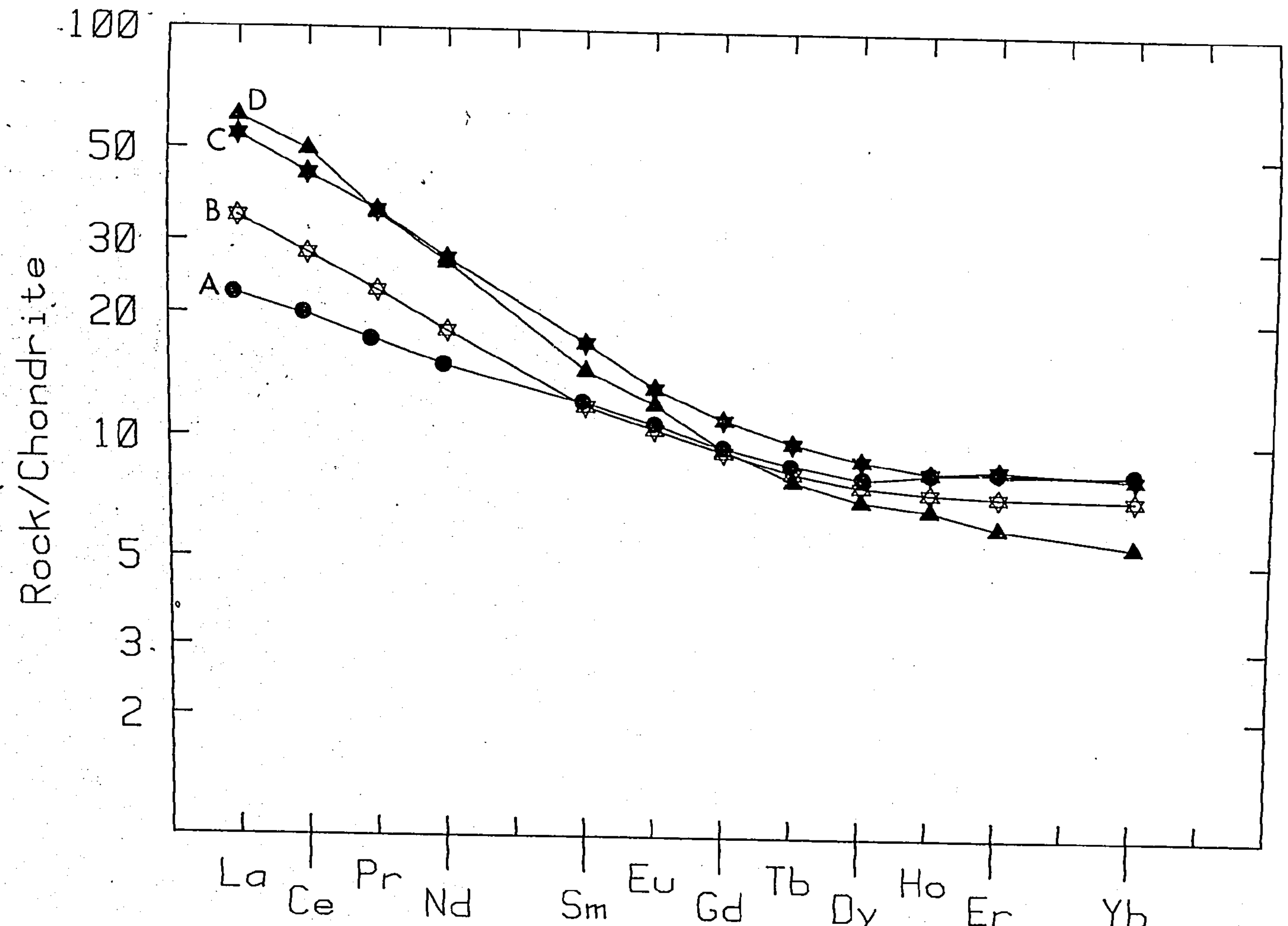


Figure 9.14 Comparison of chondrite *normalised REE* plots of Archean sedimentary *averages* with graywackes of various tectonic *settings*. A - average oceanic island arc graywacke; B - average Australian Archean shale *after* Taylor and McLennan, 1981a,b; C - average Archean shale after *McLennan, 1981b*; D - continental island arc graywacke (Sample MK29)

large variation in the data may also be because of the variation in the proportions of various source rocks in different regions.

9.6 SECULAR VARIATIONS IN THE CHEMICAL COMPOSITION OF SEDIMENTARY ROCKS

9.6.1 General Observations

Secular trends in the chemical composition of sedimentary rocks are important as they can throw substantial light on the evolution of the continental crust. The first discussion on this aspect goes back to 1909 when Daly contended that the MgO/CaO ratio in carbonates increases with increasing age. Since then, a number of workers have noted trends in various sedimentary lithologies and on various continents (Nanz, 1953; Engel et al. 1974; Ronov, 1964, 1972; Ronov and Migdisov, 1971; Veizer, 1973, 1976a,b, 1978; Veizer and Garret, 1979; Van Moort, 1973, 1974).

In most of these investigations a change from mafic to felsic composition with time has been observed. The cause of this change has been a matter of speculation. Russian workers have collected massive data and explained the trends as due to the compositional evolution of the continental crust, atmosphere and biosphere (Ronov, 1972; Ronov and Migdisov, 1971). On the other hand, many workers have attributed these trends to sedimentary recycling and associated processes such as differential solubility, diagenesis and metamorphism (Garrels and Mackenzie, 1971; Garrels et al. 1972). Recent work of Veizer and co-workers has shown that sedimentary recycling is an important factor controlling the chemical evolution of sedimentary rocks, but is superimposed on the compositional evolution of the crust (Veizer, 1973, 1976a,b, 1979; Veizer and Jansen, 1979).

In order to decipher the secular trends in the composition of sedimentary rocks, the obvious question can be asked - "Is there any clastic sedimentary facies peculiar to any geological age? " This question can not be answered satisfactorily, but the answer is probably no. This leads us to find ways for estimating bulk chemical compositions through geological time. Thus the method of selecting the facies for averaging the composition for any particular interval becomes very crucial. As pointed out by Pettijohn et al. (1972) and Schwab (1978), certain comparisons like Archean flysch with Phanerozoic cratonic platform sediments, can lead to many misleading conclusions. Schwab (1978) estimated the composition of sedimentary assemblages for Archean, Early Proterozoic, Late Proterozoic and Phanerozoic by weighting the lithologies according to their proportion in various sequences. These estimates form the basis of the present discussion.

The geochemical data derived from the sedimentary rocks of eastern Australia in the present work, are too limited in geographic distribution, geological age and facies to infer worldwide trends. However, the present work has important bearing on aspects of secular variation in the composition of sedimentary rocks and these are discussed below.

9.6.2 Major Element Geochemistry

Schwab (1978) showed that the bulk major element composition of sedimentary assemblages changes from Archean through Phanerozoic times. The gradual decrease in Fe_2O_3+FeO+MgO+CaO+Na_2O and the enrichment of SiO_2 were related to an evolutionary trend, from mafic to felsic. If the composition of sedimentary rocks has changed from mafic to felsic through geological time, it should be parallel to compositional change seen in sedimentary rocks from oceanic island arc (Unfractionated Sedimentary Composition) through continental island arc, (Intermediate Sedimentary Composition) to Andean type - passive margin (Fractionated Sedimentary Composition).

9.6.2a Archean Sedimentary Composition

Schwab's (1978) estimate of the average Archean sedimentary composition has been refined by McLennan (1981a; Table 9.1). A remarkable similarity is seen in all major elements, except CaO, between the average Archean and oceanic island arc sedimentary compositions (Figure 9.15). The large standard deviation associated with the mean CaO values in both averages do not permit an unequivocal judgement about the enrichment of CaO in oceanic island arc rocks. The overall similarity in the averages, clearly indicates the mafic nature of Archean sedimentary assemblages. However, in a previous section (Section 9.4), it has been contended that the major and trace element geochemical characteristics of Archean sedimentary rock are not compatible with derivation from only mafic volcanic rocks but can be best modelled by a mixture of mafic and felsic volcanic source rocks. This paradox cannot be resolved with the present data. Probably, all Archean sedimentary rocks may not represent a uniform composition but compositions in different regions may vary because of differences in source rocks and tectonic setting of the basins (cf. Hanson, 1981).

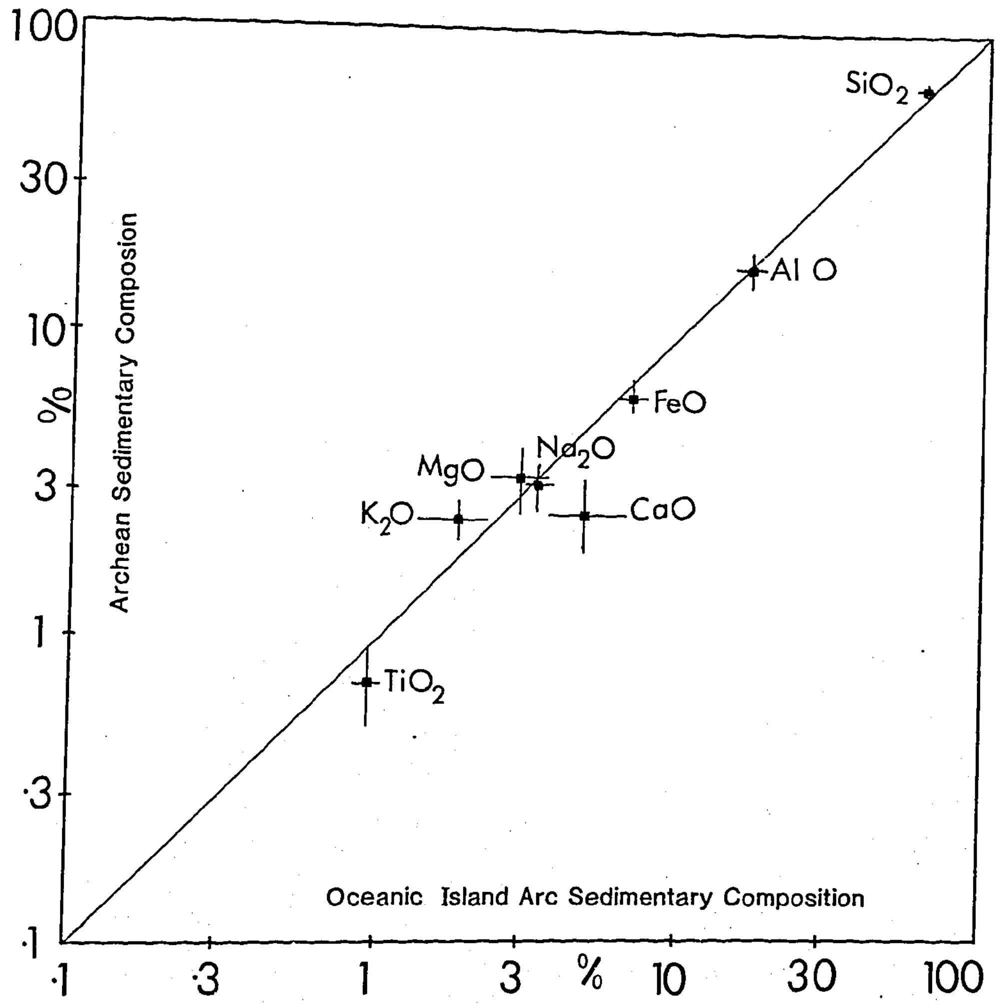


Figure 9.15 Comparison diagram of average oceanic island arc and Archean sedimentary compositions. Note the remarkable agreement between the two for most major elements, but the CaO content is higher in the oceanic island arc sedimentary average.

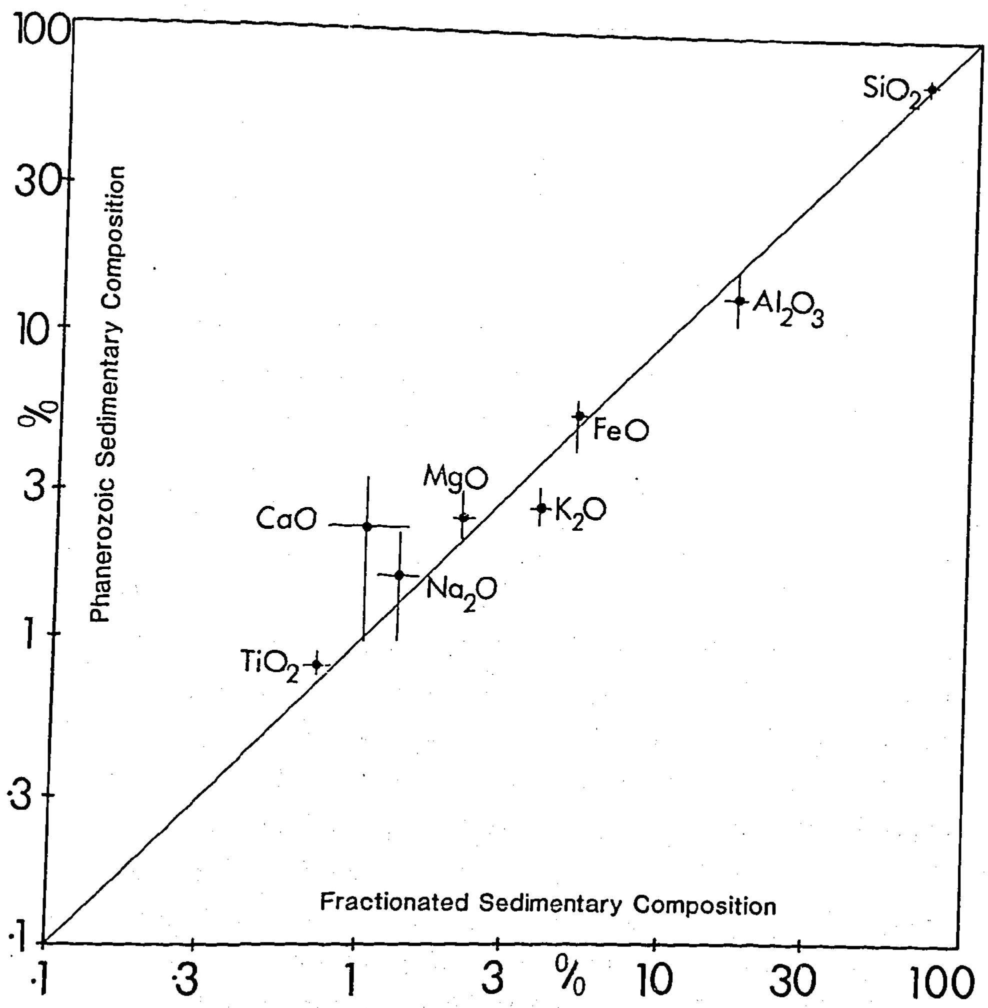


Figure 9.16 Comparison diagram of average Fractionated and Phanerozoic sedimentary compositions. Note the general similarity between the two averages, especially for the SiO_2, FeO, MgO, Na_2O and TiO_2 content. CaO is higher in the Phanerozoic average composition, whereas K_2O and Al_2O_3 is higher in the Fractionated average composition.

9.6.2b Phanerozoic Sedimentary Composition

The average Phanerozoic sedimentary composition matches reasonably well with the average Fractionated Sedimentary Composition (Andean and passive margin types) (Figure 9.16). The most significant difference is the enrichment of K_2O and Al_2O_3, and the depletion of CaO and Na_2O in the FSC. The redistribution of elements during the sedimentary cycle can account for these differences.

9.6.2c Proterozoic Sedimentary Composition

Proterozoic sedimentary rocks represent the important link of change from the Archean to Phanerozoic sedimentary compositions. Schwab (1978) showed that the composition of average Proterozoic sedimentary rocks is intermediate between the Archean and Phanerozoic averages and thus represents a gradual transition from mafic to felsic composition. On the other hand, McLennan (1981a) contended that Schwab's (1978) method, in which he included Gowganda tillites for estimating the average Early Proterozoic composition, is not correct, because tillites do not represent the "typical sedimentary rocks". McLennan's (1981a) estimate of Early Proterozoic sedimentary composition, based mainly on Huronian mudrocks, is indistinguishable from the Phanerozoic sedimentary composition.

The above discussion brings to light the importance of the method of estimating the "average" compositions of sedimentary assemblages and shows that different methods can lead to entirely different conclusions. The exclusion of tillites for estimating the average composition is not justified, rather, it has long been recognized that glacial sediments provide excellent evidence of the crustal composition because of minimal chemical weathering, and also the material derived from continental sources is homogenised during transportation (Goldschmidt, 1954).

Various independent estimates of the Proterozoic sedimentary compositions are presented in Table 9.6. The Upper Proterozoic graywackes of north-western Hogger (Algeria) were studied by Caby et al. (1977) and were thought to represent the Late Precambrian crustal composition of the area. Unfortunately, neither Schwab (1978) nor McLennan (1981a) have considered these sediments while deriving the average compositions. Compared to the continental island arc sedimentary composition, Schwab's (1978) estimate of the average Proterozoic composition is higher in FeO^t,K_2O and MgO and depleted in

Table 9.6 Various Averages of Proterozoic Clastic Sedimentary Rocks#

	(1)		(2)		(3)		(4)	
	$\bar{X}$	S.D	$\bar{X}$	S.D	$\bar{X}$	S.D	$\bar{X}$	S.D
SiO_2	67.23	3.2	70.6	4.2	64.79	6.5	67.54	2.9
TiO_2	0.73	-	0.6	0.2	0.82	0.3	0.72	0.1
Al_2O_3	15.01	0.1	14.6	2.0	15.35	1.3	14.99	0.4
FeO^*	6.78	0.9	5.6	2.3	5.47	2.2	5.95	0.7
MnO	0.31	0.1	-	-	0.13	0.06	0.01	-
MgO	2.47	0.6	2.15	0.5	2.68	1.4	2.43	0.3
CaO	1.54	0.1	1.5	0.4	4.64	3.3	2.56	1.9
Na_2O	2.57	0.3	1.65	0.5	3.91	1.1	2.71	1.1
K_2O	3.39	0.3	3.3	0.4	1.75	1.3	2.81	1.1
P_2O_5	-	-	-	-	0.21	0.06	0.07	-

Notes:

Recalculated on volatile free basis.

* Total Fe as FeO

(1) Proterozoic clastic sedimentary rock (Schwab, 1978).

(2) Proterozoic clastic sedimentary rock (McLennan, 1981a).

(3) Late Proterozoic Hoggar graywacke, Algeria (Caby et al. 1977).

(4) Average Proterozoic sedimentary composition - mean of (1), (2) and (3).

$\bar{X}$- Mean; S.D - Standard Deviation.

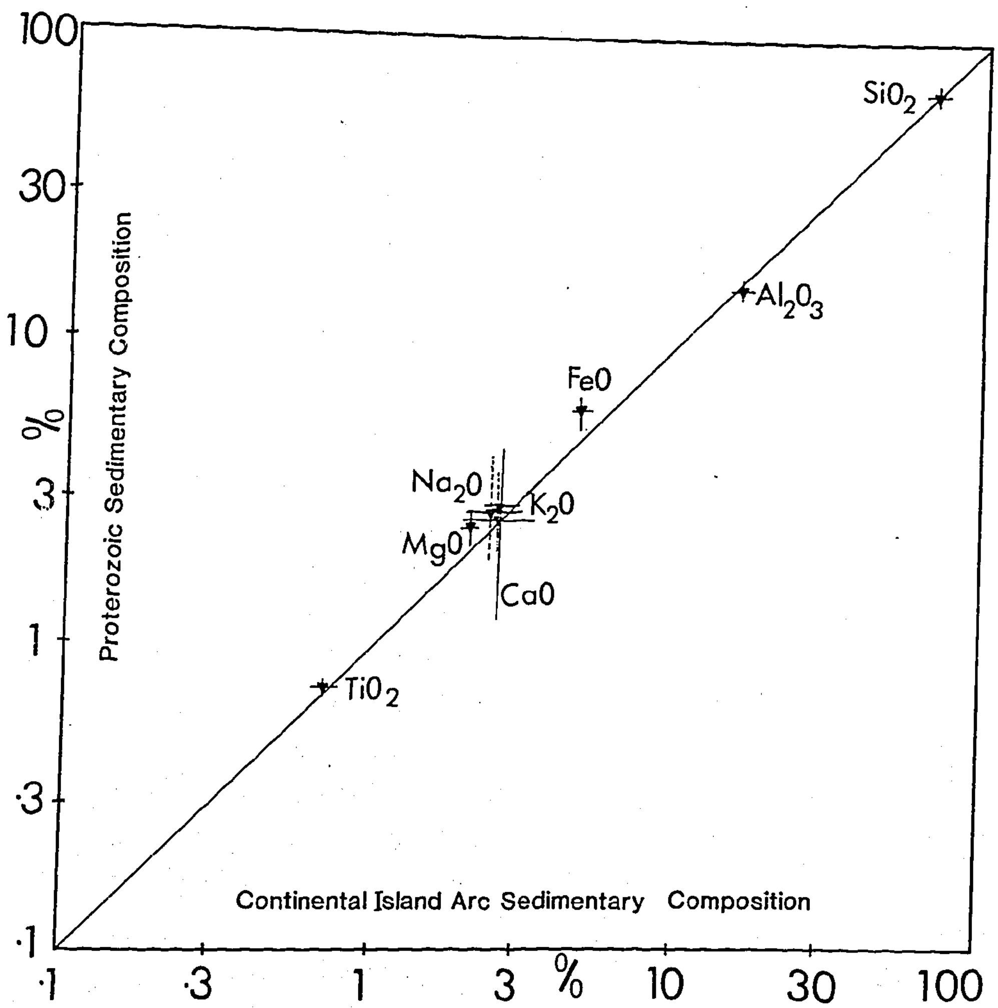


Figure 9.17 Comparison diagram of average continental island arc and Proterozoic sedimentary compositions. Note the remarkable similarity between the two compositions for most elements.

CaO but shows close similarities in in SiO_2, Al_2O_3, Na_2O & TiO_2 content. McLennan's (1981b) estimate of the average Proterozoic composition differs in most elements from the continental island arc composition. The average Hogger graywacke composition is significantly more mafic as revealed by the high enrichment of CaO, Na_2O, MgO, TiO_2 and to some extent FeO^t, and the depletion of K_2O, than the continental island arc sedimentary composition. Large uncertainties on the means, in many cases, make it very difficult to interpret the comparisons.

Presuming that the Hogger type sedimentary rocks contributed substantially to the Proterozoic crust, an average is calculated from the three estimates of Proterozoic sedimentary compositions (Table 9.6). This estimate shows an excellent similarity in all major elements with the continental island arc composition (Figure 9.17), suggesting a gradual transition from Archean to Phanerozoic. However, whether the average Proterozoic composition calculated above is a true representative of the assemblages, or is "another exercise in mathematical inbreeding" (Holland, 1978) is not known. A definite estimate of the Proterozoic sedimentary composition awaits further work in this direction.

9.6.3 Trace Element Geochemistry

Very few attempts have been made to understand the secular trends in the distribution of trace elements in clastic sedimentary rocks. Reimer (1972) noted the change in the Rb/Sr ratio with time in mudrocks and related it to the soil forming processes. The distribution of REE and Th with time in sedimentary rocks has been studied by Nance and Taylor (1976, 1977); McLennan and Taylor (1980); and Taylor and McLennan (1981a,b). These authors have contended that Archean sedimentary rocks are characterized by no detectable Eu anomaly ($Eu/Eu^* \cong 1$), a low La_N/Yb_N ratio (average $\cong$ 4.6) and low Th and ΣREE abundances; whereas Post-Archean sedimentary rocks are characterized by the presence of a negative Eu anomaly ($Eu/Eu^* = 0.64 \pm 0.05$); a high La_N/Yb_N ratio (average $= 9.2 \pm 1.5$); and high Th and ΣREE abundances. The uniformity of ΣREE and Th abundances in Post-Archean sedimentary rocks has been taken as indicative of constancy in the composition of sedimentary rocks and the upper continental crust throughout the Post-Archean period.

To what extent are these trends representative of the whole sedimentary assemblages? The above mentioned inferences on REE and

, Th are based on the comparison of Archean and Post-Archean sedimentary rocks, representing entirely different depositional systems and tectonic regimes. The Pilbara, Yilgarn and Fig Tree sequences represent the Archean geosynclinal facies whereas the Post-Archean sequences (Amadeus, Carnanvon, Canning and Perth basins) represent the aulacogens or intra-cratonic basins. These cratonic basins were sufficiently remotely located from active geosynclinal belts (where the processes of crustal additions were in progress), so that the clastic debris was only derived from the interior of the craton. Thus, these Post-Archean sedimentary assemblages may be directly related to the formation and recycling of the craton, they do not necessarily represent the sedimentary assemblages formed due to crustal addition at various geological times.

Trace element characteristics of clastic sedimentary rocks are controlled by the tectonic setting of the basin (Chapter 7). La (representing light rare earth elements), Th, U and Nb in sedimentary rocks have particularly been used to decipher crustal evolution. The variation in the average abundance of these elements with change in tectonic setting is shown in Figure 9.18. These trends are somewhat similar to the change of K_20/Na_20 in sedimentary rocks (Engel et al. 1974) and Sr^{87}/Sr^{86} in carbonates (Veizer and Compston, 1976) through geological time. The increase in La, Th, U, Nb and the La/Sc ratio from oceanic island arc through continental island arc to Andean type sedimentary rocks is parallel to the increase in K_20/Na_20 and Sr^{87}/Sr^{86} from Archean through Proterozoic towards Phanerozoic. This is probably an evolutionary trend towards a more felsic composition. The slight decrease in the abundance of La, Th, Nb and the La/Sc ratio in passive margin type sedimentary rocks, is similar to the slight decrease in K_20/Na_20 and Sr^{87}/Sr^{86} seen in Phanerozoic rocks, and may be a result of recycling. This recycling also results in the significant depletion of U and the consequent increase in the Th/U ratio in passive margin type sedimentary rocks.

9.6.4 Epilogue

Marked similarities are seen in the major element compositions of average Archean, Proterozoic and Phanerozoic clastic sedimentary rocks with that of oceanic island arc, continental island arc and Andean type-passive margin sedimentary compositions, respectively. This clearly

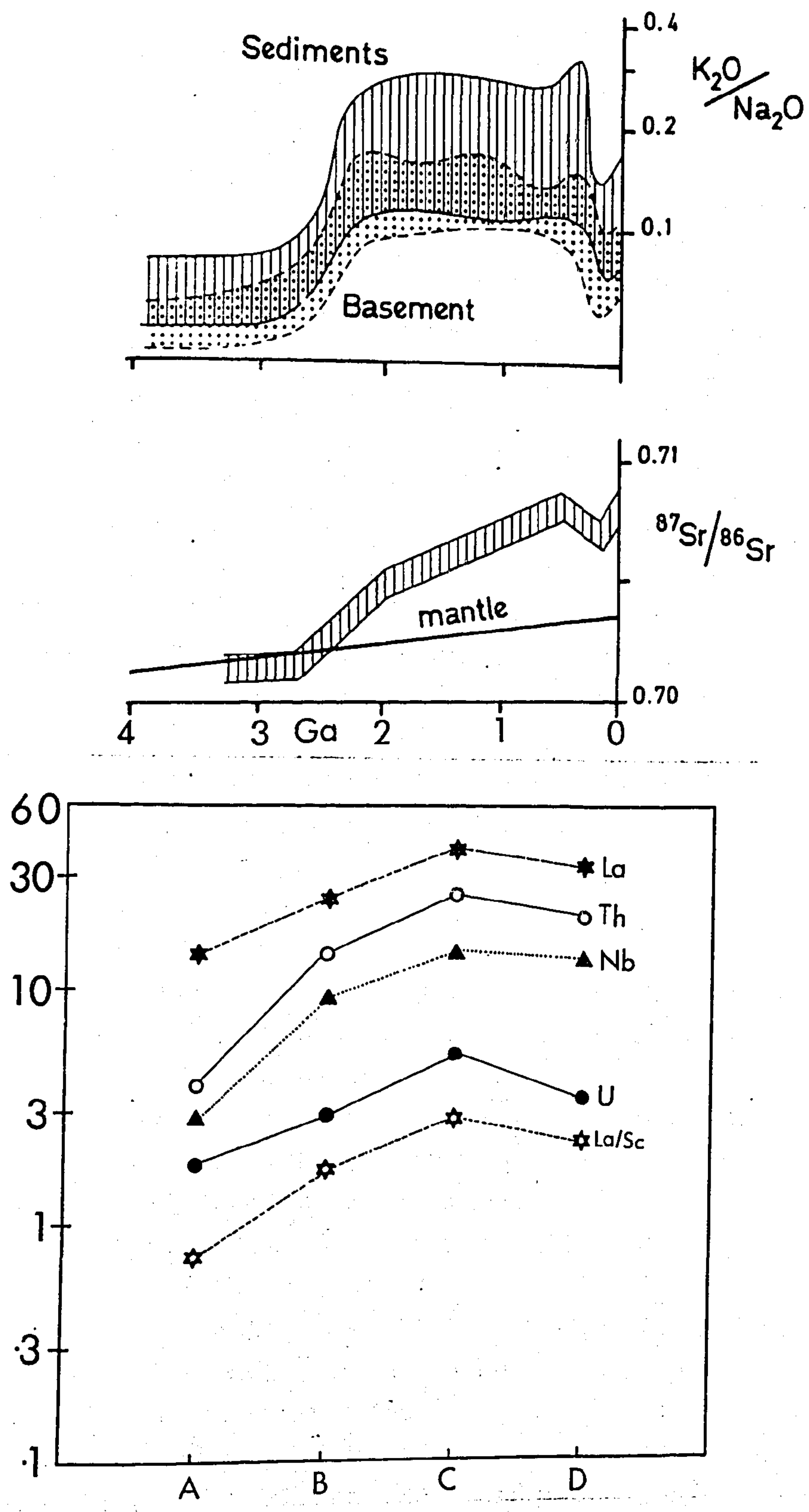


Figure 9.18 Secular trends in the K_2O/Na_2O for sediments and basement (after Engel et al. 1975), and $^{87}Sr/^{86}Sr$ in carbonates (from Veizer and Compston, 1976), through geological time (upper half of the diagram). These trends are parallel to Variation in the abundances of La, Th, Nb, U and the La/Sc ratio in clastic sedimentary rocks from oceanic island arc (A), through continental island arc (B) to Andean type (C) to the passive margins (D) (Lower half of the diagram). Abundances are in ppm (log scale).

suggests a gradual mafic to felsic trend in the bulk composition of clastic sediments from Archean through Proterozoic to Phanerozoic times. The secular trend of Sr^{87}/Sr^{86} in carbonates, and K_2O/Na_2O in clastic sedimentary rocks through geological time is parallel to the change of La, Th, Nb and U abundances, observed in sediments from oceanic island arc to continental island arc to Andean type to the passive margin type settings. This also suggests a gradual transition from mafic to felsic sedimentary compositions through time. The REE characteristics also show a similar trend. The Eu/Eu^* estimated in the Proterozoic tillites is 0.89 ± 0.13 (McLennan et al. 1979) and is intermediate between the $Eu/Eu^* \cong 1.0$ and 0.65 ± 0.05 estimated for Archean and Phanerozoic sedimentary compositions, respectively. Although certain trends have been inferred in the evolution of the sedimentary composition, it is clear that studies done in other regions, employing different methods can yield entirely different results (McLane, 1972). Thus, it is imperative that more soundly based methods of inferring compositional trends be adopted. Compositional characteristics are governed by the tectonic setting. As it would be most unreasonable to group all modern occurrences of mafic rocks together (just because they are mafic), and take the average of their compositions without regard to their tectonic settings; similarly, it would be unreasonable to estimate the average sedimentary rock composition from whatever analyses are available in literature, without regard to the tectonic settings of the basins. A better approach, will be to decipher the dominant tectonic sedimentary regimes through geological time, and then interpret the secular evolution in the composition of clastic sedimentary rocks.

9.7 EVOLUTION OF SEDIMENTARY ROCKS AND CRUSTAL GROWTH

Considerable difference of opinion exists amongst scientists regarding the processes and timings of crustal growth. Some authors argue that the bulk composition of the Archean crust was the same as the present upper crust (Condie, 1981), however, geochemical evidences favour a more mafic nature for the Archean crust (e.g. Taylor and McLennan, 1981a,b; Section 9.5). The present upper crust is of granodioritic composition, and a change from mafic to granodioritic composition and crustal growth since the Archean has been a matter of debate. The evolution of the crust has been predicted as either gradual throughout geological time by addition of new material from the mantle, or episodic, though various other extreme models (e.g. Armstrong, 1981) have also been proposed (see Taylor, 1977, 1979 for full discussion). The continual generation of the continental crust throughout geological time, has been proposed on the basis of various sedimentary evidences (Veizer and Jansen, 1979).

The Archean-Proterozoic boundary has been recognized as a very important event in the Earth's history by many workers. Evidences from sedimentary rocks favour a gradual transition from the Archean to Proterozoic (e.g. Schwab, 1978; Section 9.6). Sm-Nd and Sr isotope studies suggest that a large part of the continental crust was formed at this time (e.g. Veizer and Compston, 1976; McCulloch and Wasserburg, 1978). This has been attributed to the large scale upward transfer of granodioritic material due to intra-crustal partial material processes (e.g. Taylor, 1979; Veizer and Jansen, 1979). Estimates vary, but it has been argued that between 55-75% (and possibly up to 85%) of the total mass of the crust may have grown by 2500 my ago (Dewey and Windley, 1981; McLennan and Taylor, 1981). The K_2O/Na_2O ratio in igneous and sedimentary rocks, and the Sr^{87}/Sr^{86} ratio in carbonates show dramatic rise during this period. On the basis of isotopic data and computer simulation of recylcing models, Veizer and Jansen (1979) have envisaged a slow continental growth during the early Archean, followed by fast growth during Archean-Proterozoic boundary and slow during the subsequent periods.

The present day crustal growth probably results from the accretion of island arc material on the continental crust (Taylor, 1967, 1977; Karig and Sharman, 1975; Crook, 1980a,b). The mechanism by which growth due to continental accretion takes place is not completely understood (e.g. Karig and Kay, 1981). The formation of island arcs has been explained as due to the subduction of the oceanic lithosphere and the overlying mantle wedge to produce calc-alkaline magma.

How far back the modern plate tectonic processes operated in the history of the earth is debatable. Evidences from heat sources and their magnitude suggest that early tectonic processes were different from the modern ones (Kröner, 1981; Goodwin, 1981). However, some authors think that plate tectonic processes were active even during the Archean (Hanson, 1981). Hoffman (1980) has recognized the "Wilson Cycle" in the Early Proterozoic sequence of the Canadian Shield which suggests that plate tectonic processes were operative during that time, except that magmatism may have been more intense than at present. Paleozoic plate tectonic regimes are not as clear as those of the Meso-Cenozoic, however, the occurrence of ophiolites and blue-schists in many Paleozoic terrains indicate that plate tectonics of the modern type probably prevailed throughout the Phanerozoic (Burke and Dewey, 1973).

Oceanic island arc type sedimentary rocks are significantly different from the upper continental crust and are probably derived from the mantle and thus represent new material added to the crust (Rogers and McKay, 1972; Rogers, 1977). If crustal growth takes place through island arcs, the presence of mantle-derived sedimentary material of the accretionary prism would suggest periods of crustal growth. These rocks are not restricted to any particular period but are common throughout geological time. Pre-Mesozoic examples are of such rocks are seen in Late Proterozoic of Algeria (Caby et al. 1977); Lower Paleozoic of Southern Uplands, Scotland (Leggett, 1980); Late Paleozoic of Australia (the Tamworth Trough) and Sicker Group, British Columbia (Mukherji, et al. 1978). Meso-Cenozoic examples are common throughout the Circum-Pacific region (see Chapter 7). All these sediments are characterised by calc-alkaline andesitic detritus and low abundances of Th, U, Nb, Rb and REE (data from the Tamworth suite only). The processes of crustal growth during the Archean are not yet unequivocally established but the bulk Archean sedimentary composition is similar to the average oceanic island arc sedimentary composition (Figure 9.15). However, the geochemical characteristics of Archean sedimentary rocks in various regions are more compatible with their derivation from a mixed mafic and felsic source (Taylor and McLennan, 1981a,b; Section, 9.5). The variation in the composition of the Archean sequences may also be because of different tectonic regimes in various regions (cf. Hanson, 1981).

Geosynclinal sedimentary rocks constitute more than one third of the sedimentary assemblages of the earth (Garrels and Mackenzic, 1971). The proportion of first cycled and recycled material is difficult to estimate with the data available. However, recycled sedimentary material occurs throughout geological time, though its proportion may be minor in the Archean sequences. The presence of first cycled mantle-derived "juvenile", and abundant recycled sedimentary rocks throughout the geological column suggests that crustal addition and recycling processes were operating together, in contrasting tectonic settings, throughout geological time (except probably in the Archean). Crustal additions took place in island arc tectonic settings, where subduction related processes were operating; and recycling of the continental crust took place in the passive margins and thickened crustal regions of continental collision. Thus, the nature of preserved sedimentary rocks, and isotopic evidences (Veizer and Jansen, 1979; Moorbath, 1980) suggest crustal growth and reworking have occurred throughout geological time, though the growth has decreased and recycling increased through time. The addition of "juvenile" sedimentary material derived from the mantle or the lower lithospere throughout geological time, may have been related to time separated short "accretion-differentiation-superevents" deciphered on the basis of isotopic data (Moorbath, 1977, 1978).

CHAPTER 10

CONCLUSIONS

The main purpose of the present thesis was to examine the mineralogy and geochemistry of flysch sedimentary rocks in relation to the nature of source rocks, provenance types and tectonic settings. The major conclusions of the work are briefly summarised below.

The Paleozoic flysch sequences of eastern Australia show large variations in their mineralogical and geochemical compositions. The following five major graywacke suites are recognized on the basis of detrital mineralogy : Tamworth, Hill End, Hodgkinson, Bendigo and Cookman. The increase in maturity from Tamworth to Cookman is characterised by the progressive increase in quartzose grains and the general decrease in feldspar and lithic grains. The Tamworth suite graywackes are quartz-poor, dominantly composed of microlitic volcanic rock fragments and feldspar grains, and are derived from andesitic source rocks. The Hill End suite graywackes are quartz-intermediate, contain common felsitic volcanic fragments and feldspar grains, and are dominantly derived from felsic volcanic and sedimentary source rocks. The more quartzose Hodgkinson suite graywackes are characterised by abundant K-feldspar and polycrystalline quartzose grains, indicating their derivation from crystalline source rocks. The Bendigo suite graywackes are quartz-rich with minor feldspar and polycrystalline quartzose grains suggesting their derivation from dominantly meta-sedimentary rocks. The Cookman suite graywackes are highly quartzose with very little feldspar. Sedimentary rock fragments are common which suggests their multicycled nature and derivation from sedimentary rocks.

The mudrocks of various suites are also characterised on the basis of relative quartz, feldspar and phyllosilicate abundances. The increase in maturity in mudrocks is seen in the form of increase in phyllosilicates and decrease in tectosilicates, principally quartz and feldspar. Three broad groups of mudrocks are recognized : Tectic type (Tamworth suite); Phyllo-tectic type (Hill End and Hodgkinson suites) and Phyllic type (Bendigo and Cookman suites).

Increasing geochemical fractionation is observed in sedimentary suites with the increase in maturity. The graywackes and mudrocks of the Tamworth and Hill End suites are very similar in their bulk composition but large geochemical differences are seen between graywackes and mudrocks of the Hodgkinson, Bendigo and Cookman suites. Geochemical fractionation results in the enrichment of Si and Zr in graywackes, and the Al-group (Al, Ga), large cations (K, Rb, Ba) and ferromagnesian elements (Cr, Ni, Zn, Cu) in mudrocks. Small cations (Ca, Na, Sr), decrease with increasing geochemical differentiation and are lost in solution to form carbonates. Increasing geochemical differentiation is also accompanied by increasing textural differentiation in the form of a decrease in overall grain size, increase in the proportion of mudrocks and decrease in the proportion of graywackes.

The tectonic setting governs the relationship between compositional attributes such as provenance, relief, weathering, physical sorting and diagenesis. On the basis of similar trace element characteristics, particularly in La, Ce, Th, U, Zr, Hf, La/Y, Sc/Ni and Ni/Co, between the graywackes and various orogenic andesites, the Tamworth suite is assigned to the oceanic island arc; the Hill End suite to the continental island arc and the Hodgkinson suite to the Andean type tectonic settings. The Bendigo and Cookman suite graywackes are highly quartzose and their fractionated composition suggests a passive margin type of tectonic setting.

The major element geochemistry of arenites can be used to infer the provenance type and tectonic setting of the basin. The most discriminating parameters are total Fe as Fe_2O_3+MgO, TiO_2, and Al_2O_3/SiO_2, K_2O/Na_2O, and $Al_2O_3/(CaO+Na_2O)$ ratios. In general, there is a decrease in Fe_2O_3+MgO, TiO_2 and Al_2O_3/SiO_2; and an increase in K_2O/Na_2O and $Al_2O_3/(CaO+Na_2O)$ in arenites with the change of tectonic setting from oceanic island arc to continental island arc to Andean type to passive margin.

Immobile trace elements, e.g., La, Th, U, Zr, Nb, Y, Sc and Co are very useful in tectonic setting discrimination. In general, there is a systematic increase in La, Th, Nb and Ba/Sr, Rb/Sr, La/Y and Ni/Co and decrease in V, Sc, Ba/Rb, K/Th and K/U ratios from oceanic island arc to continental island arc to Andean and passive margin type arenites, concommitant with change in provenance type (and source rocks) from undissected magmatic arc (andesites) to dissected magmatic arc (felsic volcanics) to Andean type (crystallines) to recycled orogen - craton interior (sedimentary rocks). The most discrminating plots are La-Th, La-Th-Sc, Ti/Zr-La/Sc, La/Y-Sc/Cr, Th-Sc-Zr/10, Th-Co-Zr/10 and Rb-V-Zr.

Oceanic island arc arenites are characterised by extremely low abundances of La,Th,U,Zr,Nb,Y, and low Th/U, La/Y and high La/Sc and Ti/Zr ratios. Continental island arc arenites are discriminated from those of the oceanic island arc by their higher abundances of La,Th,U,Zr and Hf. The Andean and passive margin type of arenites are discrminated by Th-Sc-Zr/10 and Th-Co-Zr/10 plots. Passive margin type arenites can be discriminated from the Andean type by their higher abundance of Zr and lower abundance of Sc and V, due to recycling.

The mudrocks also show characteristics of the provenance types and tectonic settings. The most useful elements are Th,Nb,U,La,Sc,Zr and Y; and the most discriminating plots are La-Th, Nb/Y-Th, Nb-Zr/Th, Nb/Y-La/Sc, and Nb-Th/U. The oceanic island arc mudrocks are characterized by low abundances of La,Th,U,Zr and Nb. The continental island arc mudrocks are characterized by higher abundances of La,Th and Nb, and lower Zr/Th and higher Nb/Y ratios. The Andean type-passive margin mudrocks are characterised by higher abundances of La,Th,Nb, and Nb/Y, Th/U and lower Zr/Th ratios. The passive margin type mudrocks are discriminated from the Andean type by their higher Cr,Ni,Rb/Sr and Ba/Sr, and lower U, and Sc/Ni and V/Ni ratios, due to their recycled nature.

The nature of provenance type and tectonic setting is also reflected in the rare earth element geochemistry of clastic sedimentary rocks. There is an increase in ΣREE, La_N/Yb_N, ΣLREE/ΣHREE and a decrease in Eu/Eu^* with the increase in maturity concommitant with the change in source rocks from andesites to dacite to crystalline and sedimentary rocks. The chondrite-normalized REE patterns and associated parameters of the Tamworth, Hill End and Hodgkinson suite graywackes are similar to those of andesites of oceanic island arc, continental island arc and Andean type, respectively. The REE patterns of the Bendigo and Cookman suites are similar to turbidite sediments of the Atlantic.

The chondrite and PAAS normalized plots and REE parameters in arenites can be used to discriminate the oceanic island arc, continental island arc, Andean type and passive margin type tectonic settings.

The bulk sedimentary compositions in various tectonic settings are comparable with the crustal compositions of the region. The oceanic island arc sedimentary composition is similar to the total crustal composition. The average Andean type-passive margin major element sedimentary composition is comparable to the estimate of the upper continental crust of the shield regions, except that the former is depleted in Ca and Na, due to recycling. The continental island arc sedimentary composition is intermediate. Remarkable similarities exist between the average major element sedimentary compositions of the Archean and oceanic island arc; Proterozoic and continental island arc; and Phanerozoic and Andean type-passive margin compositions. The changes in Sr^{87}/Sr^{86} in carbonates, and K_20/Na_20 in basement and sedimentary rocks through geological time are parallel to changes in La,Th,U,Nb abundances from oceanic island arc to continental island arc to Andean type to passive margin sedimentary rocks, suggesting a gradual mafic to felsic continental growth through geological time. The mantle-derived "juvenile" and recycled sedimentary material occurs in all periods. Thus crustal growth and recycling have occurred together throughout geological time, in entirely different tectonic settings. However, the growth has decreased and recycling increased with geological time.

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Table A.1. Summary of analytical conditions for X-ray spectrometry.

ELEMENT	ANALYTICAL LINE	X-RAY TUBE	ANALYSING CRYSTAL	COLLIMATOR	DETECTOR	% RELATIVE STD DEVIATION ON BCR-1	ON W-1	DETECTION LIMIT 3σ
oxide percentages								
SiO_2	Kα	Cr	PE	Coarse	F.C	0.134		0.05
TiO_2	Kα	Cr	LiF(200)	Coarse	F.C	0.121		0.003
Al_2O_3	Kα	Cr	PE	Coarse	F.C	0.240		0.03
Fe_2O_3(total)	Kα	W	LiF(200)	Coarse	F.C	0.067		0.003
MnO	Kα	W	LiF(200)	Coarse	F.C	0.450		0.004
MgO	Kα	Cr	TAP	Coarse	F.C	0.931		0.05
CaO	Kα	Cr	LiF(200)	Coarse	F.C	0.096		0.001
K_2O	Kα	Cr	LiF(200)	Coarse	F.C	0.172		0.001
P_2O_5	Kα	Cr	Ge	Coarse	F.C	0.194		0.003
parts per million								
Ba	$L\beta_1$	W	LiF(220)	Coarse	F.C	0.29	0.75	5
Rb	Kα	Mo	LiF(200)	Fine	S.C	0.63	1.18	1
Sr	Kα	Mo	LiF(200)	Coarse	S.C	0.18	0.23	1
Pb	$L\beta_1$	Mo	LiF(200)	Fine	S.C	1.19	2.11	0.5
Th	$L\alpha_1$	Mo	LiF(200)	Fine	S.C	7.70	14.93	0.5
U	$L\alpha_1$	Mo	LiF(220)	Fine	S.C			0.5
Zr	Kα	W	LiF(200)	Coarse	S.C	0.49	0.86	1
Nb	Kα	W	LiF(200)	Fine	S.C	4.95	8.87	0.5
Y	Kα	Mo	LiF(200)	Coarse	S.C	0.55	0.84	1
La	$L\alpha_1$	W	LiF(220)	Coarse	F.C	1.65	3.88	1
Ce	$L\beta_1$	W	LiF(200)	Fine	F.C	3.09	7.98	1
Nd	$L\beta_1$	W	LiF(220)	Coarse	F.C	4.14	8.27	1
V	Kα	W	LiF(220)	Fine	F.C	0.35	0.43	1
Cr	Kα	W	LiF(200)	Fine	F.C	2.29	0.72	1
Ni	Kα	Au	LiF(200)	Coarse	S.C	11.10	0.99	0.5
Cu	Kα	Au	LiF(200)	Coarse	S.C	3.48	0.56	0.5
Zn	Kα	Au	LiF(200)	Coarse	S.C	0.46	0.45	1
Ga	Kα	Mo	LiF(200)	Coarse	S.C	1.27	2.74	0.2

Coarse collimator = 480 μ F.C = Flow Counter

Fine collimator = 160 μ S.C = Scintillation Counter

Na was determined on a modified Baird-Atomic double beam photometer with a propane-air flame, using Li as an internal standard. The technique is similar to that described by Cooper (1963) for K. All analyses were done at least in duplicate.

FeO was determined using the method of Peck (1964). This technique requires the dissolution of the powdered sample in HF over a flame followed by a titration against 0.05 N solution of potassium dichromate. All determinations were done at least in duplicate. Ferric iron was calculated by the difference from the total iron content measured by X-ray fluorescence.

The percent weight loss of a sample after heating for at least 90 minutes at 110°C was determined as H_2O^-. The H_2O^+ and CO_2 were measured by heating a sample for 30 minutes in a tube furnace at 1000 to 1050 °C in a stream of dry, CO_2-free nitrogen, following the method of Riley (1958). The H_2O and CO_2 given off from the sample were collected and weighed in microabsorption tubes containing a mixture of P_2O_5 and pumice, and "carbosorb" soda asbestos, respectively.

A.3.2 Trace Elements

The trace elements were measured in duplicate on pressed powder pellets (Norrish and Chappel, 1967). X-ray counts were automatically corrected for detector dead time and instrument drift was monitored against an internal standard. The analytical line and operating conditions were selected so as to maximize the count rate and minimise internal-element interferences. Background counts measured on either side of the peak position were selected so that interference was minimal and symmetric about the peak position for all elements. Element concentrations were calculated using the direct measurement of mass absorption (for $Sr_{k\alpha}$ and $Rb_{k\alpha}$) after corrections had been made for detector dead time, instrument drift and interelement interference.

A.3.3 Rare Earth Elements

The rare earth elements and some trace elements were determined usin[illegible] AEI MS7 spark source mass spectrograph (SSMS). The elements determined are: Th, U, Hf, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Yb. The principle and procedure involved in this technique has been extensively discussed by Taylor and Gorton (1977).

The method uses Lu_2O_3 as the internal standard, hence Lu abundance cannot be directly measured. Tm was also not measured as

Tm149 suffers a serious interference from multiple carbon molecule. Pm has no stable isotope, as such it is also not determined. An empirical correction was used for Gd, Tb, and Dy as these elements suffer a small interference from Ba and light REE. Precision and accuracy by this method is about ± 5% expressed as standard error and detection limits are ≅ 0.02 ppm. For each sample, at least two photoplates were exposed with at least 15 exposures on each plate and for many elements more than two isotopes were read. Thus between 8-20 measurements were made on each element.

A.4 X-RAY DIFFRACTION STUDIES

A.4.1 Identification of Minerals

The powdered samples of the mudrocks, on which chemical analyses have been done, were also subjected to X-ray diffraction studies for mineralogical determinations. Two types of mounts were made. An unoriented mount was made by packing the finely powdered rock into a glass holder. Oriented clay slides were made by settling a clay-water slurry containing approximately 2 μm fraction of the rock powder on a glass slide. The following diffractrographs were run on the oriented samples:

1. air-dry
2. ethylene glycoal saturated
3. heat treated at 450°C for 1 hour
4. heat treated at 600°C for 1 hour

The samples were X-rayed on a Phillip PW1050 at a goniometer speed of 1° per minute and a chart speed of 1 cm per minute, using filtered $Cu_{k\alpha}$ radiation, 1/4 degree entrance and exit slits and using a graphite monochrometer. Chlorite, illite, quartz, feldspar, biotite, calcite, kaolinite, and mixed-layered minerals were identified following the common schemes (Brown, 1961; Grim, 1968; Carroll, 1970).

A.4.2 Semi-quantitative Estimation of Minerals

The quantitative mineralogical study of mudrocks is notoriously difficult and has inherent problems due to varying factors such as crystallinity, particle orientation, chemical composition and grain size. Various methods using X-ray diffraction have been proposed but unanimity on the best method has still to be achieved (Weaver, 1958;

Biscaye, 1965; Norrish and Taylor, 1962; Scafe and Kunze, 1971). For the present work, a simplified method similar to the one adopted by Bjørlykke (1974) has been followed. The powdered sample was mixed with vaseline and run on a Sieman Type F X-ray diffraction, fitted with Omego Drive and a golden knife edge, with scan speed of 10 mm per minute and 1/2 degree entrance and exit slits, using filtered $Cu_{k\alpha}$ radiation and a graphite monochrometer. The advantage of mixing the powder with vaseline is that it avoids the preferred orientation of clay minerals, which could otherwise be overestimated. The peak areas of the minerals were used as a measure of their relative proportion in the rock. The characteristic peaks are : 7 Å (chlorite), 7.1 Å (kaolinite); 4.26 Å (quartz); 3.2 Å (feldspar) and 3.03 Å (calcite). The results are only a semi-quantitative estimation of the relative proportion of minerals present in the rock.

A.5 DETERMINATION OF QUARTZ BY INFRA-RED SPECTROSCOPY

Because of the fine-grained nature of the mudrocks, the quantitative determination of quartz using microscopes is not feasible. A chemical method is time consuming. For these reasons quartz estimation was done using an Infra-red spectroscope. Many authors have discussed the principles and procedures for the identification of minerals by Infra-red spectroscopy (Van der Marel and Beutelspacher, 1976; Larsen et al. 1972; Hlavay et al. 1978; Rosseaux 1978). The method adopted in the present work is as follows:

(1) 20 mg of the powdered sample (same as that used for XRF and XRD studies) was ground in a vibrating agate mill with 8 drops of water for 30 minutes.

(2) the ground sample was dried under a heat lamp. 0.5 mg of this was mixed with 1.0 g of oven dry reagent grade KBr and blended using a vibrating shaker for two minutes.

(3) pressed pills weighing 500 mg and 200 mg were obtained from this powder mixture by using a vacuum die.

(4) pressed pills were run on a Unicam SP1100 Infra-red spectrophotometer using the following conditions :

Scan speeds : normal

Programme : 1
Expansion : 1
Baseline : 0

For the quantitative estimation of quartz, the 798 cm^{-1} absorption peak was compared with the background at 860 cm^{-1}. The calibration curve was established using acid washed quartz as a standard.

A.6 GRAIN SIZE ANALYSIS

A.6.1 Graywackes

Grain size is an important attribute of clastic sedimentary rocks. Sieving is undoubtedly the best way of measuring the true grain size. However, in the case of well-indurated rocks, sieving techniques can not be used successfully and hence the direct measurement of grains in thin sections is the only viable alternative. However, the results obtained by the thin section study are not directly comparable to those of sieving. This subject has been discussed in great depth and various conversion equations have been proposed by a number of authors (e.g. Adams 1977; and Harrell and Erikson, 1979).

The thin sections of the graywackes used for petrological studies were also subjected to grain size determinations. The procedure followed is the slightly modified method of Harrell and Erikson (1979). The grain images were counted using Humphries semi-automatic eyepiece micrometer. The long dimension of about 200 grains in each thin section were measured and classified into $4\sqrt{2}$ classes by using this eyepiece and the attached counter. The size data were plotted as standard cumulative frequency curves on probability paper. The percentile values $\emptyset_5$, $\emptyset_{16}$, $\emptyset_{25}$, $\emptyset_{50}$, $\emptyset_{75}$, $\emptyset_{84}$ and $\emptyset_{95}$ for each sample were obtained from these curves. The percentile values thus obtained from the thin sections were converted to sieve equivalents following the equations given by Harrell and Erikson (1979). The general equation given by these authors is

$$Y \text{ (Sieve)} = a + b.X \text{ (thin section).}$$

where a and b are conversion constants.

The correlation coefficient (r) is greater than 0.900 for most percentile conversions (except that of $\emptyset_{95}$). Folk's (1974) Graphic Mean (Mz) and Inclusive Graphics Standard Deviation (S_I) were computed from these modified percentile values. To measure the accuracy of the procedure, grain size measurements were done following the procedure outlined above, on the grain mounts of various size fractions (obtained by sieving), of the recent sediments of the Angabunga River, Papua New Guinea. The values obtained for Graphic Mean and Inclusive Graphic Standard Deviation by this method are within ± 10% of the values obtained by sieving, thus attesting the valadity of the procedure adopted.

A.6.2 Mudrocks

The grain size determination of the mudrocks was comparitively harder to perform, due to their fine grain and indurated nature. The mean grain size for mudrocks was estimated from thin sections and hand specimens and is a measure of the coarseness of the rock. The standard deviation gives the textural maturity of the mudrocks and is expressed by the sorting index (after Picard, 1971) in this way :

$$S_m = \frac{\%\ \text{sand size detritus}}{\%\ \text{silt and clay fractions}}$$

The following three classes of textured maturity of mudrocks were recognised on this basis:

(1) Good sorting: more than 90% silt and clay fraction, S_m is < 0.1

(2) Fair sorting: between 75 and 90% of silt and clay fraction, S_m is between 0.1 and 0.3

(3) Poor sorting: less than 75% of silt and clay fraction, S_m is > 0.3

A.7 MODAL ANALYSIS

Considerable attention was given to the petrological determinations of graywackes. Modal analyses were performed on each thin section by counting between 300 and 400 points on each slide. The procedure adopted is slightly modified after Dickinson (1970a). Thin sections exhibiting the high influence of diagenetic and metamorphic effects were avoided. Thin sections were stained for K-feldspar and plagioclase following the technique of Norman (1974) and Wilson and Sedeora (1979). Various types of lithic grains were distinguished on the basis of textural and mineralogical characteristics. Only aphanitic polycrystalline grains were classified as lithic fragments and quartz/feldspar grains larger than 0.06 mm when occurring within lithic fragments were counted with the

Table A.2. Simplified facies classification scheme used in the present work (from Ingersoll, 1978b) and the arbitrary units (1 to 7) labelled for each facies.

Bouma sequence not applicable	Facies A:	Coarse-grained conglomerate and pebbly sandstone	1
	Facies B:	Medium- to coarse-grained massive sandstone	2
Bouma sequence applicable	Facies C:	Interbedded sandstone and mudstone, proximal turbidities	3
	Facies D:	Interbedded mudstone and sandstone, distal turbidities	4
	Facies E:	Interbedded sandstone and mudstone, overbank and interchannel deposits	5
Bouma sequence not applicable	Facies F:	Chaotic deposits, olistostromes	6
	Facies G:	Mudstone, pelagic and hemipelagic deposits	7

discrete quartz or feldspar component. Polycrystalline quartzose grains were counted separately. The polygenetic nature of matrix has been well described by Dickinson (1970a) and has also been recognized in the present work. An attempt was made to recognize the original nature of the squashed lithic fragments (pseudo-matrix) and these were counted with the appropriate grain type. All other types of interstitial material forming matrix were grouped together.

The range of variation in the mineral composition (and also in the geochemical characteristics) of each group is represented by the confidence limits on the mean and is calculated from the formula:

$$\pm L = SD.t/\sqrt{n}$$

where SD is standard deviation, n is the number of samples and t is the value obtained from statistical t-tables and depends on the confidence level selected (95% in the present work) and degrees of freedom (n-1).

A.8 FACIES ATTRIBUTES

The depositional facies and facies association studies were not done very extensively. However, each sampling locality was assigned to a facies, following Ingersoll's (1978b) classification. Arbitrary units were labelled 1 to 7 for each facies type (Table A.2) and each sample collected was assigned to one of these units. The data were used to infer the relationship between facies, texture, mineralogical and geochemical parameters.

APPENDIX B

LOCATION OF SAMPLES

Samples on which geochemical studies were done are stored in the collection of the ANU Department of Geology. These samples are listed below. The material stored is in the form of hand specimens, analysed powder of all samples, and thin sections of graywackes only. Most of the remaining samples will be retained by the author.

The lithology of the samples is indicated by G for graywackes and M for mudrocks. Sample localities are indicated by grid references (easting followed by northing). The map sheets are indicated by the following abbreviations (given as suffix to grid reference):

B	Bathurst	(topographic 1:100 000)
O	Orange	(topographic 1:100 000)
T	Tareela	(topographic 1:31680)
N	Nundle	(topographic 1:25000)
TM	Tamworth	(Geological 1:250 000)
M	Manilla	(Geological 1:250 000)
Mb	Melbourne	(Topographic 1:250 000)
Ms	Mossman	(Topographic 1:250 000)

Thesis No.	ANU Rock No.	Formation	Lithology	Location
TAMWORTH TROUGH				
MK11	43391	Lowana	G	386 514 T
MK12	43392	Lowana	G	387 516 T
MK13	43393	Lowana	G	387 516 T
MK14	43394	Noumea	G	361 241 M
MK15	43395	Noumea	G	361 241 M
MK16	43396	Noumea	G	363 240 M
MK17	43397	Noumea	G	363 240 M
MK22	43398	Yarrimi	G	398 152 TM
MK23	43399	Pyramid Hill Arenite	G	398 137 TM
MK24	43400	Pyramid Hill Arenite	G	399 135 TM
MK25	43401	Baldwin	G	221 179 N

Thesis No.	ANU Rock No.	Formation	Lithology	Location	
MK20	43402	Crow Mt. Creek Beds	G	371 236	M
MK21	43403	Crow Mt. Creek Beds	G	271 236	M
MK46	43404	Crow Mt. Creek Beds	G	271 236	M
MK18	43405	Noumea	M	363 240	M
MK34	43406	Lowana	M	387 516	T
MK35	43407	Noumea	M	361 241	M
MK36	43408	Noumea	M	361 241	M
MK38	43409	Noumea	M	361 241	M
MK41	43410	Pyramid Hill Arenite	M	399 135	T
MK43	43411	Baldwin	M	244 181	N
MK44	43412	Baldwin	M	224 181	N
MK45	43413	Goonoo Goonoo Mudstone	M	206 152	N
MK37	43414	Noumea	M	361 241	M
MK42	43415	Silver Gully	M	235 246	N
MK19	43416	Crow Mt. Creek Beds	M	363 240	M
MK39	43417	Crow Mt. Creek Beds	M	363 240	M
MK40	434418	Crow Mt. Creek Beds	M	363 240	M
HILL END TROUGH					
MK26	43419	Turondale	G	459 394	B
MK27	43420	Turondale	G	459 396	B
MK28	43421	Turondale	G	358 385	B
MK29	43421	Turondale	G	358 383	B
MK30	43423	Turondale	G	456 383	B
MK31	43424	Turondale	G	452 404	B
MK56	43425	Turondale	G	452 404	B
MK57	43426	Turondale	G	454 410	B
MK63	43427	Waterbeach	G	450 382	B
MK64	43428	Waterbeach	G	449 383	B
MK70	43429	Waterbeach	G	445 386	B
MK71	43430	Waterbeach	G	445 386	B
MK72	43431	Waterbeach	G	446 387	B
MK76	43432	Cunningham	G	403 454	B
MK60	43433	Cunningham	G	409 452	B
MK61	43434	Cunningham	G	409 452	B

Thesis No.	ANU Rock No.	Formation	Lithology	Location
MK59	43435	Merrions Tuff	G	413 372 B
MK65	43436	Merrions Tuff	G	418 376 B
MK67	43437	Merrions Tuff	G	419 376 B
MK75	43438	Merrions Tuff	G	420 370 B
MK74	43439	Merrions Tuff	G	420 370 B
MK2	43440	Chesleigh	G	480 369 B
MK4	43441	Chesleigh	G	475 370 B
MK47	43442	Chesleigh	G	470 375 B
MK49	43443	Chesleigh	G	477 377 B
MK50	43444	Chesleigh	G	472 377 B
MK3	43445	Chesleigh	G	252 410 0
MK7	43446	Chesleigh	G	252 425 0
MK8	43447	Chesleigh	G	259 406 0
MK1	43448	Cookman	G	469 382 B
MK5	43449	Cookman	G	470 385 B
MK6	43450	Cookman	G	475 396 B
MK53	43451	Cookman	G	474 395 B
MK54	43452	Cookman	G	472 400 B
MK9	43453	Cookman	G	262 392 0
MK10	43454	Cookman	G	262 392 0
MK77	43455	Cookman	G	262 392 0
MK32	43456	Turondale	M	459 394 B
MK33	43457	Turondale	M	459 385 B
MK58	43458	Turondale	M	452 404 B
MK73	43459	Waterbeach	M	445 386 B
MK62	43460	Cunningham	M	409 452 B
MK65	43461	Merrions Tuff	M	420 370 B
MK48	43462	Chesleigh	M	477 370 B
MK51	43463	Chesleigh	M	477 377 B
MK52	43464	Chesleigh	M	480 369 B
MK55	43465	Cookman	M	472 400 B
BENDIGO TROUGH	(Rock-stratigraphic names have not been defined)			
MK95	43466	Ordovician	G	251 803 Mb
MK96	43467	Ordovician	G	251 802 Mb
MK97	43468	Ordovician	G	251 802 Mb

Thesis No.	ANU Rock No.	Formation	Lithology	Location	
MK98	43469	Ordovician	G	252 799	Mb
MK99	43470	Ordovician	G	284 900	Mb
MK103	43471	Ordovician	G	253 799	Mb
MK104	43472	Ordovician	G	283 900	Mb
MK100	43473	Ordovician	M	302 867	Mb
MK101	43474	Ordovician	M	282 898	Mb
MK102	43475	Ordovician	M	283 899	Mb
HODGKINSON BASIN					
MK81	43476	Hodgkinson	G	269 923	Ms
MK82	43477	Hodgkinson	G	268 925	Ms
MK83	43478	Hodgkinson	G	268 925	Ms
MK84	43479	Hodgkinson	G	268 925	Ms
MK85	43480	Hodgkinson	G	285 864	Ms
MK86	43481	Hodgkinson	G	286 863	Ms
MK87	43482	Hodgkinson	G	286 862	Ms
MK88	43483	Hodgkinson	G	287 861	Ms
MK89	43484	Hodgkinson	G	288 860	Ms
MK90	43485	Hodgkinson	G	265 925	Ms
MK91	43486	Hodgkinson	G	265 925	Ms
MK93	43487	Hodgkinson	G	258 927	Ms
MK92	43488	Hodgkinson	M	254 956	Ms
MK94	43489	Hodgkinson	M	286 863	Ms

APPENDIX C
AN INTRODUCTION TO THE MULTIVARIATE STATISTICAL METHODS

Recent developments in analytical techniques, especially in geochemistry, have made it possible for researchers to accumulate a large amount of data. Proper representation, of the data involving many variables, is always a difficult task. Though bilinear and triangular plots are very useful in giving information, one is always uncertain which plot exhibits the best results. Multivariate met ods allow us to consider changes in several properties simultaneously and help in interpreting the data by condensing it into more meaningful form and by revealing relationships between variables or groups of variables which may not be apparent from graphical displays.

Multivariate techniques have been used in geology on various types of data e.g. chemical analysis, carbonate petrology, detrital mineralogy, paleontologic variables, stream suspended load and discharge and others. Davis (1973) and Le Maitre (1981) have reviewed the uses of multivariate analyses in geology. Multivariate methods are an extremely powerful tool because they allow us to manipulate more variables than one can judge at one time. However, most of these methods have complicated theoretical structures and operational methodology. The choice of the method to be used is also important. The method of multivariate statistical analysis depends on the type of investigation pursued.

Multivariate statistical analyses were mainly carried out in the present investigation to supplement the geological inferences. The main purposes are to confirm the differentiation and grouping of various suites established on the basis of geological knowledge, to understand the factors which control the variation in the data, the relation between various variables, and to identify the discriminant variables. Multivariate methods employed were : principal component, discriminant function and cluster analyses. A brief introduction to each technique is given below.

C.1. PRINCIPAL COMPONENT ANALYSIS

The technique of principal component analysis was developed by psychologists and has now been extensively used in the natural and social sciences. The technique has been described in detail by many authors (e.g. Harman, 1967; Cooley and Lohnes, 1971). Application of this technique in geology is reviewed by Harbaugh and Merriam (1968), Joreskog et al. (1976) and Le Maitre (1981).

The technique is designated to reduce the complexity of a set of data by reducing the number of "variables" which need to be considered. The principal component analysis takes into account the correlation between two or more of the originally measured variables to construct a smaller number of new "variables" known as "factors", which are combinations of the originally measured variables. The factors are most commonly thought to represent the underlying causative variations which produce the observed variables. However, the interpretation is not implicit in the analysis, rather it is imposed by the investigation. Each factor can then be interpreted in terms of a geological process that is responsible for the variation and co-variation in the data.

In this analysis, the correlation coefficient matrix between various variables is calculated from the raw data. N vectors of unit length are plotted in n dimensional space, where each vector represents a variable and N is the number of variables. Although N vectors are free to occupy N number of dimensions, they may occupy fewer dimensions. Principal component analysis heavily depends on these fewer dimensions if they exist and brings them out. Orthogonal axes are placed within the n-dimensional cluster of vectors and are used as a reference system for describing the vector orientations. Using the principal component methods, the reference axes are placed so that the sum of the squares of the vector projections on Axis A is maximum. Axis B is placed perpendicular to Axis A, but oriented so that the vector projections are at a maximum, and so on until there are N axes. The result of this process is a factor matrix which holds the co-ordinates of the vectors.

The principal component axes are rotated so that the vectors are closely associated with new reference axes. This can be achieved by performing the varimax method of rotation. After rotating the axes, a new set of vector co-ordinates, the rotated factor matrix, is then obtained. This matrix has axes as its columns and variables as its rows. The values within the matrix indicate the contribution (or loading) which that variable makes to the axes. Thus each axis is a linear combination of the variables. Absolute values of these loadings close to unity indicate a large contribution, and the sign indicates the type of contribution. Thus for each case on each axis, obtain

$$F = a_1x \pm a_2x \pm \ldots\ldots\ldots\ldots\ldots \pm a_ix$$

where a is the factor loading for variable i and x is the observed standardised value for that case. F is termed the factor score for that case on that particular axis.

The relative importance of each factor is expressed by two measures, each of which is related to the proportion of the original data variation attributable to the factors. The eigenvalue is the squares of the factor length (in a geometric interpretation) and represents the proportion of the total original data variance attributable to the factor corresponding to that eigenvalue. The other measures to be used are called communalities which are the sums of the squares of the factor loadings within each factor. As the number of factors is reduced, the communalities decrease, providing an index of the efficiency of that particular analysis.

Although the number of geologically significant factors will be less than the number of original measured variables, the actual choice of the number of factors is not clearly defined. Three criteria are in common use in geology (Davies, 1973):

(1) Take the number of factors which together explain 80-90% of the total variance.

(2) Take the point at which the graph of eigenvalue vs axis number flattens out as the diagnostic number of factors.

(3) Choose those factors which account for at least as much of the total data variation as was accounted for by one of the original (standardized) variables. This is done by examining the magnitude of the eigenvalues and only retaining those factors which have eigenvalues greater than unity.

In this study, criterion 3 was used and it was found that when criterion 3 is fulfilled, criterion 2 is also satisfied. The amount of variance of the original data set explained was mostly ∿ 80%. To explain the other 20% of the original variance often required an unreasonable number of added factors with eigenvalues far less than one and had uninterpretable geological meaning.

Principal component analyses are of two types : R-mode which determines the correlation between variables (elements) and Q-mode which determines the association between individuals (cases). In the present study, both types of principal component analyses were performed, the R-mode in order to group together related variables into smaller number factors and the Q-mode in order to determine the association of samples. The program "FACTOR" in the SPSS package (Nie et al. 1975) available on the UNIVAC 1100 computer on campus at the ANU was used. Factor scores for each samples produced by R-mode analysis during the run were plotted to determine the association between the samples.

There are two methods of calculating the eigenvalue and eigenvector which can give entirely different results (Le Maitre 1981): variance-covariance (or dispersion matrix) and correlation matrix. The method of dispersion matrix is advantageous when variables are measured in the same units e.g. all wt % or all ppm. In the correlation matrix method, the raw data are scaled so that every variable has zero mean and unit variance and then uses the dispersion method. The method of correlation matrix is advantageous only when variables are measured in different units e.g. wt % and ppm. This method is adopted for the present work since the variables are measured in different units.

However, this method has one main drawback. Principal component analysis depends heavily on correlation coefficients, which compares the variation of one element to another. Data which always sums to a constant, e.g., 100% in the many cases, has a strong effect on this. This is known as the closure problem and can be explained if one considers a rock composed only of quartz and feldspar grains. The two components have a negative correlation, caused by the nature of the data which is expressed on an equal volume basis. The effect of the closed array would be less pronounced with the introduction of more variables. This aspect has been discussed in detail by Chayes and Kruskal (1966) and Miesch (1976) without achieving a solution. It has been suggested in such cases to take ratios of the variables. Ratios were taken in the present case whenever possible, however, these yield almost similar results to those obtained from the raw data. The closure problem is one which cannot be avoided in the present set of data and thus compels us to adopt a very cautious approach in interpreting the statistical results.

C.2. DISCRIMINANT FUNCTION ANALYSIS

Discriminant function analysis is a very widely used multivariate technique in geology. It is a powerful tool in classifying individual cases into pre-defined groups on the basis of multiple variables. The discriminant function analysis provides a multivariate test of the difference between two or more groups. In addition, it permits the testing of different linear combinations of the discriminatory elements so that the best linear combinations can be identified and subsequently used in classifying unknown samples.

Klovan and Billings (1967) have suggested that the discriminant function analysis may be used in the following types of investigations:

1. What is the best way to discriminate between already established groups?
2. What variables are the most important in making this discrimination?
3. Given an "unknown", to which group does it most probably belong?

The mathematical treatment of the discriminant analysis has been given in detail by several authors (e.g. Cacoullos, 1973; Cooley and Lohnes, 1971; Tatsuoka, 1971). There are also several examples of the application of this technique in solving geological problems (e.g. Middleton, 1962; Griffiths, 1966; Davies and Ethridge, 1975; Divi et al. 1980; Le Maitre, 1981).

The objective in this analysis is to get a discriminant function of the form

$$di = a_i x_1 + b_i x_2 + c_i x_3 + \ldots\ldots\ldots\ldots + p_i x_p$$

such that the pre-defined populations have maximum separation along the function. In the equation given above, x_1, x_2, $x_3 \ldots x_p$ are the p discriminating variables; a_i, b_i, c_i, $\ldots\ldots p_i$ are the discriminating function co-efficients; and d_i is the discriminant score. The standardized discriminating co-efficients associated with variables give the relative importance of the variables in separating the groups along the discriminant function.

The number of discriminant functions to be obtained is one less than either the number of groups or the number of variables, whichever is less. For each discrimination function, Wilks' lambda indicates the statistical significance, the canonical correlation coefficient signifies the strength of the function in discriminating and the eigenvalue indicates the percentage of variation explained by the function in the original data (Nie et al. 1975).

The disadvantage of this technique is that for the "unknown" to be classified, it has to belong to one of the pre-defined groups. Inspite of this, it is a valuable technique in comparing several groups with each other. The discriminatant functions can be interpreted in the same way as factor scores in the principal component analysis. Discriminant functions provide axes along which discriminating scores can be plotted for each case, similar to the Q-mode factor analysis technique. The computer program DISCRIMINANT of the SPSS system (Nie et al. 1975) as adopted on UNIVAC 1100 at the ANU campus was used to carry out the analysis.

C.3. CLUSTER ANALYSIS

Cluster analysis is a common multivariate technique and can be used to decipher the natural grouping in the data. The advantage of this method over the principal component and discriminant function analysis is that prior knowledge of the group membership of cases is not required. However, the disadvantage is that new objects can not be introduced into the scheme without repeating the analysis.

Cluster analysis is a straight-forward, logical, pair-by-pair comparison between samples, variables or objects. In this analysis, samples are first compared for similarity and are then merged into a number of distinct groups in which the samples are more similar to each other. Then the most similar groups are merged sequentially until they form one group. The result of the cluster analysis can be presented in an easily understood two dimensional hierarchical diagram (dendrogram) on which the natural breaks between the groups are clear. The investigator can also pick groups at any desired level of similarity or dissimilarity.

The computer package CLUSTAN (Wishart, 1970) has been used for performing the cluster analysis. Several methods are available in this package to perform this analysis. The choice of a suitable distance measure is always a problem in cluster analysis. Several workers have used a distance function as a measure of similarity. The formula between two objects in a multidimensional hyperspace of M variables is (after Parks, 1966):

$$D_{1,2} = \sqrt{[\sum_{i=1}^{M} (X_{i1} - X_{i2})^2 / M]}$$

where X equals the normalised (transformed to range from 0.0 to 1.0) values of the variables. The actual distance between the samples would be a function of the number of variables used, so that the sum of the squared differences is divided by the number of variables used. This gives the mean squared difference, which is really the variance of the differences between the measurements of the two samples. The simple distance function is the square root of this variance, and is thus the standard deviation of the difference. This is also known as the 'elucidian squared distance'.

Ferguson and Winer (1980) observed that the "Canberra Metric" method developed by Lance and Williams (1967) has advantages over other methods, especially in a data set where closure problems are prominent. They also pointed out that although "Canberra Metric" is listed as one of the options available on the CLUSTAN package, the metric available is not based on a sound mathematical formula and gives erroneous results. To overcome this, P. Winer (in Ferguson and Winer, 1980) modified the computer package to accommodate the true "Canberra Metric". This subroutine was borrowed from Winer, however, the program did not work successfully. In the new version of CLUSTAN, which has just been released the "Canberra Metric" method has been completely taken out of the package.

The "elucidian squared distance" method was followed in the present study. There are various ways which can be used to link clusters. The most common are nearest neighbour (single linkage), furthest neighbour (complete linkage) and group average (average linkage). There is another method of linking the various groups on the CLUSTAN package, which is called Ward's method or 'error sum method'. According to Wishart (1970) this is possibly the best of the hierarchical options. The error sum of squares is defined as the sum of the distances from each individual to the centroid of its parent clusters. Ward proposed this hierarchical method in which the clusters are fused so that there is the least increase in the error sum. Wishart (1970) found this method works with the distance co-efficient. In the present study, Ward's method of linking is adopted with elucidation squared distance as the clustering method.

APPENDIX D
PETROGRAPHY OF GRAYWACKES

D.1 TAMWORTH TROUGH

The Tamworth Trough graywackes are dominantly composed of feldspar or lithic grains, with no appreciable change in their mineralogy throughout the sequence. The only exception is the Crow Mountain Creek graywackes, which are significantly more quartzose than most other graywackes of the sequence and hence have been described separately.

D.1.1 Typical Graywackes

The graywackes are massive, well indurated, generally greyish-green to dark green litharenites (Table D.1). Feldsarenites form a minor component of the sequence (Table D.1, Sample Nos. MK14, MK15). Grain size varies greatly but medium grained graywackes predominate.

TEXTURE

The detrital grains are dominantly composed of feldspar and volcanic rock fragments, with minor pyroxene and quartz grains (Figure D.1a,b). The graywackes exhibit moderate to poor sorting. The feldspar grains are angular to subangular, and elongate in shape whereas the lithic grains are generally subrounded and equant. Grains are seen floating in a chloritic groundmass and calcitic cement; however tangential to flat contacts between detrital grains are also observed.

MINERALOGY

Quartz: Quartz is minor, averaging around 5% in the whole sequence and most grains are monocrystalline with uniform sharp extinction. Fractures filled with green chloritic material are common. Grains with inclusions of devitrified glass now represented by microcrystalline quartz are also observed. Some quartz grains are hexagonal in form. Polycrystalline quartzose grains are few, mostly rounded and of chert. Grains of micrographic granite are very rare.

Feldspar: Feldspar is predominantly plagioclase with a negligible proportion of K-feldspar. Plagioclase grains which occur both as discrete detrital grains and as phenocrysts in volcanic rock fragments, have similar shapes. The grains are angular to subangular (Figure

Table D.1 Modal Composition of Graywackes from the Tamworth Trough

Serial No.*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sample No.	MK11	MK12	MK13	MK14	MK15	MK16	MK17	MK22	MK23	MK24	MK25	MK20	MK21	MK46	T24
Quartz															
Monocrystalline	3.5	4.4	2.5	1.7	10.7	1.8	5.0	3.0	5.6	3.6	2.1	30.7	1.3	8.6	18.4
Polycrystalline	1.3	1.9	0.9	0.6	0.9	0.2	1.5	0.0	1.3	1.0	0.4	1.5	4.4	2.7	0.2
Plagioclase	21.0	20.8	21.1	68.8	60.5	3.8	12.1	13.1	26.0	21.9	21.9	12.2	54.7	48.1	36.2
K-feldspar	0.7	0.4	0.9	0.6	0.6	1.7	1.0	0.1	0.2	0.4	0.3	0.0	1.2	0.7	0.5
Vol. Rock Frag.	43.1	36.7	17.6	5.2	3.4	63.9	31.2	33.8	32.6	22.3	38.5	2.5	12.1	4.0	1.7
Sed. Rock Frag.	0.6	1.2	1.9	1.0	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0
Biotite	-	-	-	-	-	-	-	-	-	-	-	4.8	3.0	6.6	4.2
Chlorite	4.6	2.6	1.3	8.8	1.1	0.4	1.5	0.3	1.3	0.5	0.9	0.0	0.2	5.0	0.2
Calcite	8.9	0.9	5.5	1.5	2.1	5.5	14.6	46.3	8.2	12.7	3.4	0.6	0.0	0.0	0.2
Pyroxene	2.8	2.1	1.5	0.6	0.5	1.3	0.4	0.7	1.3	4.1	2.6	0.0	0.7	0.0	0.0
Epidote	1.9	1.6	0.4	1.3	0.7	1.8	3.8	0.7	1.7	1.5	13.2	1.5	2.1	3.7	1.6
Opaque Minerals	5.2	4.4	4.2	1.9	1.1	12.0#	0.8	1.7	1.3	1.5	1.7	1.9	1.0	1.7	1.6
Accessories	0.7	0.9	0.6	1.2	2.1	1.3	3.8	0.7	0.9	3.0	3.4	0.4	0.7	0.2	0.2
Matrix	5.2	22.1	41.4	6.5	16.3	6.4	22.7	0.0	19.7	27.4	11.5	43.5	19.1	17.9	35.1
Mz (ø)	1.54	1.68	3.13	1.86	1.33	0.53	2.88	1.27	1.92	3.07	1.34	2.73	1.59	1.10	2.90
S_I (ø)	1.04	0.78	0.60	0.83	0.95	0.95	0.39	0.71	1.10	0.82	0.82	0.70	0.90	0.59	0.65

* Serial No. 1 to 11 : Typical Tamworth Trough Graywackes
12 to 15 : Crow Mountain Creek Beds

\# Includes 6% Ferruginous cement

FIGURE D.1

Representative Graywackes of the Tamworth Trough

(a) Feldspar, pyroxene (near the bottom right hand corner) and microlitic volcanic rock fragments in sample MK11.

(b) Abundant feldspar grains in sample MK14. Note the angular nature of the grains.

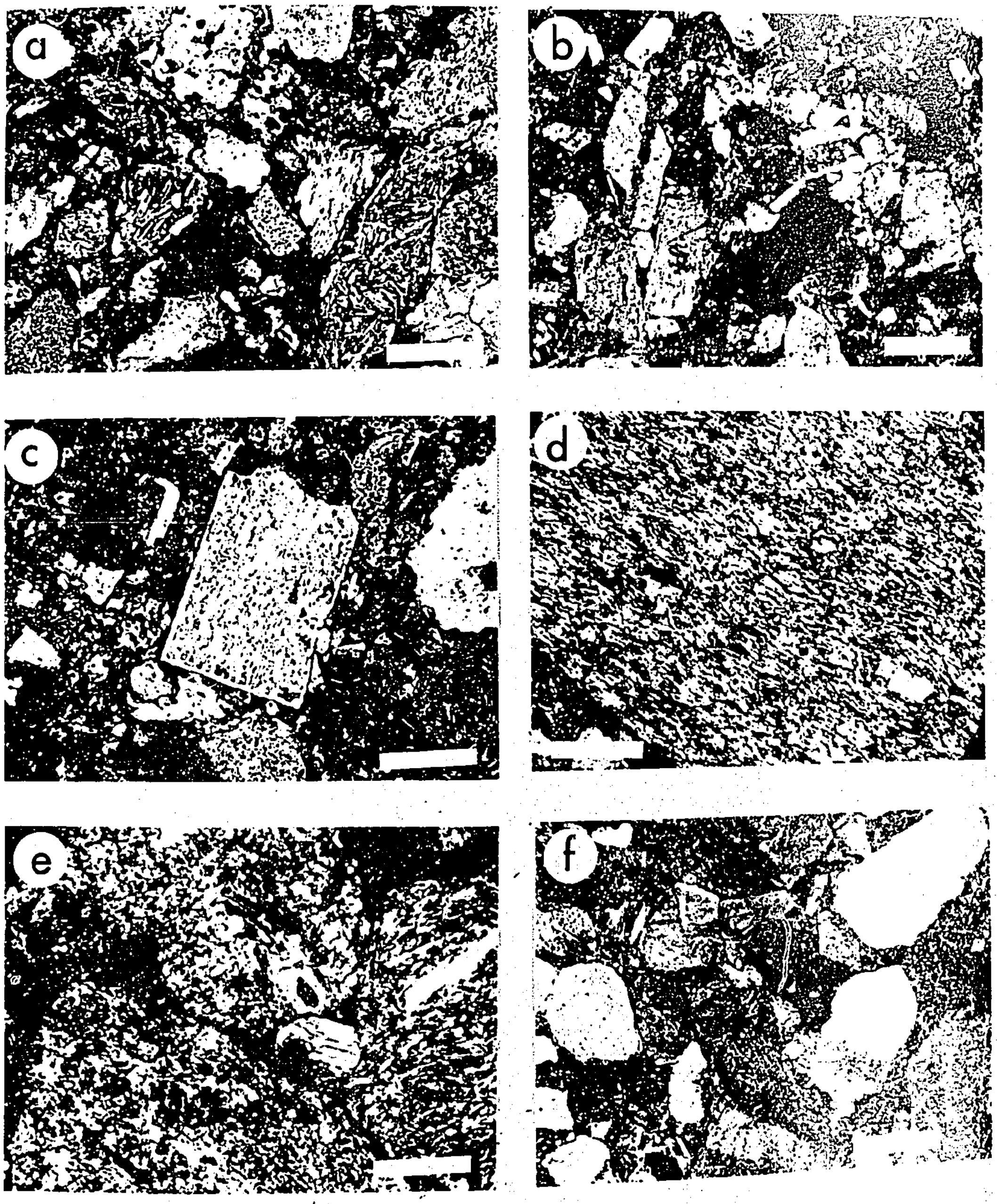
(c) Angular plagioclase and volcanic rock fragments in sample MK23. Note the inclusions in the plagioclase.

(d) Microlitic volcanic rock fragment in sample MK14.

(e) Volcanic rock fragments and pyroxene (between the three lithic grains) in sample MK14.

(f) Common quartz and abundant feldspar grains in sample MK46 of the Crow Mountain Creek Beds.

The scale bar in (a) to (e) = 0.5 mm.


a
b
c
d
e
f

D.1b.c). Most plagioclase grains are now converted to albite (n_β = 1.533 $\pm$ 0.002; $An_{0.5}$). Inclusions of prehnite, epidote, pumpellyite, calcite and apatite are common. A few grains of Ca-plagioclase, not altered to albite exhibit sharp multiple twinning. Rare orthoclase grains are heavily clouded and sericitised.

Rock Fragments: Lithic grains form the most important constituent of the rock and are dominantly volcanic. These grains usually contain plagioclase and less frequently pyroxene phenocrysts set in a groundmass consisting mainly of chlorite and epidote. The phenocysts are commonly altered and replaced in the same way as discrete grains. Rock fragments in which lath shaped plagioclase crystals form a trachytic texture are the most common (Figure D.1d). Other common textures are hyalopilitic, pilotaxitic and vitric, all included here under microlitic type (Figure D.1a,b,c,e). Grains having porphyritic texture are generally uncommon. Sedimentary rock fragments are rare and generally squashed and deformed.

Pyroxene: Pyroxene grains generally form between 1 and 2% of the whole rock. Chappell (1968) has noted up to 13% of pyroxene in graywackes of the Baldwin Formation. These occur both as free grains (Figure D.1e) and as phenocrysts in volcanic fragments and are generally subangular to subrounded, colourless, light brown or pale green. Some show simple twinning. Refractive index and 2V determinations suggest that these are augite in composition. The grains show variation from completely fresh to exceedingly altered.

Chlorite: Chlorite is seen as replacements of detrital grains, as part of matrix, or as groundmass in the volcanic rock fragments. It is generally colourless to pale green and is present in small patches. Unoriented microcrystalline patches of chlorite, probably formed by the devitrification of volcanic glass, are common.

Epidote: This is a very common diagenetic mineral and is seen in almost all the thin sections examined. It is generally dirty brown and greenish and occurs with the groundmass as well as replacing detrital grains.

Calcite: Calcite is a common mineral but varies in abundance, commonly it occurs as the replacement mineral of plagioclase grains. Graywackes of the Yarrimie Formation from the Tamworth Municipal Quarry contain up to 46% of calcite, occurring as cement.

Accessories: Diagenetic prehnite and pumpellyite are observed in almost all thin sections. Prehnite is an alteration product in both detrital grains and groundmass. Pumpellyite generally occurs in very small amounts as small irregular sheaf-like aggregates in detrital grains and groundmass. It is strongly pleochroic from colourless to pale yellow and green. Grains of apatite and sphene also occur as accessory minerals.

Opaque Minerals: Magnetite, ilmenite and titano-magnetite constitute the opaque minerals and generally form between 2 and 4% of the whole rock. The minerals vary from unaltered to completely altered. Alteration to "leucoxene" is very common. In some grains, lamallae of "leucoxene" are seen in otherwise unaltered opaque minerals.

Matrix: Matrix shows a large variation in its abundance and mainly consists of chlorite and epidote with some accessory minerals. Matrix is polygenetic but various types are difficult to distinguish due to compaction.

D.1.2 Crow Mountain Creek Beds

Crow Mountain Creek graywackes differ significantly from "typical" graywackes of the Tamworth Trough. The major differences in mineralogical characteristics are highlighted below.

The Crow Mountain Creek graywackes are more quartzose, containing common quartz and plagioclase grains and subordinate volcanic rock fragments (Figure D.1,f). Quartzose grains make up from 4 to 31% of the rock (Table D.1). Monocrystalline grains generally predominate and commonly have embayments filled with chlorite. Polycrystalline quartzose grains are few, however, sample MK21 is conspicuous due to the dominance of polycrystalline quartz over the monocrystalline type (Table D.1). Volcanic rock fragments are both microlitic and felsitic types and are considerably less abundant than in the typical graywackes of the Tamworth Trough. A large part of lithic grains are squashed, to yield abundant matrix which is marked by the deformed shape of the pasty material and shows a remarkable resemblance to the scruffy groundmass of the volcanic fragments. Prehnite and pumpellyite are almost completely absent but metamorphic biotite is very common. This is probably due to the deformation and tectonism suffered by these rocks due to their close proximity to the Peel Fault system and the associated granitic intrusion.

D.2 HILL END TROUGH

The sedimentary sequence of the Hill End Trough contains graywackes of various compositional types. On the basis of composition and stratigraphic occurrences, the graywackes representing the various formations can be grouped into the following three classes:

(1) Turondale, Waterbeach, Merrions Tuff and Cunningham Formations

(2) Chesleigh Formation

(3) Cookman Formation

D.2.1 Turondale, Waterbeach, Merrions Tuff and Cunningham Formations

Graywackes of this group are both pyroclastic and epiclastic in nature. The pyroclastic beds are coarse-grained, massive and thick and contain abundant felsic volcanic material (Cas, 1977, 1978). In the present work, only epiclastic sediments were selected for petrological and geochemical analyses, though even these beds contain some pyroclastic material.

TEXTURE

The graywackes contain quartz, feldspar and rock fragments, disseminated in a chloritic groundmass (Figure D.2a.b). Sorting is poor to moderate due to large variations in the detrital grain sizes. Quartz grains are angular to subrounded; feldspar grains are mainly tabular and angular; and lithic grains are subrounded to rounded and equant in shape. The original grain fabric and shapes are often distorted due to deformation and metamorphism. Grains are floating but plane, concavo-convex and tangential contacts are also common.

MINERALOGY

Quartz: It is present in varied proportions, forming between 8 and 50% of the whole rock (Table D.2). Quartz is dominantly monocrystalline and of volcanic type, showing definite hexagonal and bipyramidal shapes, with embayments filled with phyllosilicates (Figure D.2b,c). However, "common" quartz having undulose extinction and inclusions of apatite and zircon are commonly present. Polycrystalline quartzose grains are not very abundant and are fine sand to silt sized chert grains made up of a mosaic of microquartz with calcite specks.

Table D. 2 Modal Composition of Graywackes from the Hill End Trough

Serial No.*	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample No.	MK26	MK27	MK28	MK29	MK30	MK31	MK56	MK57	MK63	MK64	MK70	MK71	MK72	MK76	MK60	MK61	MK59	MK66	MK67	MK75	MK74
Quartz																					
Monocrystalline	12.5	29.7	26.7	38.9	36.7	29.8	28.8	8.4	35.9	15.0	21.7	25.3	23.9	46.7	41.6	35.7	23.1	36.6	32.8	30.0	50.9
Polycrystalline	1.0	1.8	4.0	1.1	2.2	0.6	1.4	0.0	1.3	0.7	0.0	0.0	0.0	2.1	0.8	0.5	0.0	0.7	1.4	0.6	0.2
Plagioclase	16.9	7.6	14.3	26.1	20.2	23.5	15.2	9.4	3.4	11.6	12.2	4.3	3.8	5.2	13.9	8.0	8.3	5.4	6.1	9.8	5.1
K-feldspar	0.5	0.2	0.0	0.3	0.5	2.2	2.1	0.4	0.6	0.9	0.2	0.6	0.4	0.4	0.9	0.3	4.1	0.0	0.2	2.0	0.2
Vol. Rock Frag.	22.4	16.9	10.7	0.7	0.8	2.1	9.5	19.2	13.9	16.5	25.9	16.2	6.9	5.1	11.5	16.5	26.5	11.7	25.9	27.8	12.9
Sed. Rock Frag.	0.4	0.7	7.1	0.0	0.0	0.0	1.7	36.6	10.3	11.3	2.2	6.2	3.2	13.1	2.1	11.5	9.2	9.5	6.5	3.6	3.5
Chlorite	4.4	2.4	0.0	4.9	8.8	4.3	4.0	0.0	0.0	2.5	0.0	0.0	0.0	0.5	2.1	0.0	0.0	1.6	0.9	2.6	0.4
Muscovite	0.4	1.5	0.8	0.8	2.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0	0.0	0.0	0.7	0.9	0.0	0.4
Biotite	0.0	0.0	1.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	2.1	0.0	2.7	0.0	0.0	0.0	0.0
Calcite	1.0	0.0	0.0	0.0	0.0	1.6	0.9	5.1	0.6	21.6	23.4	11.7	8.5	0.7	0.0	9.9	1.0	0.4	0.5	1.4	7.8
Epidote	3.3	2.6	3.6	2.3	19.9	19.3	9.5	2.5	1.7	4.3	4.9	10.1	8.0	0.7	4.0	3.2	5.5	11.6	6.5	8.0	3.9
Accessories	0.8	0.9	0.6	3.4	0.7	0.8	0.9	1.2	0.8	0.7	0.5	1.0	1.1	0.5	0.6	1.3	1.2	1.4	1.6	1.0	2.2
Opaque Minerals	1.5	0.9	1.0	1.9	2.0	1.2	0.3	4.5	3.2	1.8	1.5	2.6	1.3	1.2	0.4	0.4	0.2	1.1	1.4	1.2	2.9
Matrix	35.1	34.8	29.6	19.6	34.6	14.2	25.6	12.7	28.3	13.1	7.8	22.1	43.0	22.9	20.2	12.6	13.3	19.4	15.0	12.0	9.6
Mz (ø)	1.11	2.09	2.15	1.47	1.14	1.30	1.29	2.94	3.68	1.62	3.54	3.58	3.66	1.65	2.97	2.02	1.88	3.28	2.36	2.89	3.59
S_I (ø)	0.91	0.80	0.75	0.82	0.94	0.79	0.90	0.54	0.39	0.79	0.81	0.40	0.35	0.85	0.41	0.77	0.74	0.19	0.89	0.75	0.40

* Serial Nos. 1 to 8 : Turondale Formation
9 to 13 : Waterbeach Formation
14 to 16 : Cunningham Formation
17 to 21 : Merrions Tuff

FIGURE D.2

Representative Graywackes of the Hill End Suite

(a) Abundant felsitic volcanic fragments common quartz and feldspar in sample MK26.

(b) Volcanic quartz, (upper right hand side), feldspar, abundant sedimentary and volcanic rock fragments in sample MK57.

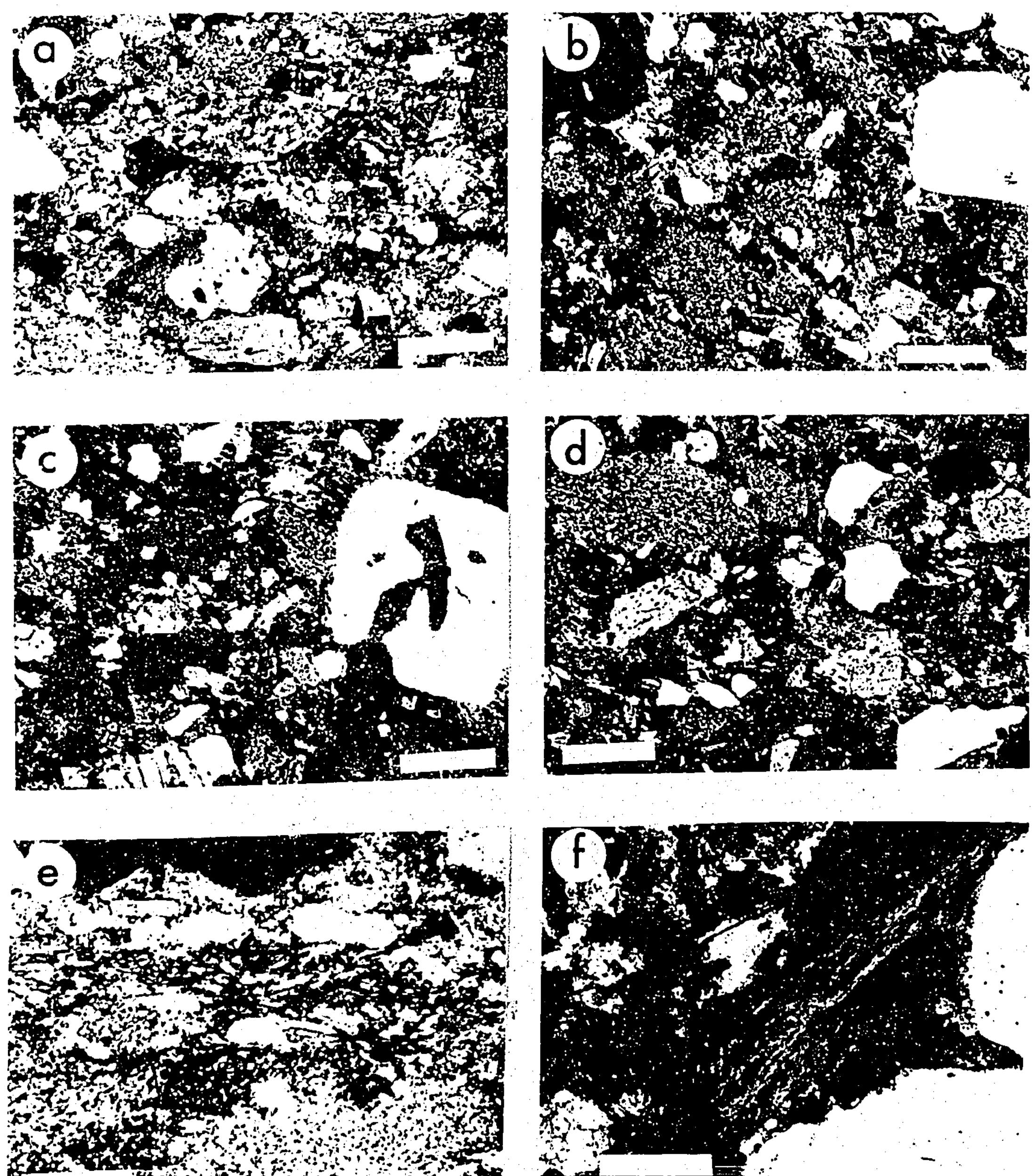
(c) Volcanic quartz (right side) having embayments filled with phyllosilicates; feldspar and lithic grains in sample MK70.

(d) Quartz, feldspar and lithic grains in sample MK64. Note the bleb inclusions of chlorite in the feldspar grains.

(e) Diagenetically altered volcanic rock fragment in sample MK59.

(f) Devitrified chlorite in sample MK30.

The scale bar in (a) to (e) = 0.5 mm and in (f) = 0.2 mm.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Feldspar: Feldspar is common in these graywackes and mainly consists of plagioclase. They are dominant in graywackes of the Turondale Formation. Refractive index determinations show that the plagioclase is now of albitic composition. Grains exhibit clouding to various degrees. Twin lamellae are normally diffused but occassionally sharp (Figure D.2c). Bleb inclusions of low birefringent homogeneous chlorite are common (Figure D.2d). Similar blebs are also seen in vitriclasts and are divitrified and chloritised glass. Common inclusions of epidote, calcite and chlorite in plagioclase suggest that the plagioclase was more calcic originally. K-feldspar grains are not very common, usually have a cloudy appearance and are replaced by phyllosilicates, epidote and sometimes albite.

Rock Fragments: Volcanic and argillaceous lithic grains are present in various proportions and are similar to megaclasts of conglomerates. Felsitic volcanic fragments are the most common (Figure D.2a). In these fragments, phenocrysts mainly of plagioclase and quartz occur in a groundmass made up of a continuous homogeneous fibrous mat of chlorite. Much of this groundmass was originally glassy material which is now devitrified and chloritised and differs from the clastic, ragged and platy matrix of the graywackes. Volcanic grains exhibiting holocrystalline, microlitic and pilotaxitic textures are also present. The modification of volcanic rock fragments due to diagenesis and metamorphism is common, especially in the higher grade (Figure D.2e). Argillaceous rock fragments dominate in some samples (Figure D.2b), they are sand sized, rounded to well-rounded and are made up of phyllosilicates with minor fine-grained quartz. Often they are squeezed between the competent grains.

Chlorite: Devitrified chlorite forming pseudomorph shards occur as angular, cuspate and vesicular fragments (Figure D.2f), now extensively replaced by aggregates of fine granular dirty epidote. Minor chlorite also occurs as the inclusions in plagioclase grains.

Mica: Muscovite is minor and occurs in the form of small flakes with the matrix. In the higher zone of metamorphism, biotite is commonly seen as associated with matrix and replacing detrital grains.

Calcite. Calcite occurs as part of the groundmass and as inclusions in plagioclase and volcanic rock fragments. Most of it formed due to the release of calcium during albitisation.

Epidote: Epidote is ubiquitous in these graywackes and occurs as dirty aggregates of granules forming part of the matrix and inclusions in plagioclase and volcanic rock fragments. This suggests the diagenetic origin of epidote.

Opaque Minerals: Magnetite and ilmenite are the common opaque minerals and their alteration yields common "leucoxene" and minor ferruginous cement.

Accessories: Small and well rounded detrital grains of tourmaline, zircon and apatite constitute the accessory minerals, which form less than 1% of the whole rock. Occassional small, green and highly pleochroic horneblende grains are also present in the Turondale graywackes.

Matrix: Matrix forms a prominent component of these graywackes and is highly recrystallised. In the lower zone of metamorphism, it is mainly composed of chlorite, mica and epidote whereas in the higher zone, biotite is formed. Matrix is polygenetic but most of it is probably epimatrix. However, 'pseudo-matrix' formed due to the squashing of lithic grains, is also common.

D.2.2 Chesleigh Formation

Considerable mineralogical variation was noted in graywackes of this stratigraphic unit (Table D.3). Graywackes of the western section (near the Hill End township) contain common feldspar and volcanic rock fragments and in general are similar to other graywackes of the Hill End trough described in the previous section. Graywackes of the eastern section (Sofala region) are more quartzose and less feldspathic. The proportion of volcanic rock fragments varies in the graywackes but they are conspicuous by their presence even in quartzose graywackes. The petrographic description of the Chesleigh Formation graywackes is more or less similar to the one given for other graywackes in section D.2.1 and hence only important features are given below.

Monocrystalline quartz with slight to strong undulose extinction and containing inclusions of apatite and zircon, form the dominant detrital grains (Figure D.3b). However, some quartz grains have rounded embayments filled with phyllosilicates, indicating their derivation from volcanic sources. Polycrystalline quartzose grains made up of chert are common. Plagioclase constitute the major proportion of feldspar grains and are both twinned and untwinned (Figure D.3a). Untwinned grains

Table D.3 Modal Composition of Graywackes of the Chesleigh Formation, Hill End Trough

Serial No.*	1	2	3	4	5	6	7	8
Sample No.	MK2	MK4	MK47	MK49	MK50	MK3	MK7	MK8
Quartz								
Monocrystalline	43.3	41.6	38.2	24.5	36.6	35.7	23.7	65.1
Polycrystalline	1.8	10.2	1.6	6.4	4.5	2.2	12.1	5.8
Plagioclase	2.0	0.8	1.4	15.3	2.5	10.2	12.8	6.4
K-feldspar	0.4	0.0	1.0	2.5	0.2	0.4	0.6	0.7
Vol. Rock Frag.	3.0	25.0	8.0	7.8	2.7	1.6	0.4	4.7
Sed. Rock Frag.	30.8	1.2	1.2	1.1	18.7	1.0	5.5	2.2
Chlorite	0.0	0.0	0.0	3.6	0.0	0.0	0.0	0.0
Muscovite	0.0	0.0	0.0	1.1	0.0	0.0	3.7	0.0
Biotite	0.0	0.0	0.0	0.0	0.0	8.8	12.8	5.1
Calcite	0.0	0.0	3.6	0.4	0.0	1.2	5.1	4.7
Epidote	0.0	0.0	1.6	21.6	0.0	34.1	0.9	3.4
Accessories	1.1	1.2	0.0	0.0	0.8	0.4	0.4	0.0
Opaque Minerals	0.9	1.2	2.8	0.7	0.4	0.0	3.7	0.4
Matrix	16.8	19.0	40.6	14.9	33.7	4.5	18.3	1.6
Mz (ø)	2.44	2.23	3.50	2.51	2.81	2.27	2.08	1.78
S_I (ø)	0.77	0.66	4.68	0.75	0.37	0.85	0.80	0.81

* Serial Nos. 1 to 5 : Sofala section
6 to 8 : Hill End section

FIGURE D.3

Representative Graywackes of the Chesleigh and Cookman Formations

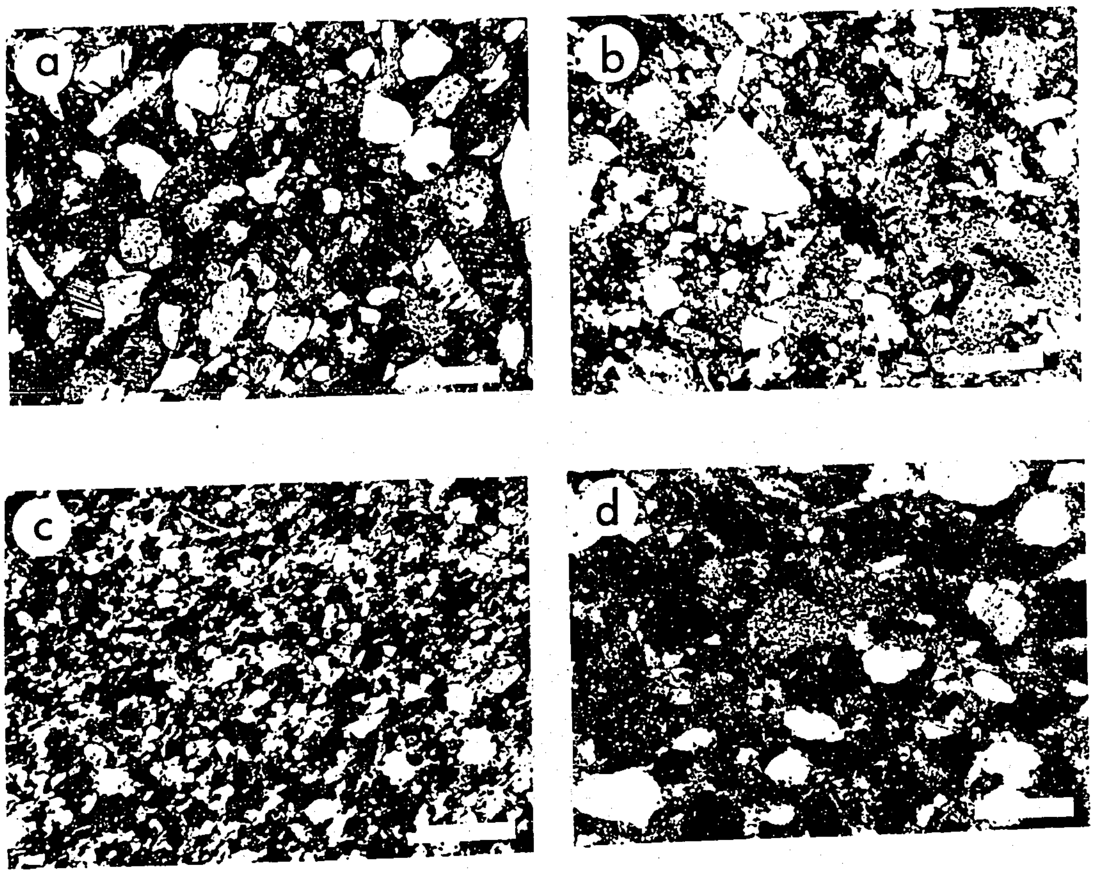
(a) Common feldspar, quartz and volcanic rock fragments in sample MK49 of the Chesleigh Formation.

(b) Quartzose graywacke containing sedimentary and volcanic lithic grains. Sample MK2 of the Chesleigh Formation.

(c) Fine grained highly quartzose graywacke of the Cookman Formation. Sample MK53.

(d) Abundant quartz and sedimentary rock fragments in sample MK54 of the Cookman Formation.

The scale bar in (a) to (d) = 0.5 mm.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are strongly vacuolised and sericitised giving a turbid appearance. Volcanic and sedimentary rock fragments are present in various proportions (Table D.3). Volcanic fragments are probably of the felsitic type, though their exact nature is difficult to discern due to post-depositional modifications. Calcite, chlorite, epidote and sericite are present as inclusions in plagioclase and volcanic rock fragments, as well as forming part of the matrix. Zircon, horneblende, tourmaline, sphene, apatite and rutile constitute the accessory minerals. Hornblende grains are rare and display strong pleochroism, negative and oblique extinction and a large 2v. Matrix is prominent in most graywackes and is recrystallised, dense, dark, scruffy and consists of phyllosilicates with minute grains of quartz, sericite and chlorite. Largely, it is epimatrix, however some pseudo-matrix, formed due to the degradation of argillaceous rock fragments, is also present.

D.2.3 Cookman Formation

Graywackes of the Cookman Formation are generally fine grained, greyish-white and exhibit common graded bedding and parallel laminations.

TEXTURE

The detrital assemblage is fine to medium grained, moderate to well sorted and consists of dominant quartz grains with a subordinate amount of lithic grains (Table D.4; Figures D.3c.d). The original fabric and shape of grains is sometimes modified due to metamorphism and deformation. Grain contacts are both plane and tangential.

MINERALOGY

Quartz: Monocrystalline quartz grains exhibiting slight to strong undulose extinction and containing common inclusions of apatite and rutile form the most abundant constituent of the graywackes. Well rounded chert and arenaceous rock fragments constitute the common polycrystalline quartzose grains.

Feldspar: Feldspar is almost all plagioclase and generally forms less than 1% of most graywackes, however in sample MK9 it constitutes about 4% of the rock (Table D.4). The grains are of very fine sand size, well rounded and show multiple twinning.

Table D.4 Modal Composition of Graywackes of the Cookman Formation, Hill End Trough

Serial No.*	1	2	3	4	5	6	7	8
Sample No.	MK1	MK5	MK6	MK53	MK54	MK9	MK10	MK77
Quartz								
Monocrystalline	78.5	72.0	59.2	91.2	50.1	73.1	54.3	93.1
Polycrystalline	6.2	7.9	1.5	1.6	1.1	1.2	0.0	0.0
Plagioclase	0.6	0.3	0.6	0.2	0.0	3.8	0.0	0.4
K-feldspar	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0
Vol. Rock Frag.	0.6	0.3	1.2	0.0	1.1	0.0	0.0	0.0
Sed. Rock Frag.	4.6	11.8	14.7	2.1	40.4	2.1	4.8	1.7
Muscovite	1.1	2.0	5.2	0.6	0.8	4.3	0.0	0.6
Biotite	0.0	0.0	0.0	0.0	0.0	12.1	35.3	3.4
Accessories	0.0	0.3	0.6	0.6	0.8	0.8	0.5	0.2
Opaque Minerals	0.0	2.0	0.3	0.4	1.1	0.6	2.6	0.4
Matrix	9.0	3.0	16.3	3.3	4.7	1.9	2.4	0.5
Mz (ø)	3.10	1.58	2.41	2.40	3.50	2.82	2.91	3.60
S_I (ø)	0.56	0.59	0.76	0.55	0.39	0.40	0.65	0.47

* Serial Nos. 1 to 5 : Sofala section
6 to 8 : Hill End section

Rock Fragments: Argillaceous rock fragments constitute the major portion of lithic grains. These are often squashed and squeezed and are made up of phyllosilicates and fine quartz. Volcanic rock fragments form only ≅ 1% of the whole rock and their original texture is obscured by post-depositional modifications.

Mica: Muscovite is common and both detrital and diagenetic in nature. The large flakes bent around the quartz grains are detrital whereas most small flakes replacing the framework grains are probably diagenetic in origin. Diagenetic biotite, occurring as irregular brown or greenish-brown flakes, is common in graywackes of the western section.

Opaque Minerals: Rounded to well rounded, very fine sand sized magnetite and ilmenite grains constitute less than 1% of the whole rock.

Accessories: A few small well rounded grains of zircon, tourmaline and sphene together with rare detrital epidote and strongly pleochroic hornblende are present.

Matrix: Matrix is not very abundant and commonly forms less than 5% of the whole rock (except in MK1 and MK6; Table D.4) whereas it usually constitutes more than 15% of the whole rock in most other graywackes. It is of the epi- and pseudo-types and the relative proportions are difficult to estimate due to recrystallisation.

D.3 BENDIGO TROUGH

The graywackes are grey to greyish-white in colour, commonly graded but sometimes laminated and contain occassional micaceous and carbonaceous partings.

TEXTURE

The graywackes are fine to medium grained, moderately sorted and contain predominantly rounded to subrounded quartz, subordinate feldspar grains and common matrix (Figures D.4a,b; Table D.5). A parallel arrangement of mica flakes is commonly visible. Detrital grains are usually floating but at times have long and pointed contacts.

MINERALOGY

Quartz: Monocrystalline grains of varied sizes dominate the quartz assemblage and exhibit slight to strong undulose extinction (Figure D.4a,c). Vacuoles and acicular inclusions are common. Grains are

Table D.5 Modal Composition of Graywackes of the Bendigo Trough

Serial No.	1	2	3	4	5	6	7	8	9
Sample No.	MK95	MK96	MK97	MK98	MK99	MK103	MK104	BT 4	BT5
Quartz									
Monocrystalline	58.0	40.7	65.8	59.7	57.4	52.9	46.5	78.4	69.2
Polycrystalline	10.7	6.1	1.5	10.2	4.7	3.5	5.4	3.5	5.4
Plagioclase	2.6	1.8	1.0	2.1	3.2	1.4	2.2	1.6	1.9
K-feldspar	0.1	0.0	0.2	0.0	0.0	0.2	0.0	0.0	0.0
Sed. Rock Frag.	0.7	10.7	3.0	0.4	1.8	0.5	0.0	0.8	0.5
Muscovite	5.0	23.5	14.0	9.9	14.8	18.3	17.6	1.2	15.5
Chlorite	1.1	4.5	1.5	1.1	3.7	1.8	7.8	0.0	0.0
Accessories	0.9	4.9	1.8	0.7	1.6	1.8	1.9	2.0	0.5
Opaque Minerals	0.0	0.0	0.0	0.7	0.0	0.1	0.0	0.1	0.0
Matrix	20.8	7.6	11.3	15.2	12.8	20.0	18.6	12.5	6.5
M_z (ø)	1.23	3.25	2.13	1.59	1.89	2.02	2.59	2.73	1.55
S_I (ø)	0.59	0.45	0.85	0.86	0.83	0.59	0.66	0.77	0.57

FIGURE D.4

Representative Graywackes of the Bendigo Trough

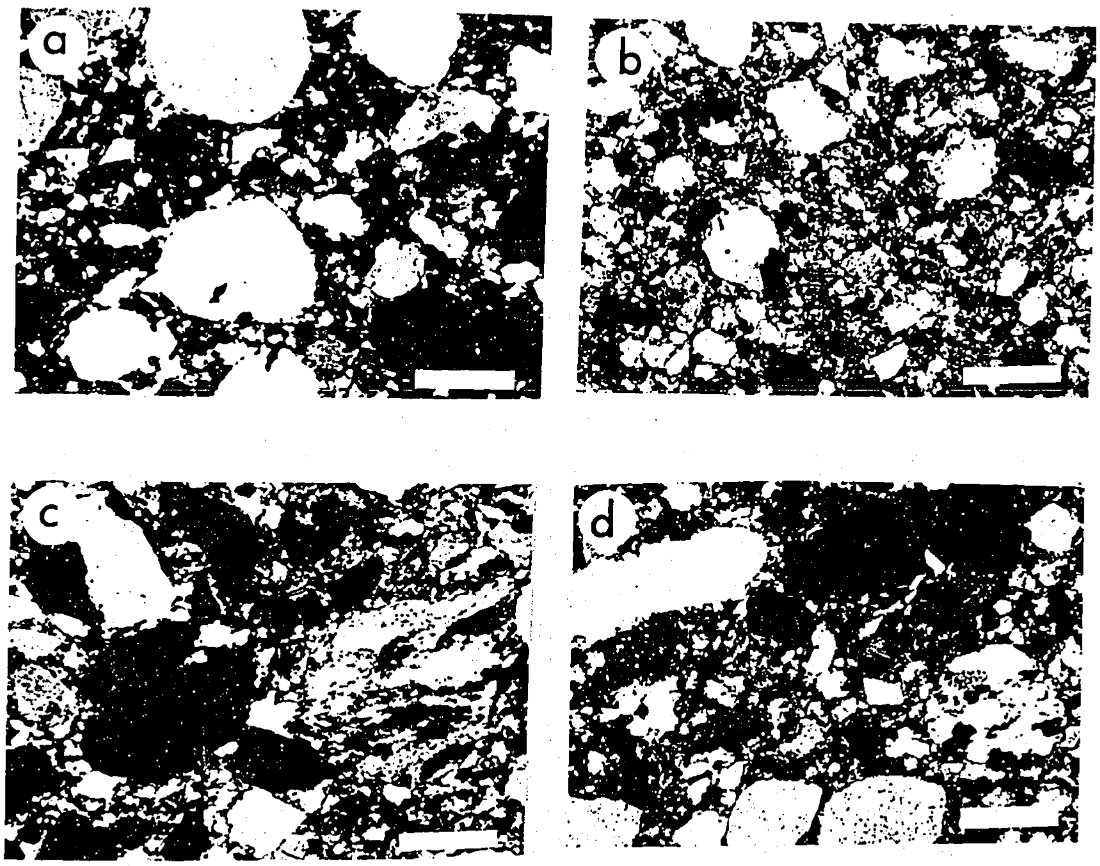
(a) General texture of the Bendigo Trough graywackes. Note the abundant well rounded monocrystalline quartz and one polycrystalline quartzose grain. Sample MK95.

(b) Fine-grained graywacke dominantly composed of monocrystalline quartz grains, with a few polycrystalline quartzose and feldspar grains. Sample MK104.

(c) Polycrystalline quartzose grain made up of elongated and sutured quartz crystals in Sample MK99.

(d) Typical quartz-rich graywacke of the Bendigo Trough. The polycrystalline quartzose grain shows coarse interlocking mosaic of crystals. Sample MK99.

The scale bar in (a) to (e) = 0.5 mm.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generally rounded to well rounded but their margins are often corroded by recrystallised matrix. Polycrystalline grains are common and of two types: composite and chert. Composite grains are made up of many elongate and sutured individuals showing slight to perfect orientation (Figure D.4c,d). Some grains also show coarse interlocking mosaic of crystals (Figure D.4a). Silty and speckled chert grains are common and form 1-2% of the whole rock.

Feldspar: Fine sand sized, well rounded feldspar grains constitute 1 to 3% of the whole rock (Figure D.4b). Most grains are plagioclase and show polysynthetic twinning. K-feldspar grains are rare.

Rock Fragments: Lithic grains are of the argillaceous type and form a small proportion of the graywackes, except in one sample (MK96) in which they form ≅ 11% of the whole rock (Table D.5). Often these grains are deformed and squashed.

Muscovite: Muscovite is very common and occurs as shreds and plates, oriented parallel to bedding. Many flakes are bent and broken and sometimes deformed around quartz grains.

Chlorite: Chlorite shows a large variation in its abundance and occurs as small flakes associated with the groundmass.

Accessories: Small and well rounded grains of tourmaline, zircon, rutile and apatite constitute about 2% of the whole rock (except sample MK96 which contains ≅ 5%). Tourmaline is the most dominant accessory mineral and some grains exhibit probable authigenic overgrowth.

Matrix: Matrix is an essential constituent of these graywackes and is mainly composed of sericite, chlorite and minute quartz grains. Matrix is of various types and reliable estimates are difficult to achieve. Most of it is probably of detrital derivative (i.e. of the ortho— or epi— type) and only a minor fraction, seen as replacing the detrital grains, is of diagenetic origin.

D.4 HODGKINSON FORMATION

The Hodgkinson Formation graywackes are light to dark grey and greyish-green in colour, indurated, commonly graded, often laminated and show large variations in their grain sizes.

TEXTURE

Graywackes are composed of rounded to subangular quartz, feldspar, and lithic grains of varying sizes (Figures D.5a,b,c). Sorting is moderate to poor and the original shape and roundness of the grains is often distorted due to post-depositional modifications. Grains are mostly floating but often grain boundaries could be long or concavo-convex.

MINERALOGY

Quartz: This is the most abundant constituent of the graywackes (Table D.6). Monocrystalline grains, having slight to strong undulose extinction and rutile inclusions, are dominant (Figures D.5a,b). Polycrystalline grains are very common, generally have more than 2 or 3 subindividuals and are of the following types (see also discussion in Chapter 4, Section 4.5.3): (a) most common are the "metamorphic" type of quartzose grains having numerous elongated, sutured crystals (Figure D.5c,d) and a coarse interlocking mosaic of crystals. (b) "polygonised" type quartzose grains having straight boundaries and slight undulose extinction of individual crystals (Figure D.5e). They are derived from granites. Minor, small and well rounded chert grains, containing phyllosilicate specks, are also present.

Feldspar: Plagioclase, orthoclase and microcline in various proportions constitute the feldspar component (Table D.6). Medium grained subrounded plagioclase grains are of albite-oligoclase composition and contain quartz and mica inclusions (Figures D.5b,c). Orthoclase grains are rounded and sericitised. Microcline grains are large, rounded and exhibit cross-hatched twinning (Figures D.5a,b). A few perthite grains are also observed.

Rock Fragments: Volcanic, metamorphic and sedimentary lithic grains constitute this component. Volcanic rock fragments (Figure D.5f) are present in various proportions, forming upto 9% of the whole rock (Table D.6), and are of the felsic-intermediate type containing feldspar and quartz phenocrysts. Their original texture is altered due to post-depositional modifications. Foliated phyllitic and "mica-tectonite" (a term of Graham et al. 1976; Figure D.5e) grains constitute the metamorphic rock fragments, which are quite common. Argillaceous rock fragments, composed of phyllosilicates and minute quartz grains, are abundant (Figure D.5e) and commonly squashed.

Table D.6 Modal Composition of Graywackes of the Hodgkinson Formation

Serial No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
Sample No.	MK81	MK82	MK83	MK84	MK85	MK86	MK87	MK88	MK89	MK90	NQ7	NQ11	NQ12	NQ13	NQ15	NQ20	NQ21	NQ25	NQ43	NQ50	NQ52
Quartz																					
Monocrystalline	36.8	42.9	41.0	34.0	39.6	38.8	51.9	46.0	44.8	44.0	38.6	48.4	29.6	36.4	38.0	43.5	43.5	25.7	43.4	43.8	35.4
Polycrystalline	16.0	9.4	9.0	10.8	6.1	1.9	9.8	8.9	9.0	15.8	7.7	14.1	16.8	5.8	10.0	9.8	7.4	13.4	4.2	7.1	8.4
Plagioclase	5.5	5.4	7.7	4.9	3.2	5.7	3.3	10.5	6.6	7.0	5.8	5.7	5.4	4.3	5.4	10.0	9.1	8.0	3.0	14.9	12.3
K-feldspar	2.6	7.1	3.7	6.6	6.5	3.3	8.3	6.9	11.0	4.4	4.1	5.9	4.7	3.8	8.8	5.5	6.2	4.9	6.0	10.5	8.4
Vol. Rock Frag.	2.1	1.1	0.9	1.9	7.2	4.7	3.0	0.7	4.1	4.2	1.1	9.5	1.5	2.1	1.1	1.3	2.6	1.0	7.0	3.4	0.0
Sed. Rock Frag.	9.6	2.6	2.2	1.7	3.9	6.2	3.6	1.7	0.2	2.1	4.9	0.5	3.0	3.4	1.8	2.5	0.6	7.9	3.4	0.5	0.6
Meta Rock Frag.	3.8	1.5	0.9	1.4	5.9	1.9	0.9	1.8	0.0	1.8	2.1	1.6	1.5	0.2	1.8	1.7	0.2	1.9	1.2	1.0	0.9
Muscovite	2.6	3.5	4.7	5.1	3.3	8.1	6.2	2.4	9.2	2.4	6.9	7.8	2.2	4.6	2.3	2.6	2.3	6.6	3.2	6.7	8.0
Chlorite	0.8	0.4	0.6	0.3	0.0	0.3	0.0	0.4	0.6	0.9	0.0	0.5	0.4	0.4	0.5	0.4	0.6	0.3	0.2	0.0	0.7
Calcite	0.9	0.7	0.4	0.0	1.9	1.9	1.2	0.4	0.6	2.1	0.4	0.0	0.0	0.4	0.0	0.0	0.0	0.0	1.0	1.0	0.6
Accessories	3.2	2.6	3.5	3.9	1.5	0.6	1.8	3.3	2.3	0.6	5.8	1.6	2.2	4.8	2.7	2.1	3.8	3.5	3.0	0.7	7.4
Opaque Minerals	0.4	0.4	0.4	0.7	1.7	0.6	1.5	0.7	0.4	1.2	0.9	0.0	0.9	0.7	0.5	0.4	0.4	0.3	0.6	0.7	0.6
Matrix	16.0	22.5	25.0	28.8	19.1	26.1	8.6	16.3	11.2	13.5	21.6	4.3	31.8	33.2	27.0	20.0	23.4	26.4	23.9	9.6	16.8
Mz (ø)	1.33	1.81	2.08	2.15	2.93	2.93	1.69	2.16	1.99	2.25	2.54	1.86	1.59	2.86	2.03	1.55	1.65	2.82	3.21	1.56	2.16
S_I (ø)	0.91	0.83	0.90	0.78	0.52	0.41	0.96	0.85	0.97	0.75	0.62	0.83	0.95	0.52	0.85	0.97	0.76	0.66	0.55	0.76	0.70

FIGURE D.5

Representative Graywackes of the Hodgkinson Formation

(a) General texture of the Hodgkinson Formation graywackes. Mono- and polycrystalline quartzose, K-feldspar, plagioclase and lithic grains in sample MK85.

(b) Quartz, microcline, plagioclase and lithic grains in sample MK82.

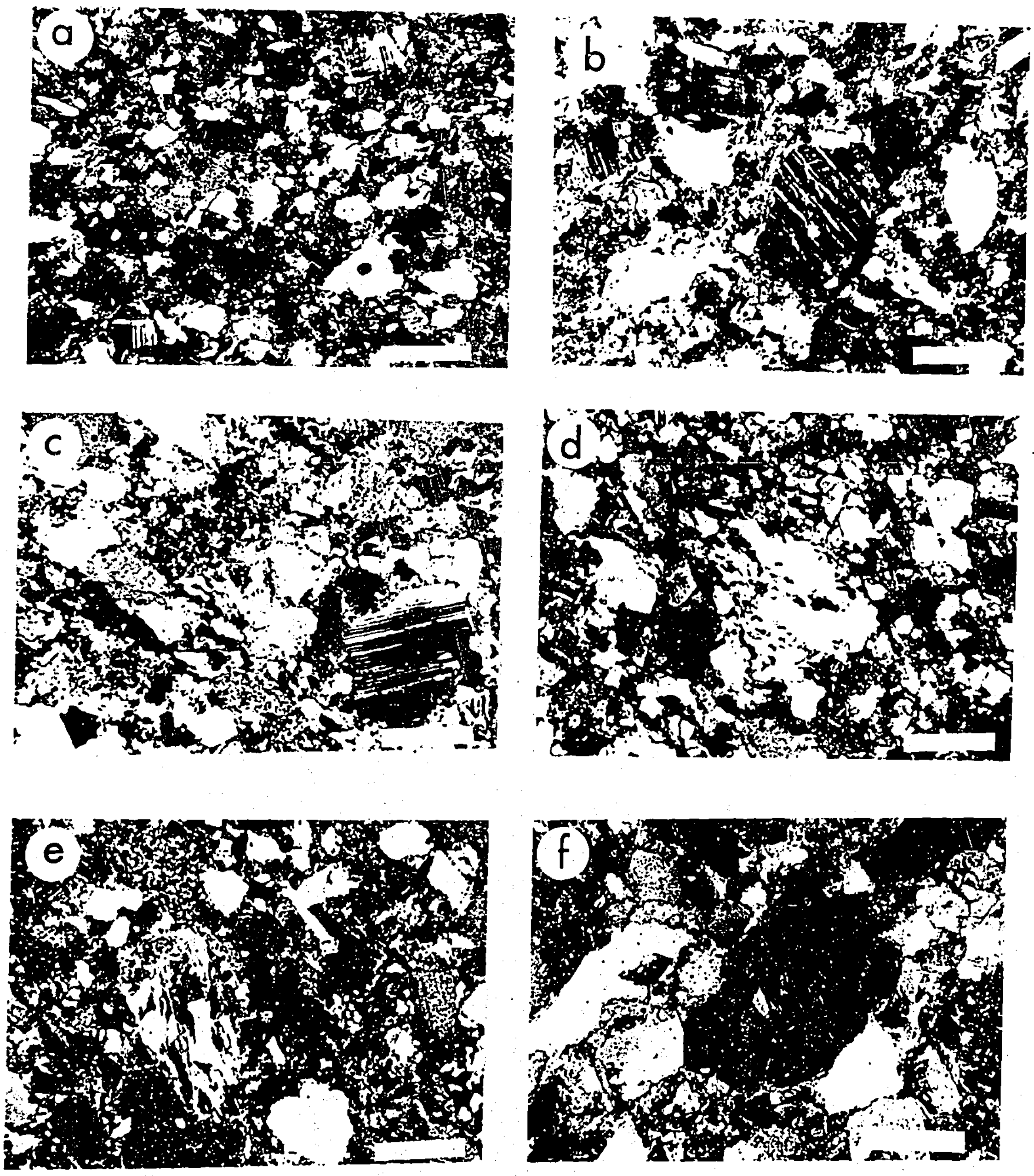
(c) Mono- and polycrystalline quartzose grains, plagioclase, K-feldspar and lithic grains in sample MK87.

(d) Polycrystalline quartzose grain having sutured quartz crystals. Sample MK88.

(e) Common, lithic grains in sample MK86. Note the 'mica-tectonite' grain (slightly left of the middle of the figure).

(d) Volcanic rock fragment in Sample MK81.

The scale bar in (a) to (e) = 0.5 mm and in (f) = 0.2 mm.


a
b
c
d
e
f

Muscovite: Detrital muscovite is an essential component of these graywackes and occurs as minute to large flakes, sometimes bent and deformed. The clustering of flakes is occassionally seen. Some muscovite also occurs in lithic grains, as in "mica-tectonites".

Chlorite: Minor chlorite and greenish-tinted biotite flakes are seen associated with matrix.

Calcite: Calcite forms less than 2% of the whole rock and normally occurs as replacing plagioclase grains or associated with the matrix.

Accessories: Rounded zircon, tourmaline, sphene, epidote and pyroxene grains constitute the accessory minerals in order of their decreasing abundance. Rare bright grains of apatite are also present. Rare reaction rims are seen around pyroxene grains.

Opaque Minerals: Fine sand sized magnetite and ilemite grains, forming $\cong$ 1% of the whole rock, constitute the opaque minerals. Pyrite grains are also occassionally seen.

Matrix: Matrix is very common and mainly made up of phyllosilicates with minor quartz and rare dirty epidote. Much of the matrix is recrystallised and hence its exact nature is difficult to discern. However, replacement of detrital grains by matrix is common. Some argillaceous fragments are squashed and deformed to yield pseudo-matrix.

APPENDIX E

CHEMICAL COMPOSITION OF PALEOZOIC CLASTIC SEDIMENTARY ROCKS OF EASTERN AUSTRALIA

Table E.1 Chemical composition of graywackes of the Tamworth Trough*

Sample#	MK11	MK12	MK13	MK14	MK15	MK16	MK17	MK22	MK23	MK24	MK25	MK20	MK21	MK46
SiO_2	56.73	65.81	64.35	53.69	69.22	57.74	55.01	27.46	52.90	50.24	57.56	59.75	67.71	65.48
TiO_2	1.27	0.90	0.65	0.42	0.24	1.00	1.07	0.61	0.99	0.88	0.93	1.09	0.61	0.96
Al_2O_3	15.14	13.36	14.36	20.03	16.03	15.49	16.64	9.46	15.20	17.36	16.00	16.92	14.74	14.94
Fe_2O_3	1.68	1.50	1.22	1.47	0.59	1.84	1.65	2.47	1.71	1.54	1.35	1.34	1.34	0.97
FeO	5.90	3.06	2.90	4.30	1.16	5.85	6.07	3.72	5.60	7.11	4.37	6.55	2.74	4.46
MnO	0.20	0.14	0.12	0.07	0.03	0.15	0.15	1.11	0.16	0.23	0.19	0.15	0.08	0.10
MgO	2.67	1.94	1.49	2.77	0.74	2.74	2.70	1.77	3.88	3.66	3.89	2.50	1.42	1.61
CaO	4.25	3.26	3.41	2.12	2.30	4.24	6.49	27.07	6.41	7.92	5.65	3.41	2.26	2.98
Na_2O	5.35	4.13	3.33	5.90	5.79	5.65	3.60	2.67	4.62	4.12	4.30	4.39	4.73	4.35
K_2O	1.52	2.42	2.43	1.35	0.97	0.84	1.21	0.27	0.39	0.25	0.45	0.67	0.95	0.56
P_2O_5	0.23	0.19	0.30	0.10	0.04	0.23	0.25	0.16	0.13	0.15	0.16	0.28	0.19	0.26
S	0.08	0.09	0.03	0.14	<0.02	0.16	0.08	0.20	0.14	0.06	0.08	0.06	0.11	0.11
H_2O+	2.87	1.59	2.96	2.94	1.36	2.74	3.54	1.99	3.38	2.91	3.15	2.63	1.64	1.93
H_2O-	0.40	0.21	0.82	0.49	0.17	0.16	0.22	0.28	0.24	1.50	0.13	0.60	0.21	0.36
CO_2	1.53	1.18	1.03	0.33	0.85	1.12	0.37	20.32	2.97	1.50	0.78	0.29	0.79	0.48
rest	0.12	0.18	0.53	0.22	0.16	0.13	0.17	0.10	0.18	0.17	0.17	0.25	0.23	0.23
	99.95	99.96	99.93	99.88		100.07	99.72	99.66	99.90	99.61	100.07	99.79	99.75	99.78
O=S	0.04	0.04	0.01	0.07		0.08	0.04	0.10	0.07	0.03	0.04	0.03	0.05	0.05
	99.91	99.92	99.92	99.81	99.65	99.99	99.68	99.56	99.83	99.53	100.03	99.76	99.70	99.73
Trace elements														
Ba	180	710	1180	620	380	130	440	55	140	100	140	260	320	260
Rb	19	41	49	31	17	10	13	4	5	4	5	14	22	14
Sr	72	314	2850	790	696	134	214	274	529	555	582	784	1042	839
Pb	11	9	10	6	4	6	6	6	6	5	6	15	13	13
Th	4	3	3	4	1	2	2	1	2	2	1	11	6	8
U	1	1	<1	1	<1	1	2	1	<1	1	<1	4	2	3
Zr	117	107	95	107	76	132	125	26	110	85	77	272	114	195
Nb	2	3	2	2	<1	2	2	<1	3	2	2	9	5	7
Y	25	24	31	9	8	26	29	13	20	20	10	27	12	21
La	11	10	16	6	6	9	10	2	12	7	7	26	13	22
Ce	29	25	39	14	12	23	27	8	29	19	19	64	30	52
Nd	14	13	17	5	6	15	16	5	13	10	11	27	13	24
Sc	26	19	15	8	5	25	27	23	21	24	16	20	14	19
V	161	89	51	77	31	176	172	138	193	199	157	177	89	136
Cr	31	22	20	22	20	35	35	40	79	46	64	29	21	26
Mn	1570	1080	905	515	230	1140	1190	3610	1240	1770	740	1140	620	795
Co	19	11	7	9	4	23	23	16	28	31	29	22	41	19
Ni	6	5	4	6	4	9	9	14	23	15	26	11	17	7
Cu	10	7	6	5	4	62	49	32	20	20	39	18	8	13
Zn	118	90	70	64	28	94	109	70	111	110	111	149	89	126
Ga	18	12	15	19	16	18	18	11	13	19	19	23	17	18

* Samples MK 20, MK21, MK 46- Crow Mt. Creek Beds

Table E.2 Chemical composition of mudrocks of the Tamworth Trough*

Sample#	MK18	MK34	MK35	MK36	MK37	MK38	MK41	MK42	MK43	MK44	MK45	MK19	MK39	MK40
SiO_2	60.16	68.22	60.11	69.20	44.14	65.83	57.66	61.94	66.01	64.93	63.47	70.42	66.02	66.86
TiO_2	0.90	0.63	0.69	0.62	0.89	0.60	0.49	0.76	0.74	0.75	0.79	0.51	0.61	0.64
Al_2O_3	15.56	12.29	18.41	12.97	18.94	13.15	11.35	14.75	14.86	15.08	16.38	14.48	15.22	15.03
Fe_2O_3	1.70	3.07	4.02	1.47	1.36	1.52	5.02	1.00	5.04	5.19	5.26	1.02	1.02	0.82
FeO	4.40	0.59	0.86	2.38	5.34	4.71	0.35	5.68	0.45	0.73	0.84	2.29	4.07	3.51
MnO	0.15	0.05	0.05	0.04	0.21	0.07	0.03	0.07	0.04	0.04	0.03	0.06	0.06	0.07
MgO	2.04	1.09	2.06	1.88	2.47	2.49	1.19	3.96	1.46	1.62	1.58	0.96	1.83	1.88
CaO	5.99	2.73	1.35	1.85	9.07	1.51	8.55	1.60	0.62	0.71	0.51	1.30	1.48	1.65
Na_2O	1.66	0.76	1.88	3.09	3.08	2.70	1.08	4.36	0.97	1.27	1.38	5.39	2.38	3.43
K_2O	2.17	3.73	3.73	1.47	2.86	1.40	1.65	2.03	1.91	1.70	2.46	0.79	2.77	2.05
P_2O_5	0.25	0.10	0.16	0.13	0.17	0.14	5.18	0.06	0.10	0.09	0.14	0.16	0.12	0.10
S	0.05	<0.02	<0.02	0.48	0.27	0.49	<0.02	<0.02	<0.02	<0.02	<0.02	0.09	<0.02	<0.02
H_2O+	3.53	3.32	3.63	2.38	3.66	3.23	3.04	3.34	3.96	4.10	4.10	1.47	2.72	3.37
H_2O-	0.40	1.65	1.90	0.31	0.69	1.39	2.55	0.10	2.48	2.17	1.33	0.19	0.34	0.20
CO_2	0.75	1.51	0.74	2.00	6.57	1.39	1.41	0.01	1.58	1.93	1.38	0.48	1.24	0.50
rest	0.17	0.25	0.28	0.19	0.36	0.21	0.21	0.17	0.17	0.16	0.15	0.13	0.18	0.22
	99.88			100.46	100.08	100.83						99.74		
O=S	0.02			0.24	0.13	0.24						0.04		
	99.86	99.99	99.87	100.22	99.95	100.59	99.76	99.83	100.39	100.47	99.80	99.70	100.06	100.33
Trace elements														
Ba	510	1150	1320	460	1340	500	280	660	380	330	270	190	460	340
Rb	37	90	127	53	85	45	66	18	57	51	104	28	118	81
Sr	231	400	185	153	697	296	309	271	245	271	129	340	232	651
Pb	7	8	7	10	7	8	14	4	7	10	13	11	20	17
Th	2	6	5	7	5	5	6	6	5	5	9	8	13	12
U	1	2	2	6	2	4	2	1	2	2	2	2	3	2
Zr	164	157	118	109	122	99	148	146	121	118	150	127	138	160
Nb	2	3	3	5	3	3	5	4	4	3	7	5	7	7
Y	30	21	24	21	25	18	109	12	25	20	25	22	24	27
La	12	14	38	19	14	21	115	3	26	12	20	18	25	26
Ce	29	31	91	41	32	45	226	8	25	26	43	43	59	59
Nd	19	13	40	17	14	16	97	4	28	15	20	20	23	23
Sc	22	17	18	16	25	17	18	20	21	20	20	10	16	15
V	119	62	130	308	257	236	100	91	121	121	140	77	107	106
Cr	26	22	48	43	42	45	44	28	40	39	57	30	48	45
Mn	1200	410	360	305	1590	530	245	530	335	345	265	480	475	510
Co	16	7	10	15	19	14	13	27	11	10	17	14	16	10
Ni	7	4	14	24	19	17	16	11	12	16	23	9	19	14
Cu	31	27	53	45	60	52	23	3	67	61	41	20	32	29
Zn	92	70	120	97	148	196	73	24	96	101	97	77	102	101
Ga	19	14	23	14	21	15	14	22	19	19	19	14	18	19

* Samples MK 19 MK39, MK40 - Crow Mt. Creek Beds.

Table E.3 Chemical composition of graywackes of the Hill End suite

Sample#	MK61	MK59	MK65	MK67	MK75	MK74	MK2	MK4	MK47	MK49	MK50	MK3	MK7	MK8
SiO_2	72.30	70.88	77.86	74.01	69.14	76.41	81.94	81.66	72.96	64.83	83.14	59.27	62.48	78.80
TiO_2	0.50	0.61	0.58	0.81	0.82	0.51	0.46	0.50	0.49	0.63	0.41	0.96	1.09	0.42
Al_2O_3	9.99	12.68	10.00	10.43	12.27	9.41	8.52	8.67	12.07	14.90	8.43	17.36	15.37	8.54
Fe_2O_3	0.53	0.71	0.74	0.84	0.76	0.56	1.01	1.19	0.90	1.57	0.76	2.74	2.24	0.58
FeO	2.13	2.44	1.95	3.51	4.67	2.23	1.72	1.60	2.28	3.80	1.45	3.00	3.12	0.94
MnO	0.04	0.04	0.03	0.05	0.10	0.04	0.02	0.02	0.06	0.07	0.02	0.11	0.07	0.05
MgO	1.28	1.16	1.23	1.41	2.11	1.01	1.27	1.27	1.18	2.81	0.96	2.22	1.90	0.56
CaO	4.03	1.67	1.05	1.33	2.11	2.37	0.13	0.14	1.47	1.81	0.16	5.97	3.00	2.25
Na_2O	1.81	2.66	1.98	1.85	3.29	2.37	0.63	0.47	3.01	4.50	1.48	3.02	2.41	1.55
K_2O	2.02	3.82	1.65	1.66	1.12	1.35	1.76	2.07	1.89	1.56	1.65	1.68	2.68	3.46
P_2O_5	0.05	0.06	0.37	0.11	0.12	0.12	0.09	0.10	0.13	0.13	0.10	0.28	0.18	0.11
S	<0.02	0.06	0.07	0.08	<0.02	0.10	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
H_2O+	1.82	1.64	2.04	2.50	2.56	1.54	2.00	1.93	1.71	2.67	0.71	2.60	3.01	0.77
H_2O-	0.06	0.13	0.07	0.05	0.08	0.16	0.09	0.09	0.39	0.09	0.08	0.16	0.24	0.23
CO_2	3.25	1.00	0.41	0.71	0.65	1.53	0.07	0.03	1.10	0.31	0.16	0.10	1.93	1.33
rest	0.19	0.22	0.16	0.17	0.19	0.16	0.13	0.17	0.15	0.18	0.13	0.19	0.17	0.14
		99.78	100.19	99.52		99.87								
O=S		0.03	0.03	0.04		0.05								
	100.02	99.75	100.16	99.48	99.99	99.82	99.86	99.99	99.79	99.86	99.64	99.66	99.89	99.73
Trace elements														
Ba	720	920	260	390	480	340	330	410	410	470	320	430	360	500
Rb	85	108	81	77	52	66	71	99	79	60	81	58	45	118
Sr	227	242	83	96	221	166	22	22	113	222	47	514	296	117
Pb	16	21	12	16	19	17	12	19	18	15	10	17	8	16
Th	11	15	12	13	12	11	11	15	14	11	10	10	5	11
U	3	3	3	3	2	2	2	3	2	2	3	3	4	2
Zr	196	183	400	306	262	339	249	348	173	160	220	137	99	180
Nb	9	1	9	11	10	6	9	9	9	7	8	8	3	7
Y	27	25	34	26	23	26	21	23	26	21	21	24	16	17
La	29	27	36	24	20	32	18	19	34	24	26	25	32	18
Ce	53	60	80	52	24	33	53	55	65	45	57	58	72	43
Nd	21	21	32	19	18	26	16	17	27	19	20	23	28	16
Sc	12	12	12	16	17	9	8	10	13	18	7	20	24	9
V	68	64	70	120	133	55	65	73	70	142	62	81	91	40
Cr	41	42	48	56	70	47	63	67	48	79	55	31	83	38
Mn	325	320	235	425	770	285	150	180	445	580	125	860	580	400
Co	4	9	10	12	18	18	6	12	9	17	7	11	16	7
Ni	8	8	9	10	14	14	20	25	15	13	17	5	25	7
Cu	6	6	30	10	9	18	11	13	13	14	9	2	52	3
Zn	45	58	49	71	82	54	69	69	56	79	46	112	124	31
Ga	11	13	10	12	14	6	9	11	13	7	10	18	15	8

Table E.3 (cont.)

Sample#	MK26	MK27	MK28	MK29	MK30	MK31	MK56	MK57	MK63	MK64	MK70	MK71	MK72	MK76	MK60
SiO_2	64.79	75.52	73.75	75.23	63.90	64.44	72.77	70.52	74.68	63.70	64.00	66.48	68.59	75.78	78.29
TiO_2	1.05	0.61	0.57	0.57	0.87	0.85	0.22	0.48	0.49	0.93	0.73	0.47	0.44	0.64	0.63
Al_2O_3	14.66	11.29	11.75	12.22	13.54	13.78	11.43	12.75	10.80	12.08	10.63	13.63	13.91	11.16	9.42
Fe_2O_3	0.98	0.79	0.90	0.79	1.44	1.49	0.48	0.34	1.08	1.04	0.54	1.00	0.59	1.19	1.32
FeO	5.55	2.76	3.44	0.59	4.65	5.06	1.18	2.57	3.50	5.53	1.85	2.65	3.12	2.80	2.26
MnO	0.07	0.04	0.05	0.02	0.09	0.12	0.03	0.07	0.11	0.20	0.28	0.19	0.16	0.05	0.03
MgO	2.10	1.31	1.38	0.43	2.36	2.65	0.64	1.18	1.75	2.07	0.62	1.15	1.29	1.26	0.97
CaO	1.79	0.68	0.75	4.46	4.55	4.20	4.51	3.56	0.70	4.20	8.63	4.03	2.66	0.78	0.67
Na_2O	3.33	2.59	2.63	2.13	3.22	2.67	3.30	1.87	2.52	2.78	3.17	2.59	2.21	2.23	2.08
K_2O	1.67	1.80	1.71	1.80	0.53	0.58	1.36	1.65	1.45	0.77	1.10	2.15	2.43	1.78	1.68
P_2O_5	0.12	0.11	0.10	0.07	0.10	0.13	0.04	0.06	0.10	0.11	0.12	0.12	0.10	0.11	0.04
S	<0.02	<0.02	<0.02	0.05	<0.02	0.02	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
H_2O+	2.71	2.26	2.03	0.71	2.34	2.83	1.21	2.14	1.69	2.89	1.61	1.92	1.96	1.91	1.82
H_2O-	0.08	0.09	0.11	0.08	0.14	0.12	0.01	0.03	0.11	0.17	0.08	0.16	0.03	0.10	0.22
CO_2	0.65	0.10	0.85	0.25	2.39	0.79	2.55	2.51	0.87	3.03	6.36	2.80	1.93	0.01	0.54
rest	0.21	0.20	0.19	0.14	0.13	0.14	0.13	0.17	0.16	0.16	0.18	0.20	0.20	0.19	0.20
				99.54		99.97	99.90								
O=S				0.02		0.01	0.02								
	99.76	100.15	100.21	99.52	100.25	99.86	99.88	99.90	100.21	99.64	99.92	99.56	99.62	99.99	100.17
Trace elements															
Ba	580	760	670	460	210	180	400	450	350	150	300	560	620	680	680
Rb	73	79	76	86	22	25	69	81	64	36	52	98	115	82	66
Sr	197	124	144	177	185	224	231	297	139	222	327	242	200	137	111
Pb	17	14	13	19	11	10	19	18	16	13	17	18	15	14	13
Th	12	13	14	7	4	5	11	14	13	9	11	15	15	14	12
U	2	3	3	2	1	1	2	3	3	2	2	3	2	3	3
Zr	232	246	249	164	154	167	156	243	252	175	392	255	209	280	336
Nb	13	9	9	7	9	9	7	11	9	10	11	8	9	10	11
Y	30	23	24	15	13	15	24	30	23	22	34	34	33	27	36
La	30	24	19	17	15	16	23	19	25	20	20	27	31	28	42
Ce	57	56	46	39	34	37	52	47	51	45	49	58	61	30	59
Nd	23	21	18	15	12	14	20	20	21	18	21	23	26	21	25
Sc	22	14	13	12	22	23	9	13	13	25	12	16	15	14	13
V	160	86	86	47	129	123	16	48	88	172	61	74	73	90	81
Cr	57	51	48	35	55	57	21	28	59	109	58	50	50	49	52
Mn	540	345	400	185	735	940	235	525	855	1570	2150	1450	1230	415	205
Co	10	9	7	10	17	17	3	5	10	11	15	28	10	10	5
Ni	11	10	11	6	9	12	3	5	18	20	15	22	20	11	12
Cu	5	6	6	4	4	4	3	4	10	9	13	17	11	6	9
Zn	95	55	64	57	103	106	38	64	72	95	51	80	71	60	59
Ga	18	13	14	11	16	18	13	14	13	15	8	14	15	13	10

Table E.4 Chemical composition of mudrocks of the Hill End suite

Sample#	MK32	MK33	MK48	MK51	MK52	MK58	MK62	MK66	MK73
SiO_2	62.10	70.37	66.62	67.08	74.71	66.62	66.50	67.90	67.24
TiO_2	0.62	0.49	0.32	0.52	0.58	0.49	0.59	0.60	0.47
Al_2O_3	17.33	12.95	15.37	12.79	12.33	16.18	16.13	15.69	16.43
Fe_2O_3	1.33	1.53	1.70	2.93	1.40	1.91	3.89	1.02	1.21
FeO	2.81	2.64	2.21	2.25	2.14	1.30	0.99	3.58	3.34
MnO	0.05	0.06	0.10	0.08	0.03	0.02	0.04	0.05	0.12
MgO	1.65	1.65	1.33	2.07	1.40	1.03	1.66	2.00	1.78
CaO	5.88	3.10	0.41	2.50	0.19	1.91	0.02	0.72	0.74
Na_2O	1.99	0.78	3.44	1.18	1.34	1.83	0.55	0.94	1.43
K_2O	2.78	3.01	5.69	3.13	2.89	5.51	3.65	3.78	3.46
P_2O_5	0.11	0.06	0.14	0.13	0.12	0.11	0.06	0.13	0.10
S	0.12	0.12	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
H_2O+	2.87	2.03	1.73	3.16	2.47	1.90	4.13	2.69	2.99
H_2O-	0.07	0.10	0.46	0.72	0.07	0.11	0.64	0.09	0.14
CO_2	0.38	1.32	0.21	1.36	0.20	0.67	1.11	0.30	0.25
rest	0.22	0.22	0.31	0.18	0.19	0.23	0.21	0.19	0.21
	100.31	100.43							
O=S	0.06	0.06							
	100.25	100.37	100.04	100.08	100.06	99.82	100.17	99.68	99.91
Trace elements									
Ba	700	960	1790	550	590	860	700	590	830
Rb	134	136	149	134	141	239	172	173	165
Sr	169	169	140	137	39	172	80	56	144
Pb	23	13	22	13	14	31	23	18	21
Th	18	16	19	12	18	20	20	20	19
U	4	3	4	3	3	4	4	3	3
Zr	332	135	173	118	238	261	188	186	160
Nb	10	9	7	8	12	9	13	11	10
Y	29	29	19	21	33	38	17	28	32
La	33	27	25	22	24	32	12	22	27
Ce	79	62	48	51	56	69	31	46	32
Nd	29	24	17	19	21	28	9	20	24
Sc	14	16	10	14	12	12	16	17	18
V	75	75	45	100	59	57	67	96	81
Cr	43	64	34	79	78	36	85	76	51
Mn	415	465	770	635	240	160	305	425	955
Co	10	12	5	14	20	5	12	8	6
Ni	8	13	9	29	31	9	31	24	18
Cu	6	11	30	34	15	11	28	10	11
Zn	62	65	75	92	82	48	150	80	81
Ga	19	15	13	14	16	19	19	20	20

Table E.5 Chemical composition of graywackes and mudrock of the Cookman suite*

Sample#	MK1	MK5	MK6	MK53	MK54	MK9	MK10	MK77	MK55
SiO_2	82.63	87.99	87.06	94.47	86.51	88.27	75.71	82.39	61.99
TiO_2	0.25	0.17	0.24	0.18	0.23	0.35	0.63	0.13	0.89
Al_2O_3	11.18	7.14	7.35	3.32	7.80	5.56	10.75	9.71	22.25
Fe_2O_3	<0.05	0.18	0.67	<0.05	0.43	0.81	1.73	0.32	1.25
FeO	0.17	0.22	0.16	0.13	0.23	0.55	2.14	0.21	0.42
MnO	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	0.04	0.01	0.01
MgO	0.12	0.25	0.44	0.08	0.25	0.43	1.37	0.19	1.34
CaO	0.01	0.02	0.04	0.02	0.04	0.17	0.42	0.10	0.02
Na_2O	0.01	0.02	0.02	0.01	0.02	1.07	1.54	4.45	0.10
K_2O	0.33	0.97	1.38	0.24	1.49	1.33	3.11	1.33	6.32
P_2O_5	0.02	0.05	0.08	0.06	0.13	0.07	0.17	0.02	0.03
S	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
H_2O+	3.75	2.23	2.15	1.37	2.20	0.80	1.68	0.74	4.57
H_2O-	0.59	0.12	0.10	0.07	0.07	0.09	0.15	0.15	0.10
CO_2	0.80	0.07	0.01	0.24	0.17	0.06	0.12	0.10	0.45
rest	0.09	0.09	0.11	0.08	0.14	0.13	0.19	0.11	0.26
O=S									
	99.95	99.52	99.81	100.27	99.71	99.70	99.75	99.96	100.00
Trace elements									
Ba	75	180	250	85	420	220	370	370	850
Rb	19	46	63	11	72	63	155	36	291
Sr	18	115	105	92	145	42	62	123	61
Pb	25	21	18	10	21	17	12	26	13
Th	16	9	11	6	12	10	20	15	29
U	3	1	2	1	2	2	3	4	4
Zr	334	129	195	246	170	444	363	133	211
Nb	10	4	5	4	6	7	13	6	19
Y	37	13	21	14	27	14	39	37	38
La	27	36	30	18	39	15	57	45	54
Ce	63	73	72	41	91	35	113	51	120
Nd	25	26	32	20	43	14	45	44	43
Sc	6	4	4	3	5	5	10	4	21
V	11	19	23	16	26	24	61	6	137
Cr	28	31	35	47	36	44	78	16	133
Mn	8	22	24	6	29	82	335	49	83
Co	<1	1	1	1	1	3	9	1	6
Ni	<1	<1	2	<1	3	3	25	1	13
Cu	3	2	3	1	3	6	16	1	3
Zn	2	7	7	2	9	22	70	19	24
Ga	6	7	8	3	9	7	12	7	29

* Sample MK55- Mudrock, all other graywacks.

Table E.6 Chemical composition of graywackes and mudrocks of the Hodgkinson suite*

Sample#	MK81	MK82	MK83	MK84	MK85	MK86	MK87	MK88	MK89	MK90	MK91	MK93	MK92	MK94
SiO_2	78.13	76.71	74.87	73.79	77.81	73.78	80.31	77.45	74.34	80.73	73.68	79.40	62.69	61.51
TiO_2	0.40	0.43	0.47	0.53	0.41	0.49	0.36	0.43	0.49	0.40	0.47	0.41	0.61	0.63
Al_2O_3	11.00	11.00	11.48	12.68	9.90	11.00	9.36	10.37	11.85	9.58	11.90	9.45	17.60	18.24
Fe_2O_3	0.79	0.62	0.62	0.81	0.55	0.56	0.41	0.55	0.71	0.60	0.72	0.39	3.00	3.42
FeO	1.57	1.78	2.02	2.25	2.06	2.99	1.39	1.60	2.39	1.50	2.19	2.00	2.65	2.28
MnO	0.05	0.05	0.05	0.05	0.04	0.06	0.04	0.05	0.06	0.03	0.04	0.04	0.04	0.05
MgO	0.92	0.78	0.89	0.92	0.88	1.24	0.66	0.82	1.19	0.75	1.17	0.75	1.50	1.75
CaO	0.91	1.11	1.71	1.45	1.12	1.88	0.69	0.81	1.18	0.76	1.12	0.88	0.58	0.52
Na_2O	2.79	2.63	2.51	2.63	1.77	1.95	1.83	2.38	2.52	1.67	1.99	1.99	1.19	1.02
K_2O	2.11	2.77	2.80	2.93	2.01	1.78	3.37	3.10	3.16	2.47	2.90	1.70	3.83	4.29
P_2O_5	0.07	0.07	0.06	0.10	0.07	0.09	0.07	0.09	0.10	0.08	0.09	0.07	0.11	0.11
S	<0.02	<0.02	0.05	0.06	<0.02	0.05	0.05	<0.02	0.04	<0.02	0.04	0.02	<0.02	<0.02
H_2O+	1.41	1.51	1.34	1.37	1.57	1.79	0.88	1.11	1.53	0.84	1.51	1.93	3.16	3.10
H_2O-	0.02	0.08	0.03	0.05	0.14	0.18	0.09	0.11	0.14	0.04	0.09	0.05	0.53	0.62
CO_2	0.50	0.48	0.78	0.33	1.08	2.14	0.33	0.53	0.39	0.13	1.67	1.14	2.42	2.25
rest	0.16	0.17	0.18	0.20	0.13	0.14	0.16	0.17	0.18	0.14	0.17	0.13	0.21	0.23
			99.88	100.15		100.12	100.00		100.27		99.75	100.35		
O=S			0.02	0.03		0.02	0.02		0.02		0.02	0.01		
	100.84	100.19	99.86	100.12	99.55	100.10	99.98	99.57	100.25	99.74	99.73	100.34	100.12	100.03
Trace elements														
Ba	490	550	540	570	330	300	710	680	640	410	490	300	680	640
Rb	99	115	124	134	106	100	117	116	124	117	138	95	189	244
Sr	141	184	169	188	89	104	145	155	170	69	124	104	98	61
Pb	22	25	23	25	24	23	26	26	24	22	17	23	24	35
Th	22	23	23	24	17	19	13	14	14	19	19	16	26	29
U	5	4	4	5	4	4	3	3	3	4	4	4	4	8
Zr	186	188	221	269	173	182	114	133	135	196	221	198	184	194
Nb	10	11	11	13	10	13	7	9	10	13	14	9	17	16
Y	28	27	29	32	24	27	16	19	20	27	28	21	30	36
La	40	37	39	42	29	33	24	29	25	32	31	32	38	46
Ce	84	80	85	94	67	76	52	60	57	72	71	73	75	99
Nd	29	28	29	33	23	27	18	22	19	26	25	25	30	36
Sc	7	7	7	8	8	10	5	7	10	6	9	8	16	18
V	45	45	50	56	47	55	38	46	63	36	46	43	91	108
Cr	21	21	25	28	26	35	20	25	39	17	24	27	49	67
Co	6	7	10	11	11	12	13	8	12	8	8	10	16	16
Ni	7	7	9	9	11	15	7	11	17	8	11	11	16	35
Cu	5	6	6	9	12	16	4	7	12	2	8	8	39	44
Zn	48	47	56	64	58	70	31	40	61	47	62	49	91	131
Ga	14	15	14	17	12	15	11	13	16	11	15	12	24	25

* Samples MK92 & MK94- Mudrocks, all other graywackes

Table E.7 Chemical composition of graywackes and mudrocks of the Bendigo suite *

Samples	MK95	MK96	MK97	MK98	MK99	MK103	MK104	MK100	MK101	MK102
SiO_2	90.02	78.52	79.12	91.38	83.73	83.05	80.74	78.66	57.42	58.91
TiO_2	0.38	0.72	0.60	0.31	0.49	0.49	0.44	0.43	0.74	0.77
Al_2O_3	4.47	10.27	9.76	3.70	7.58	7.09	8.64	7.83	20.08	19.32
Fe_2O_3	0.22	0.68	0.59	0.29	0.69	0.51	0.90		2.57	2.46
FeO	1.04	2.38	2.16	0.78	1.47	1.62	1.67	0.87	4.26	3.93
MnO	0.01	0.02	0.03	0.03	0.02	0.01	0.02	0.01	0.05	0.05
MgO	0.58	1.32	1.40	0.41	0.96	0.93	1.29	0.57	3.46	3.19
CaO	0.14	0.22	0.25	0.17	0.17	0.14	0.20	0.06	0.20	0.24
Na_2O	0.84	1.82	1.65	0.83	1.51	1.35	1.52	0.08	0.44	0.58
K_2O	0.82	1.89	1.88	0.60	1.19	1.27	1.46	2.29	5.00	4.82
P_2O_5	0.10	0.18	0.14	0.11	0.14	0.11	0.14	0.21	0.12	0.15
S	0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.11	<0.02	<0.02
H_2O+	0.66	1.82	1.52	0.48	1.26	3.00	1.71	1.53	4.00	3.76
H_2O-	0.12	0.15	0.11	0.08	0.16	0.14	0.19	0.56	0.46	0.58
CO_2	0.58	0.18	0.05	0.25	0.70	0.50	1.09	3.81	1.09	1.22
rest	0.12	0.20	0.17	0.09	0.14	0.14	0.09	0.40	0.25	0.25
	100.12							97.42		
O=S	0.01							0.05		
	100.11	100.38	99.44	99.51	100.21	100.35	100.10	97.37	100.14	100.25
Trace elements										
Ba	160	400	400	124	230	250	270	2310	870	840
Rb	40	92	91	30	60	62	74	112	247	237
Sr	28	46	44	32	49	34	43	201	35	38
Pb	11	18	16	9	16	18	3	28	28	23
Th	25	28	20	18	24	23	14	13	23	24
U	5	6	5	4	4	4	2	9	4	4
Zr	401	550	384	315	370	422	16	97	136	161
Nb	8	15	11	7	10	10	3	10	17	16
Y	25	39	32	20	22	29	40	54	35	36
La	34	44	37	25	33	35	27	24	34	38
Ce	79	106	84	59	74	61	62	52	74	87
Nd	27	34	28	20	26	29	23	17	27	31
Sc	4	10	10	3	6	6	7	9	19	19
V	26	63	57	20	32	37	45	256	126	122
Cr	28	60	51	22	35	35	40	63	109	107
Co	6	13	13	6	7	7	10	4	22	21
Ni	6	20	19	3	14	11	6	13	54	47
Cu	4	12	11	5	8	7	2	53	44	37
Zn	22	60	53	17	39	40	13	12	133	122
Ga	5	13	13	4	8	9	10	13	29	28

* Samples MK100, MK101,& MK102- mudrocks, all other graywackes.

APPENDIX F

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TRACE-ELEMENT GEOCHEMISTRY AND SEDIMENTARY PROVINCES: A STUDY FROM THE TASMAN GEOSYNCLINE, AUSTRALIA

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ABSTRACT

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The abundances of La, Th, U and Hf have been determined in flysch sequences of the Tasman Geosyncline, Australia. The arc-derived graywackes differ from those of rifted continental margins and marginal basins, in containing low abundances of La, Th, U and Hf (La = 9.2 ± 1.7 ppm; Th = 1.4 ± 0.6 ppm; U = 0.52 ± 0.2 ppm; Hf = 2.1 ± 0.6 ppm), reflecting similar low abundances in the andesitic source-rocks. Graywackes of rifted continental margins and marginal basins, in contrast, are "mature" and characterised by high abundances of La, Th, U and Hf (La = 39 ± 9.9 ppm; Th = 16 ± 0.6 ppm; U = 3.40 ± 0.5 ppm; Hf = 7.9 ppm), mirroring increased abundances in the granitic and sedimentary source-rocks. Sedimentary rocks deposited in inter-arc basins show wide dispersion but have characteristics intermediate between these two types. The Th/U ratio for magmatic arc sediments is 2.7. For most other sedimentary rocks it remains uniform at 4.5 ± 0.3. For sediments having andesitic and dacitic rocks as provenance the La/Th ratios are 6.7 and 4.5, respectively. This ratio remains constant at 2.6 for most quartzose sedimentary rocks.

INTRODUCTION

Two recent publications on Th—U and Th—rare-earth element geochemistry of sedimentary rocks discuss the significance of these element abundances for models of crustal evolution (McLennan and Taylor, 1980; McLennan et al., 1980). A marked difference in abundance of La, Th, U, and Th/U and La/Th ratios between sedimentary rocks of Archean and Post-Archean age has been attributed to differences in composition of the exposed portions of the continental crust. In these studies data on sedimentary rocks have been grouped into Archean and Post-Archean. To date, no study has been undertaken to examine the relationship between tectonic settings of ancient or modern continental margins and the geochemical characteristics of sedimentary rocks.

Rare-earth elements (REE) and Th are particularly useful for studying provenance because of their low solubility during weathering and diagenetic processes. Geosynclinal clastic sequences are ideally suited for such an investigation since the sedimentary rocks have undergone little chemical weathering. Chemically precipitated rocks are also rare in this regime.

The purposes of the present paper are to document the effect of provenance on Th, U, La, Hf, and Th/U and La/Th ratios in flysch sedimentary rocks, and to examine the relation between tectonic settings and geochemical characteristics of the sedimentary basins. The region chosen for study is the Paleozoic Tasman Geosyncline of eastern Australia.

GEOLOGICAL SETTING

The Tasman Geosyncline constitutes the eastern third of the Australian continent. Its geological history, which spans the Palaeozoic Era, is described by Brown et al. (1968), Scheibner (1978) and other workers. Crook (1980) has discussed its origin in terms of the development of island arcs and adjacent troughs which were progressively accreted onto the Australian continental margin.

Samples of graywackes and mudrocks representing each suite from the following zones of the Tasman Geosyncline were analysed: Tamworth Trough, New South Wales; Hill End Trough, New South Wales; Bendigo Trough, Victoria; and Hodgkinson Basin, Queensland (Fig.1).

Tamworth Trough

The Tamworth Trough of the Tasman Geosyncline lies in the northern part of New South Wales. The Devonian—Carboniferous flysch sequence is ~ 2000 m thick and composed of monotonous graywackes and mudrocks with minor lenticular biostromal limestones and radiolarian argilites. The dominance of feldspars and volcanic rock fragments and low abundance of quartz grains indicate an andesitic source terrain. The Tamworth Trough sequence was deposited in a fore-arc basin having a magmatic arc in the west and a subduction complex in the east (Scheibner, 1976).

Hill End Trough

The Silurian—Devonian flysch sequence of the Hill End Trough is ~ 5000 m thick. The sequence is comprised of graywackes, mudrocks, tuffs and minor conglomerates. The graywackes are sub-quartzose in nature with abundant feldspar and lithic grains. A wide range in the mineralogical nature of the graywackes is seen but the abundance of volcanic rock fragments and some sedimentary rock fragments indicate the provenance to be mainly composed

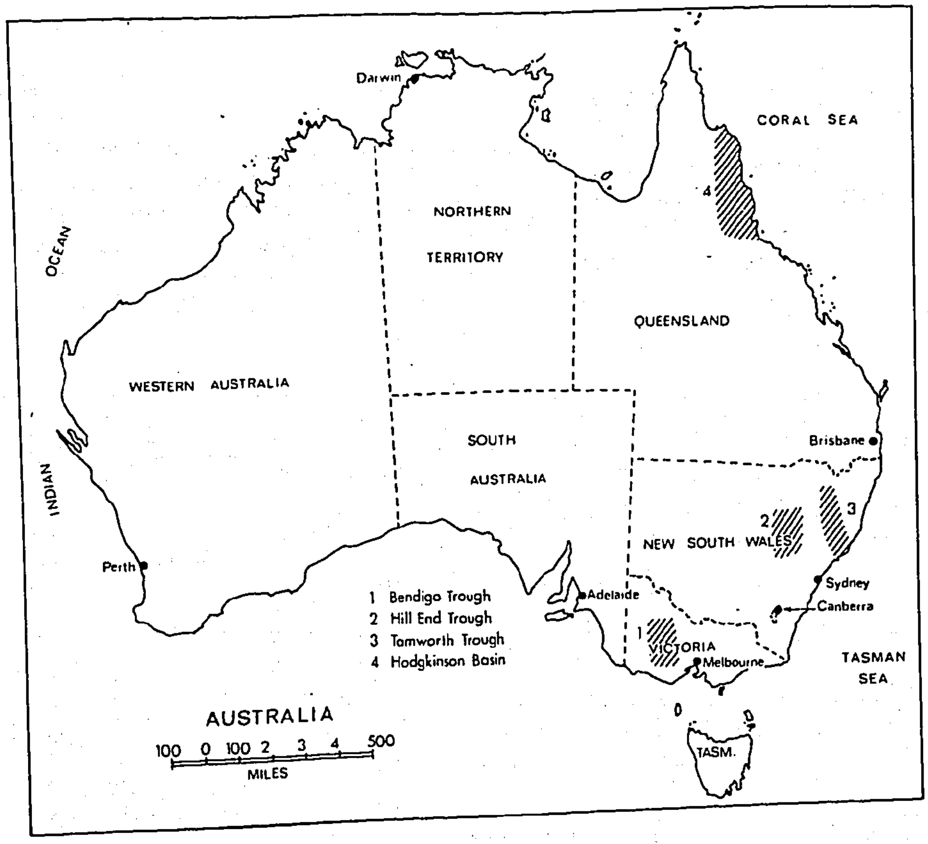


Fig. 1. Location of sedimentary basins.

of felsic volcanic rocks with some contribution from the older sedimentary rocks. The flysch sequence was deposited in an inter-arc basin formed by the limited extension of crust in which active silicic volcanism and older sedimentary material was added (Cas and Jones, 1979).

Hodgkinson Basin

Graywackes, mudrocks and conglomerates of Devonian age comprise the flysch sequence of the Hodgkinson Basin in northern Queensland. The graywackes are sub-quartzose to quartzose in nature with common feldspar and lithic grains. The polycrystalline quartzose lithic grains and abundant detrital mica indicate their derivation from the crystalline rocks composed of granites, gneisses and schists. The sedimentary rocks were deposited in a marginal basin formed due to uplift of the basement near the edge of the continental margin.

Bendigo Trough

The Bendigo Trough comprises a thick sequence of Ordovician graywackes and mudrocks in Victoria. The graywackes contain abundant monocrystalline quartz grains. The highly matured nature characterised by depletion of labile grains indicates their recycled origin. The Bendigo Trough sequence was deposited in a marginal basin with sediments derived from a recycled orogen.

TABLE I

Lithological, mineralogical and geochemical data of the sedimentary rocks

Basin	Lithology*1	Maturity*2	Abundance (ppm)				Th/U	La/Th
			La	Th	U	Hf		
*Tamworth Trough**3:								
M216	G	0	11	2.1	0.59	2.2	3.6	5.2
M277	G	0	10	0.88	0.32	1.8	2.8	11.0
M282	G	0	8	1.3	0.44	2.5	3.0	6.2
M283	G	0	6.3	0.72	0.28	1.6	2.6	8.8
M284	G	0	5.4	0.72	0.26	1.3	2.8	7.5
M285	G	7	6.8	1.4	0.84	1.2	1.7	4.9
B10	G	0	7.2	1.1	0.4	2.0	2.8	6.5
MK14	G	2	7.9	3.02	0.99	2.6	3.05	2.62
MK16	G	4	11.4	1.49	0.57	3.4	2.61	7.58
MK43	M	13	25.94	3.77	1.23	3.5	3.07	6.88
Hill End Trough:								
M4	G	74	22.36	12.54	2.71	11.8	4.62	1.78
M49	G	35	35.73	8.52	1.77	3.8	4.81	2.85
MK26	G	22	29.04	12.06	2.96	8.0	4.07	2.40
MK29	G	45	21.86	5.54	1.27	4.9	4.36	3.95
MK57	G	11	27.55	12.77	2.53	7.3	5.05	2.07
MK65	G	56	20.51	15.22	3.17	6.2	4.80	1.35
MK66	G	26	24.65	6.96	1.33	3.8	5.23	3.54
MK59	G	30	31.42	12.90	3.04	5.6	4.24	1.96
MK54	G	98	33.75	7.49	1.80	5.0	4.16	4.51
MK51	M	32	25.35	9.97	2.14	3.3	4.66	2.54
MK58	M	39	37.13	13.55	3.19	7.0	4.25	2.74
MK66	M	58	45.00	9.35	2.77	11.9	3.38	4.81
MK73	M	58	31.42	15.31	3.12	3.8	4.91	2.05
MK55	M	85	73.12	23.79	3.25	7.0	7.32	3.07
Hodgkinson Basin:								
MK84	G	54	39.29	16.09	3.8	8.2	4.23	2.44
MK86	G	64	35.15	15.84	3.75	5.4	4.22	2.22
MK92	M	70	37.78	18.96	3.71	6.4	5.11	1.99
Bendigo Trough:								
MK97	G	85	43.15	16.36	3.42	10.1	4.78	2.64
MK101	M	89	51.62	22.72	3.88	4.3	5.86	2.27

*1 *Lithology*: G = graywacke; M = mudrock.
*2 *Maturity*: for graywackes, (mineralogical maturity index) = [(quartz)/(quartz) + (feldspar) + (rock fragments)] × 100; for mudrocks, (clay maturity index) = [(total clay minerals)/(total clay minerals) + (quartz)] × 100
*3 Data for samples *M216* to *B10* from Chappell (1968) and Nance and Taylor (1977).

ANALYTICAL TECHNIQUES

La, Th, U and Hf determinations were made by spark-source mass spectrometry, using the method of Taylor and Gorton (1977). Precision and accuracy by this method is ~ ± 5% expressed when standard error and detection limits are ~ 0.02 ppm. Modal composition studies on graywackes were done by point counting and mineralogical determinations on mudrocks were done by semi-quantitative X-ray diffraction methods in which the peak areas of different minerals were used as a measure of their relative proportion in the rock. The data are presented in Table I.

RESULTS

Thorium and uranium

Mineralogical maturity and clay maturity indices (defined in Table I), for graywackes and mudrocks, respectively, have been found useful in provenance determination. Th and U abundances in graywackes increase from the Tamworth Trough through Hill End, to the Hodgkinson Basin—Bendigo Trough, in response to change of provenance from andesite, through dacite, to granites and to older sedimentary rocks as is evident from the nature of the detrital grains (Table I). The lithic grains of the Tamworth and Hill End troughs are dominantly microlitic and felsitic types, respectively. The detrital grains of the Hodgkinson Basin and the Bendigo Trough are dominantly polycrystalline and monocrystalline quartz type, respectively. This relationship is also seen in associated mudrocks where there is an increase in Th and U abundances in mudrocks with the increase of clay maturity index (Fig. 1). Mudrocks are generally enriched by ~ 20% in Th and U compared to associated graywackes in each suite. This can be attributed either to selective adsorption of Th and U on clay minerals and their retention in heavy resistates such as zircons, in finer fractions (Adams and Weaver, 1958). Enrichment trends of Th and U in different types of graywackes and mudrocks are similar to trends seen in igneous rocks towards more silica-rich rock types (Heier, 1978).

A low Th/U ratio of around 2.8 is observed in sediments of Tamworth Trough (Figs. 2 and 3). For all other types of graywackes and mudrocks, the Th/U ratios are uniform around 4.5 ± 0.3, independent of the nature of the source-rocks. Highly recycled mudrocks exhibit high Th/U ratios of around 6 because of oxidation of U^{4+} to U^{6+} and its removal as soluble $(UO_2)^{2-}$. Thus the low Th/U ratios (~ 2.5—3.0), typical of island-arc volcanic rocks change rapidly to those typical of sedimentary rocks (~ 4.5). The similarity in the Th/U ratio of graywackes and shales indicates that the Th/U ratio changes before most of the conventional mineralogical or major-element (e.g., K/Na) indices of maturity are affected. Recycling of sediments themselves leads to a further loss of U and an increase in Th/U ratio of ~ 6.

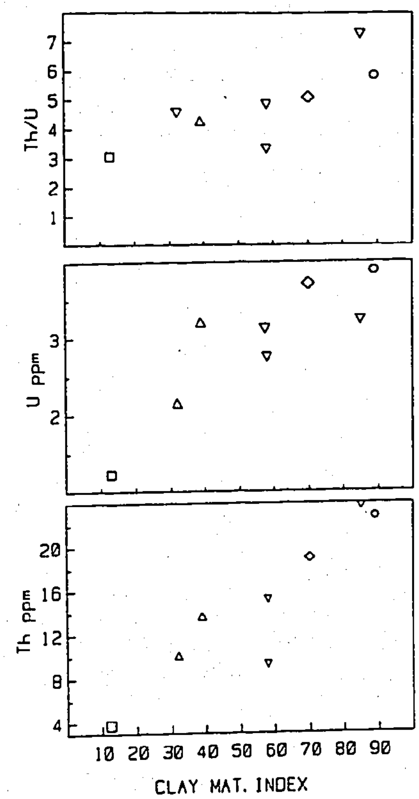


Fig. 2. Variation in Th, U and Th/U ratio with clay maturity index in mudrocks (*open square* = Tamworth Trough; *open triangle* = Hill End Trough (dominantly felsic volcanic detritus); *open inverted triangle* = Hill End Trough [dominantly older sedimentary detritus]; *open hexagon* = Hodgkinson Basin; *open circle* = Bendigo Trough).

Thorium and rare-earth elements

A positive correlation between Th and light REE (expressed as La) occurs in flysch sedimentary rocks (Fig. 4). The influence of the parent-material on La and Th abundances in sedimentary rocks can be well depicted in this plot as graywackes and mudrocks of different tectonic setting occupy distinct fields. Tamworth Trough sedimentary rocks are characterised by low abundances of La and Th and higher La/Th ratios (La/Th = 6.7 ± 2.0). Graywackes and mudrocks from the Hill End Trough occupy a wider field due to mixing of felsic volcanic and sedimentary components in various proportions. Sedimentary rocks, having a La/Th ratio of around 4.5 in this field, consist of detritus dominantly from felsic volcanic sources. The Hodgkinson Basin and Bendigo Trough sedimentary rocks have higher abundances of La and Th in marked contrast to the Tamworth and Hill End troughs. La/Th ratios of most clastic sedimentary rocks (except volcanogenic sediments of Tamworth and Hill End troughs) are ~ 2.6, in agreement with a value of 2.7 reported for the upper crust (McLennan et al., 1980).

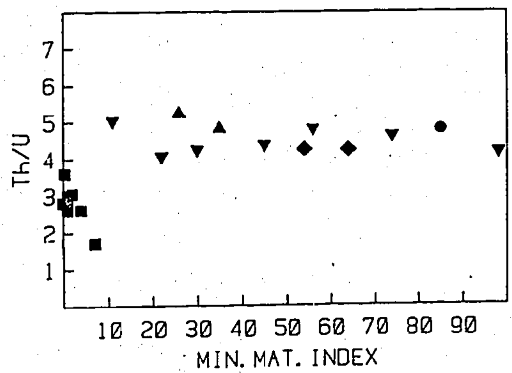
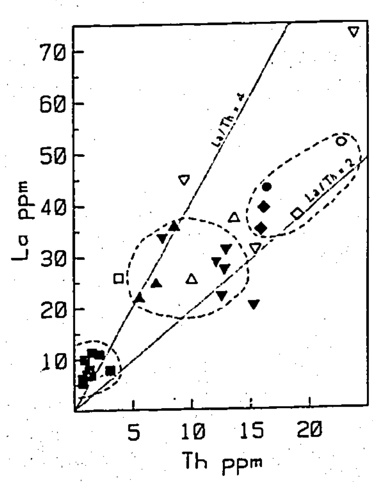


Fig.3. Plot of Th/U ratio vs. mineralogical maturity index in graywackes (*solid square* = Tamworth Trough; *solid triangle* = Hill End Trough [dominantly felsic volcanic detritus]; *solid inverted triangle* = Hill End Trough [dominantly older sedimentary detritus]; *solid hexagon* = Hodgkinson Basin; *solid circle* = Bendigo Trough).



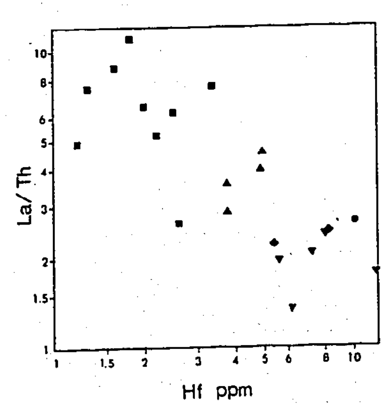


Fig.4. Plot of La vs. Th for graywackes and mudrocks (symbols as in Figs. 1 and 2) (graywackes: *solid* symbols; mudrocks: *open* symbols).

Fig.5. Plot of La/Th vs. Hf (logarithmic scale) in graywackes (symbols as in Fig.3).

Hafnium

Hf shows an inverse relationship with La/Th ratios in graywackes (Fig. 5). Hf increases as the source-rocks change from andesite through dacite to granites and sedimentary rocks as evident from the nature of detrital mineralogy. The enrichment of Hf in graywackes in this manner is analogous to the enrichment of this element in silica-rich igneous rocks due to differentiation (e.g., Erlank et al., 1978). Tamworth Trough graywackes show a low abundance of Hf (~ 2 ppm) similar to the low abundance of Hf in andesites (Ewart et al., 1968; Taylor et al., 1969; Gill, 1970). Graywackes derived dominantly from dacitic rocks (part of the Hill End Trough) show Hf abundances of around 4—5 ppm. All other quartzose and subquartzose graywackes have Hf contents greater than 5 ppm, corresponding to their low La/Th ratio of 2.6 (Fig. 5).

SEDIMENTARY PROVINCES AND GEOCHEMICAL CHARACTERISTICS

In recent years, it has generally been recognised that plate tectonics govern the relationship between sandstone detritus, source-rock and the nature of sedimentary basins (Crook, 1974; Schwab, 1975; Dickinson and Suczek, 1979; Bhatia and Taylor, 1980; Dickinson and Valloni, 1980; Valloni and Maynard, 1981). The present work shows that graywackes deposited on active continental margins (fore-arc basin, e.g. Tamworth Trough) differ significantly from others and are characterised by low abundances of La, Th, U and Hf (Table II). In the inter-arc basin (e.g., Hill End Trough), felsic volcanic material is added from the dissected arc and the graywackes show higher abundances of La, Th, U and Hf. Graywackes deposited on passive

TABLE II

Nature of basin and geochemical characteristics of sedimentary rocks

Tectonic nature	Basin studied	Provenance	Source-rocks
Fore-arc basin	Tamworth Trough	undissected magmatic arc	andesites
Embryonic inter-arc basin	Hill End Trough	dissected magmatic arc	dacites and sedimentary rocks
Rifted continental margin and marginal basin	Hodgkinson Basin and Bendigo Trough	tectonic highlands and recycled orogen	granites, gneisses and sedimentary rocks

*[1] *Lithology*: G = graywackes; M = mudrocks.
*[2] N = number of samples.
*[3] Uncertainties represent 95% confidence limits on the means.
*[4] Means of the individual ratios.

continental margins and collision orogens (rifted continental margins and marginal basins, e.g. Hodgkinson Basin and Bendigo Trough) derive material from granites, gneisses and older sedimentary rocks of the recycled orogen and tectonic highlands, and are highly mature. These are characterised by correspondingly higher abundances of La, Th, U and Hf (Table II).

Sediments of fore-arc basins are also characterised by high La/Th and low Th/U ratios (La/Th = 6.7; Th/U = 2.7). In contrast, except for some volcanogenic sediments of inter-arc basins, most other sediments show uniform high Th/U and low La/Th ratios of 4.5 ± 0.3 and 2.6 ± 0.3, respectively.

Mudrocks associated with graywackes in each basin appear to show similar trends as those in graywackes (Table II) but more data are needed.

CONCLUSIONS

There is an increase in La, Th, U and Hf abundances as the parent-material varies from andesite, through dacite, to granites and sedimentary rocks in response to change of tectonic setting of sedimentary basins from magmatic arc, through inter-arc, to rifted continental margin—marginal basin. High La/Th and low Th/U ratio in graywackes and mudrocks indicates a substantial contribution from volcanic provenances.

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Lithology[*1]	N[*2]	Abundance (ppm)				Th/U[*3,*4]	La/Th[*3,*4]
		La[*3]	Th[*3]	U[*3]	Hf[*3]		
G	9	8.2 ± 1.7	1.4 ± 0.6	0.52 ± 0.2	2.1 ± 0.6	2.8 ± 0.4	6.7 ± 2.0
M	1	25	4.0	1.2	3.5	3.1	6.9
G	9	27 ± 4.5	10 ± 2.7	2.2 ± 0.6	6.3 ± 2	4.6 ± 0.3	2.7 ± 0.9
M	5	42	14.4	2.9	6.6	4.9	3.0
G	3	39 ± 9.9	16 ± 0.6	3.4 ± 0.5	7.9 ± 5.9	4.4 ± 0.8	2.4 ± 0.4
M	2	45	20	3.8	5.4	5.5	2.1

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