HYDROTHERMAL ZONING:

A STUDY OF THE LEAD-ZINC ORES OF ZEEHAN, TASMANIA

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A thesis submitted as a requirement for admission to the degree of Doctor of Philosophy of the Australian National University
Except where otherwise acknowledged in the text, all observational, experimental and interpretative work summarised in this thesis is solely that of the author.

K. L. Williams.
### CONTENTS

**VOLUME I.**

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td>II</td>
<td>Acknowledgements</td>
<td>5</td>
</tr>
<tr>
<td>III</td>
<td>Hydrothermal zoning</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>General review</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Examples of zoned deposits</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>The hydrothermal environment</td>
<td>37</td>
</tr>
<tr>
<td>IV</td>
<td>The Zeehan field</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>Communications, physiography and climate</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>History</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Previous investigations</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>Regional tectonic and stratigraphic setting</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Geology of the Heemskirk-Zeehan district</td>
<td>59</td>
</tr>
<tr>
<td>V</td>
<td>Mineralogy, paragenesis and zonal relationships in the Zeehan ores</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>Previous descriptions</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>The present study</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>Paragenetic relationships</td>
<td>83</td>
</tr>
<tr>
<td></td>
<td>Zonal relationships</td>
<td>163</td>
</tr>
<tr>
<td>VI</td>
<td>Geochemical studies</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>171</td>
</tr>
<tr>
<td></td>
<td>Minor elements in sphalerite</td>
<td>174</td>
</tr>
<tr>
<td></td>
<td>Geothermometric implications</td>
<td>182</td>
</tr>
<tr>
<td></td>
<td>Trace element studies</td>
<td>212</td>
</tr>
<tr>
<td>VII</td>
<td>The Queen Hill ores</td>
<td>285</td>
</tr>
<tr>
<td>VIII</td>
<td>Summary and conclusions</td>
<td>292</td>
</tr>
<tr>
<td></td>
<td>REFERENCES</td>
<td>308</td>
</tr>
</tbody>
</table>
APPENDIX I: The geology, mineralogy and mineral production of individual mines and prospects

APPENDIX II: Analytical methods

Selection of methods

Details of methods:
- Electron microprobe analysis
- Atomic absorption methods
INDEX TO TABLES AND FIGURES.

Table:

<table>
<thead>
<tr>
<th>Table</th>
<th>On or following page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Emmons' &quot;reconstructed vein system&quot;</td>
<td>9</td>
</tr>
<tr>
<td>2. Edwards' general paragenetic sequence</td>
<td>10</td>
</tr>
<tr>
<td>3. Colour and composition of sphalerite</td>
<td>122</td>
</tr>
<tr>
<td>4. Stannite assays</td>
<td>141</td>
</tr>
<tr>
<td>5. Zonal variations in mineralogy</td>
<td>163</td>
</tr>
<tr>
<td>6. Zonal changes in sphalerite composition</td>
<td>175</td>
</tr>
<tr>
<td>7. Mineralogical effects of isothermal changes in bulk chemical composition of sphalerite-bearing assemblages</td>
<td>204</td>
</tr>
<tr>
<td>8. Trace elements in pyrite</td>
<td>225</td>
</tr>
<tr>
<td>8b. Pyrite trace element correlations</td>
<td>237</td>
</tr>
<tr>
<td>9. Trace elements in sphalerite</td>
<td>238</td>
</tr>
<tr>
<td>9b. Sphalerite trace element correlations</td>
<td>255</td>
</tr>
<tr>
<td>10. Trace elements in siderite</td>
<td>256</td>
</tr>
<tr>
<td>10b. Siderite trace element correlations</td>
<td>263</td>
</tr>
<tr>
<td>11. Trace elements in galena</td>
<td>266</td>
</tr>
<tr>
<td>11b. Galena trace element correlations</td>
<td>282</td>
</tr>
</tbody>
</table>

Appendix I:

A1. Electron microprobe analyses of crustified sphalerite A94

Appendix II:

A2. Atomic absorption analytical conditions A177

Figure:

<table>
<thead>
<tr>
<th>Figure</th>
<th>On or following page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2. Locality maps</td>
<td>1</td>
</tr>
<tr>
<td>3,4. Cornwall zoning</td>
<td>14</td>
</tr>
<tr>
<td>5,6. Zoning at Freiberg and Central City, Colo.</td>
<td>19</td>
</tr>
<tr>
<td>7. Zeehan stratigraphy</td>
<td>52</td>
</tr>
<tr>
<td>8,9. Regional structure</td>
<td>52</td>
</tr>
<tr>
<td>10,11. Regional and local geology</td>
<td>59</td>
</tr>
<tr>
<td>12. Mine localities</td>
<td>59</td>
</tr>
<tr>
<td>13. Heemskirk granite</td>
<td>66</td>
</tr>
<tr>
<td>14. Fault and vein patterns</td>
<td>69</td>
</tr>
<tr>
<td>15. Structural evolution</td>
<td>69</td>
</tr>
<tr>
<td>16. Waller's &quot;zoning&quot;</td>
<td>77</td>
</tr>
<tr>
<td>17. Twelvetrees &amp; Ward's zonal system</td>
<td>77</td>
</tr>
<tr>
<td>18-21 Photomicrographs</td>
<td>88</td>
</tr>
<tr>
<td>22-27 Photomicrographs</td>
<td>94</td>
</tr>
<tr>
<td>28-33 Photomicrographs</td>
<td>103</td>
</tr>
<tr>
<td>34-38 Photomicrographs</td>
<td>122</td>
</tr>
</tbody>
</table>

(continued)
vi.

Figures (continued):

<table>
<thead>
<tr>
<th>Figure:</th>
<th>On or following page:</th>
</tr>
</thead>
<tbody>
<tr>
<td>39-42 Photomicrographs</td>
<td>126</td>
</tr>
<tr>
<td>43-44 Photomicrographs</td>
<td>134</td>
</tr>
<tr>
<td>45. Zoning of gangue mineralogy</td>
<td>163</td>
</tr>
<tr>
<td>46. Areal distribution of zones</td>
<td>169</td>
</tr>
<tr>
<td>47. Vertical distribution of zones</td>
<td>169</td>
</tr>
<tr>
<td>48. FeS in sphalerite</td>
<td>174</td>
</tr>
<tr>
<td>49. MnS in sphalerite</td>
<td>174</td>
</tr>
<tr>
<td>50. FeS histograms</td>
<td>174</td>
</tr>
<tr>
<td>51. FeS-MnS correlations</td>
<td>174</td>
</tr>
<tr>
<td>52. FeS in sphalerite as functions of T, $f_{S_2}$</td>
<td>183</td>
</tr>
<tr>
<td>53. Initial sphalerite temperature ranges</td>
<td>188</td>
</tr>
<tr>
<td>54. Projection on FeS-ZnS binary</td>
<td>192</td>
</tr>
<tr>
<td>55. FeS-ZnS-S isotherms</td>
<td>199</td>
</tr>
<tr>
<td>56. Sphalerite alteration compositions and temperatures</td>
<td>209</td>
</tr>
<tr>
<td>57-61 Pyrite scatter diagrams</td>
<td>225</td>
</tr>
<tr>
<td>62-71 Sphalerite scatter diagrams</td>
<td>238</td>
</tr>
<tr>
<td>72-73 Siderite scatter diagrams</td>
<td>256</td>
</tr>
<tr>
<td>74-78 Galena scatter diagrams</td>
<td>266</td>
</tr>
</tbody>
</table>
CHAPTER I: INTRODUCTION

The Zeehan mineral field is located in the vicinity of the township of Zeehan (145° 20' E, 41° 53' S), in the West Coast region of Tasmania (Fig.1). The field covers an area of approximately 25 square miles, between the south-eastern margin of the Heemskirk Granite and the township itself (Fig.2); within and adjacent to the Granite are the tin deposits of the adjacent Heemskirk mineral field, while to the east and north-east are the Dundas, Renison Bell and Rosebery fields.

Between 1887 and 1913 the Zeehan district was a flourishing, though small-scale producer of silver-lead ores. For various reasons (see below), activity since 1913 has been only intermittent, and, with one minor exception, the field has been dormant since closure of the Oceana Mine in 1960. Despite their relative lack of economic success, however, the Zeehan ore deposits have long been of geological interest, since they have been widely quoted as classic examples of zoned hydrothermal ores (e.g. by Park, 1955, and Bateman, 1956). Their reputation in this respect rests on the excellent descriptions of Waller (1903, 1904) and Twelvetrees & Ward (1910); however until the recent work of Both (1966), the ores had never been subjected to detailed mineralogical examination, and lately Hall & Solomon (1962) and Solomon (1965) have questioned the validity of the supposed zoning and have stressed
Fig. 1: Locality map.

Fig. 2: Outcrop of the Heemskirk granite.
the need for more detailed studies. Furthermore, while the general concept of zoning has continued to interest students of ore genesis and many examples have been quoted in the literature (Park, 1955), remarkably few of these examples have been studied in sufficient detail to throw useful light on the geological processes involved or to provide reliable frameworks for laboratory and theoretical studies.

The concept of hydrothermal zoning is presently generally accepted among economic geologists (see Chapter III) but, because of the relative lack of detailed studies, is rather poorly defined. The present investigation was designed to obtain detailed information essential to description and interpretation of zonal regularities in the Zeehan ores, and to provide quantitative geochemical data which might assist in defining the physico-chemical environment of hydrothermal ore deposition in this and other similar deposits.

The author first visited Zeehan in 1957, while investigating the nearby nickel deposits of the Cuni field and at Trial Harbour (Williams, 1958). Several mineralogical features of the silver-lead ores attracted some attention, and, at the suggestion of the late Dr. A.B. Edwards (then Officer-in-Charge of the Mineragraphic Investigations section of the C.S.I.R.O.), a comprehensive collection was made from the workings of the Montana Silver-Lead and Oceana Mines and a pilot study of the geochemistry of Zeehan sphalerites was initiated.
Little of this work was completed before Dr. Edwards' death and the study was later resumed at the Australian National University. In 1964, a more extensive collection embracing as much as possible of the whole field was undertaken. Unfortunately, the author's original collections were no longer available; the present study has therefore necessarily been largely based on dump samples, supplemented in many cases by specimens from the collections of several Australian museums. In relatively few instances could samples be collected from outcrop or from accessible portions of old workings. The limitations imposed by such inadequate sampling are obvious and could be controlled only by careful selection procedures. All material collected was compared with descriptions from reports compiled while the mines were operating, and any doubtful samples were rejected, as were many museum specimens (most of which were poorly documented). The clear mineralogical and geochemical patterns which have emerged from the present study, and the close agreement with other descriptions, indicate that the samples employed were reasonably representative of the ore from the various mines.

In 1964, Mr. R.A. Both, then on the staff of the Tasmanian Museum, Hobart, also began a mineralogical study of the Zeehan ores, with objectives partly overlapping those of this study (Both, 1966). The two investigations were performed independently, and the substantial agreement in the results in areas of mutual
4.

interest further supports the validity of the samples employed and compensates for the unfortunate duplication of effort. Access to, and discussion of, Both's results have materially assisted the present study, and this assistance is gratefully acknowledged.
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CHAPTER III : HYDROTHERMAL ZONING

General review

The phenomenon of zoning of hypogene ore deposits has long been of interest to geologists, largely because of its significance in the study of ore genesis. The establishment of zonal patterns on regional, district or ore-body scales has obvious implications in exploration and development, while in several instances data relating to mineralogical or elemental distributions have thrown considerable light on problems of ore genesis.

The theory of zoning of hydrothermal ore deposits was first stated as a generalization by Spurr (1907), although several geologists (e.g. de Launay, 1900; Collins, 1902; Waller, 1903, 1904) had previously recognised zonal regularities in the mineralogy of individual deposits. In his study of the Zeehan lead-zinc ores, Waller (1904 - see Chapter V) showed that systematic changes in the ore mineralogy were centred around the Heemskirk granite stock, and used these relationships as evidence to suggest that the ore minerals were originally derived from the granite, a relationship which is otherwise by no means apparent in the field (in outcrop the veins are over two miles distant from the nearest granite contact).
Comprehensive reviews of the zonal theory of ore deposition have been presented by Emmons (1940), Park (1955), Park & MacDiarmid (1964), Kutina (1957, 1965) and others, and only a brief summary is presented here.

The district-scale zoning of hypogene ore deposits is generally attributed to changes imposed on ore-bearing fluids as they move upwards and outwards from their source. These changes are presumed to include generally declining temperature and pressure, and chemical changes consequent upon reaction with the wallrocks. As these changes take place, various constituents being carried in solution may successively become unstable and precipitate, causing a sequential (but possibly overlapping) deposition of ore and gangue minerals, regulated along co-ordinates of both time and space. "Each of these depositional dimensions -- time and space -- will be recorded in the ore deposit, leaving the geologist detailed evidence of the evolutionary trends in the ore-forming solution" (Park & McDiarmid, 1964).

* It has been clearly recognised that zoning is not confined to ores of magmatic origin (Park, 1955), but this group includes the majority of observed examples, and in many discussions the "hypogene" or "hydrothermal" qualification is implied (e.g. Kutina, 1965).
9.

The time sequence of mineral deposition constitutes the paragenesis of a deposit, a term which is also used, particularly by European geologists, in the completely different sense of a characteristic mineral assemblage or association. The spatial sequence is described as zoning. The paragenesis is recorded in the ore deposit in terms of the physical relationships, or textures, of the various minerals relative to each other, while the zonal patterns are manifested by systematic changes in gross mineralogy along both horizontal and vertical co-ordinates.

In a series of discussions in which the zonal theory was developed at length, Emmons (1924, 1926, 1933, 1936, 1940) attached particular significance to the role of temperature, and argued that a cooling complex solution, such as a hydrothermal solution passing outwards from a major intrusion, would precipitate its dissolved components sequentially, in the reverse order of their solubilities. While other factors might, in special circumstances, give rise to local anomalies, Emmons believed that in general the dominant effect of temperature would be such as to give rise to an overall sequence of deposition applicable to a wide variety of ore deposits. Based on observed zonal relationships, he postulated a "reconstructed vein system" (Table 1) in which he showed an empirical order of deposition of common ore and gangue minerals, away from a presumed magmatic centre, but recognizing that no single vein could be expected to include all phases of the theoretical system.
### Table 1.

**Generalised Zonal Sequence**

*(after Emmons, 1940)*.

**TOP**

1. Barren: chalcedony, quartz, barite, fluorite. Minor Hg, Sb, As.
3. Antimony: stibnite, often passing into galena with some antimonates, gold.
4. Gold-silver: argentite, As, Sb, tellurides and selenides, quartz, adularia, alunite, carbonates; minor galena, sphalerite, chalcopyrite.
5. Barren: quartz, carbonates, minor sulphides.
6. Silver: argentite, stibnite, sulphosalts, arsenopyrite; quartz, some siderite.
7. Lead: galena, Ag, sphalerite increasing with depth, some chalcopyrite; quartz and carbonates.
8. Zinc: sphalerite, galena, chalcopyrite; quartz, carbonates.
9. Copper: tetrahedrite, chalcopyrite, enargite.
10. Copper: chalcopyrite, pyrite, pyrrhotite; quartz, carbonates, feldspar.
13. Bismuth: bismuthinite, native Bi, quartz, pyrite.
15. Tin: cassiterite, quartz, tourmaline, topaz, feldspar.

**BOTTOM**

*(close to parent intrusion)*
Lindgren (1933) appears to have been rather sceptical of the general applicability of the concept of zoning; he drew attention to the complexity of the factors controlling the precipitation of any one metal from a complex solution (temperature, pressure, solvent, concentration, inter-element effects etc.) and was inclined to doubt the universal application of the zonal theory, although he himself had described several individual examples.

On the other hand, Lindgren (1937), Bastin (1950), Edwards (1954) and others concerned with the study and interpretation of microtextures independently showed that most hypogene orebodies, whether magmatic, hydrothermal, pegmatitic, pneumatolytic or metamorphic, show paragenetic similarities which can be combined into a generalised paragenetic sequence, analogous to and closely resembling Ermons' "reconstructed vein system" (Table 2). It is unlikely that the correlation can be fortuitous, and the coincidence has long been accepted as supporting evidence for the validity of the zonal concept.

Strong emphasis has been placed on hypogene zoning by a number of European geologists, including S.S. Smirnov (1937), Bilibin (1951), Kutina (1957, 1965) and V.I. Smirnov (1960). In particular, this school has been largely responsible for stressing the concept of polyascendant zoning, which recognises that at least part of the control of sequential deposition rests not only with progressive changes in chemical and physical parameters...
Table 2.

Generalised Paragenesis.


EARLY

1. Magnetite, ilmenite, chromite, hematite.

2. Cassiterite, tantalite, wolframite, molybdenite.

3. Pyrrhotite, pentlandite, löllingite, arsenopyrite, pyrite, cobalt and nickel arsenides.

4. Chalcopyrite, sphalerite, bornite.

5. Galena, tetrahedrite, lead and silver sulphosalts, native bismuth and bismuthinite (cf. Table 1), tellurides, stibnite, cinnabar.

LATE

Gangue minerals tend to an ordered sequence from early quartz, tourmaline and topaz to late siderite, fluorite, calcite, barite and chalcedony.
along spatial co-ordinates, but also with time changes in the composition of the ore solutions as they are derived from their magmatic source. In other words, the generation of ore fluids is viewed as a (possibly intermittent) process taking place over a substantial time interval during the crystallization of the parent magma. Under these circumstances, progressive changes in the source composition of the mineralizing solutions would be reflected in systematic variations in both paragenetic and zonal relationships. Vol'fson & Nevskii (1949) emphasised the role of structural factors in the development of hydrothermal zoning, and suggested that it should be viewed as the product of parallel evolution of the ore-forming solutions in time and ore-containing fissures in space.

Pouba (1963) introduced the term polymagmatic zoning to describe relationships in the Vysoky Jesenik Mountains of Czechoslovakia where, in his opinion, Sn - W - Mo mineralisation accompanied the intrusion of granites into a region carrying an older Cu - Pb - Zn mineralisation.

The concepts of polyascension and polymagmatism were extensively discussed at the 1963 Prague Symposium on the Problems of Postmagmatic Ore Deposition (Kutina, 1963; Stenprok, 1965). Various criteria for the recognition of these processes were proposed, leaving no doubt as to the significance of the time dimension in the establishment of hydrothermal parageneses and zonal patterns. For example, hydrothermal leaching and re-deposition
such as that described by Sims & Barton (1961) and Barton, Bethke & Toulnin (1963) is evidence for changing solution-mineral equilibrium conditions.

Although many contributors to the Prague Symposium do not seem to have recognised the fact, Emmons (1940) had clearly described many of these complications. Thus he stated "In certain districts the mineral deposits do not show regular zones. The irregularities and reversals in arrangements in the positions of the deposits may be due to 1. overlapping of deposits from two or more magmatic centres; 2. retreat or advance of magmatic centers during one period of deposition; 3. deposition in a single area in different epochs of mineralization; 4. other causes not understood".

Spurr (1925) drew attention to the confused paragenesis and "telescoped" zonal relationships characteristic of some hydrothermal veins, notably those emplaced in the "subvolcanic" (Borchert, 1951) or "xenothermal" (Buddington, 1935) environment. Spurr supposed the telescoping to be due to the abrupt release of volatile "mineralizers", affecting the solubilities of the ore mineral constituents. Borchert, on the other hand, attributed it simply to the steep pressure and temperature gradients characteristic of the subvolcanic environment, producing virtually simultaneous saturation and precipitation of various components which, under less severe gradients, are commonly zoned. A survey of the literature descriptions of many zoned deposits suggests that some
degree of telescoping is characteristic of most zoned deposits, including mesothermal and epithermal types.

Zoning may be manifested in many ways, from the gross changes in type of mineralization observed on a regional scale (e.g. the Southeastern Piedmont Province of the U.S.: Pardee & Park, 1948), through systematic variations in ore and gangue mineralogy on a district scale (such as those at Zeehan) to subtle variations in minor element chemistry within a single vein or orebody, such as variations in the fineness of gold in the veins of the Kolar field of India (Pryor, 1923). The following brief descriptions have been selected to illustrate the relationships typically observed in hydrothermal deposits resembling the Zeehan ores, and to summarize those mineralogical and chemical features which commonly show zonal regularities in their distributions.

Examples of zoned deposits

Cornwall-Devon, England:

The tin-copper mineral field of Cornwall and Devon has long been recognised as a classical example of district-scale zoning. Stocks and associated satellitic bodies of Permo-Carboniferous granite intrude a complexly folded and faulted sequence of Paleozoic sediments and intercalated pre-granite basic bodies. Mineralization is most intense in the centre of the batholithic area, where it is concentrated along granite "cusps" and subsurface granite ridges (Hosking, 1951, 1963, 1964). Economic minerals are found in pegmatites, in swarms of greisen-lined veins
in the apices of the granite "cusp", and in large complex lodes transgressing the granite-sediment contacts.

Davison (1927) recognised four principal zones of mineralization, viz:

1. Tin zones, largely confined to the granite cusps but extending into the intruded sediments, and commonly overlapping with (2).

2. Copper-arsenic-tungsten zones. The overlap with tin zones may be extensive, and in many instances copper and tin were mined together (e.g. the Dolcoath Main Lode - see Hosking, 1963, 1964).

3. Lead-zinc-silver zones (with minor U, Co, Ni, and Bi).

4. Outermost "iron" zones, containing pyrite, marcasite, siderite, hematite and goethite in association with antimonial sulphosalts.

The spatial distribution of the zones reflects the general form of the granite contacts, but the zones do not parallel the contacts exactly. Hosking (1951) has shown that the zone boundaries are of flatter dip than the contacts, so that the tin zones, for example, tend to be confined to the granite near cusp apices, but to pass into the sediments down the flanks of the intrusions (Fig.3). Hosking also showed that the zoning was a little more complex than had previously been supposed; he recognised seven zones, which he divided into hypothermal (Fe-Sn-W-As-Cu) and mesothermal (Pb-Ag-Zn-U-Co-Ni-Bi-Sb-Fe) groups. The former are
Fig. 3: Zoning at Cornwall, U.K. (after Hosking, 1951)

Fig. 4: Diagrammatic representation of zonal and paragenetic relationships in the Geevor Tin Mines, Cornwall. (Simplified after Garnett, 1963.)
largely confined to the contact metamorphic aureole, while the latter tend to lie outside it; in both cases, however, there are many instances of overlap. Paragenetically, the hypothermal minerals appear to be older than the mesothermal group; hypothermal veins tend to strike parallel to the granite ridges, and in places they are displaced by mesothermal lodes, which tend to strike at right angles to the ridges. The greisen-bordered swarms in particular are partly "telescoped"; thus Hosking (1963) describes a quartz-tourmaline-cassiterite vein at St. Agnes which is separated by only a few feet from a parallel sphalerite-chalcopyrite-fluorite vein.

Hosking (1963) concluded that it is "difficult to escape from the conclusion that temperature gradients established between the granite and the land surface played an important role in the development of the primary zones...and a few lodes...were developed before the last of the granite had been emplaced......". He also noted that "Doubtless factors other than temperature played some part in determining the sites of deposition of the ore minerals...impounding bodies and the variation in the extent of fracturing were, on occasion, important limiting factors".

The time parameter was stressed by Cronshaw (1921), who listed ten separate phases of mineralization; the ore fluids were considered to have differed in composition during each phase as a consequence of progressive differentiation of the ore fluid at its source (i.e. "polyascendant zoning"). Weston-Dunn (1923)
(quoted by Garnett, 1963) considered the zoning to have arisen from differentiation of the ore fluid during its passage through the lodes, and Webb (1947) proposed that the two processes operated in conjunction.

In a detailed study of the accessible workings of the Geevor Tin Mine, Garnett (1963, 1966) traced a complex sequence of thirteen mineralization stages (Fig. 4), giving rise to an overall zoning. Within individual stages spatial zoning is not clearly defined, with the exception of "phase 9" (cassiterite + sulphides) and "phase 10" (sulphides). A distinct break between these two stages marked the onset of declining temperature of mineralization, causing pronounced telescoping of the later "phases", amounting to reverse zoning in places, and to some rejuvenation (leaching and subsequent re-precipitation of earlier phases). It seems highly probable that this mechanism, rather than the "dumping" mechanism of Spurr or Borchert, might account for many observed instances of telescoping, although temperature may not always be the controlling factor.

Hosking (1964) noted general tendencies for the iron content of wolframite to increase, and that of sphalerite to decrease, towards the later stages of the paragenetic sequence. El Shazly, Webb & Williams (1957) described parallel increases in the Ge and Ga contents of sphalerite, and decreases in In, Mn and Sn in sphalerite and Bi and Sn in galena.

It is unfortunate that the vast majority of the Cornish
deposits are no longer accessible, for they have been described in only limited mineralogical detail, and many chemical variations can now be studied only in terms of old assay data. There is, however, no question of the validity of the zonal relationships (particularly when they are considered in terms of both time and space), and the field will doubtless continue to be quoted as a classical example of the phenomenon.

**Freiberg:**

The ore veins of the Freiberg district are situated in the pre-Variscan crystalline basement rocks of the Erzgebirge Mountains. Gneisses, quartzites, schists etc. are intruded by Variscan and Tertiary granites, quartz porphyries and lamprophyres. Within the Freiberg field, a complex system of hydrothermal fissure veins is developed above a hypothetical pluton which has not been exposed, but whose topography has been inferred from geophysical data and from a well-developed zoning in the mineralogy and minor-element geochemistry of the hydrothermal veins. The following description is condensed from that of Baumann (1965).

Throughout the long history of mining in this region it has been recognised that the ore veins are not homogeneous, but that several ore formations or "parageneses" (in the European sense) can be recognised, as follows:

**I. Pyritic Lead Formation (Kiesig-blendige Bleierz, or "kb")**

1. **Pyrite"paragenesis"** (Quartz-arsenopyrite-pyrite-pyrrhotite)
18.

2. Zn-Sn-Cu"paragenesis" (Sphalerite-stannite-chalcopyrite-tetrahedrite-bornite)

3. Pb"paragenesis" (Quartz-galena)

II Hematite-barite Formation (Roteisen-Barytformation, or "eba") "Hornstone", barite, oxides of Fe, Mn, U, quartz, fluorite.

III Noble Carbonate Formation (Edle Braunspatformation, or "eb")

1. Sulphide"paragenesis" (carbonates with redeposited kb-sulphides)

2. Silver "paragenesis" (freibergite, jamesonite, pyrargyrite, argentite)

IV Fluorite-barite Lead Formation (Fluorbarytische Bleierz-formation or "fba")

Quartz, barite, fluorite, tetrahedrite, galena, sphalerite (schalenblende), melnikovite-pyrite, marcasite.

V Bi-Co-Ni-Ag formation (Edle Geschicke)

1. Arsenide "paragenesis" (Quartz, barite, fluorite, Co-Fe-Ni arsenides, pitchblende, native Bi and As)

2. Silver sulphide "paragenesis" (Carbonates, redeposited sulphides, argentian sulphantimonides, argentite, native silver, quartz, barite, fluorite)

Formations I, II and III are assigned to the Variscan metallogenesis, or "first cycle"; they are described as katathermal, mesothermal and epithermal respectively. Formations IV and V are
attributed to a second, Cretaceous-Tertiary cycle of mineralization.

Paragenetic relationships correspond with the zonal distribution; two zone sets can be distinguished, with the first (corresponding to the first or Variscan cycle) being largely confined to a N-S trending vein system and the second (Cretaceous-Tertiary) to an E-W trending system.

Despite marked telescoping, four zones can be distinguished in the Variscan veins, centred about an axis between Tuttendorf and Muldenhütten (Fig. 5; comprehensive diagrams showing zonal and paragenetic relationships in the Freiberg ores are presented by Baumann, 1965).

Zone 1: Oldest kb (pyrite-quartz) paragenesis; genetically the lowest depositional horizon in the district. Characterised by high Bi ( > 0.1%) in galena.

Zone 2: kb (Zn-Pb) paragenesis; sphalerite has high stannite and chalcopyrite contents; Bi in galena averages approximately 0.01%.

Zone 3: Minor kb and increasing eba and eb parageneses; Bi content of galena is low (less than 0.001%).

Zone 4: Sporadic eb paragenesis.

The four zones together cover an outcrop area approximately 12 km x 9 km.

Mineralogical and structural features of the Freiberg zoning have been closely studied, and in addition some data concerning minor element variations in several key minerals have been collected.
Fig. 5: Zoning at Freiberg.

Fig. 6: Zoning at Central City.
20.

These have been summarised by Baumann as follows:

A. Sphalerite: "Trace elements in the Freiberg sphalerite show a clear dependence on the mode of origin, especially the temperature of formation" (p.62). Three internally consistent groups of trace elements can be distinguished.

1. **Fe, Mn, Cu, Co, In, Ga**: All decrease in concentration with "decreasing temperature of formation". All show their highest concentrations (12% Fe, 0.4% Mn, 1.6% Cu, 40 ppm Co, 1000 ppm In, 10 ppm Ga) in kb-sphalerites of the central zone. In and Co appear to be markedly temperature dependent in their distribution.

2. **Sn, Cd**: Maxima for these elements (1.2% Sn, 8000 ppm Cd) are observed in mesothermal kb- and eb-sphalerites. Much of the tin occurs as stannite inclusions.

3. **Tl, Ag, Ge**: Maxima (600 ppm Tl, 1.0% Ag, 1000 ppm Ge) observed in epithermal (eb) sphalerite, often in schalenblende.

The regional distributions of the various trace element maxima correspond closely with the zonal trends observed in the ore mineralogy; temperature is assigned a dominant role in explaining both mineralogical and geochemical relationships.

B. Galena; According to Baumann, bismuth contents in the kb-galena can be used to plot isothermal surfaces "because they are inserted, depending on temperature, in the galena lattice in the form of
α-schapbachite (α-AgBiS₂). The isothermal surfaces so derived coincide closely with paragenetic surfaces and parallel the distributions of the sphalerite trace elements.

The Freiberg ores, although relatively complex, show some distinct resemblances to the Zeehan lodes, and the minor element data reported by Baumann encouraged the undertaking of much of the geochemical work reported in the present study.

Central City District, Colorado:

Clear mineralogical zoning in the hydrothermal ores of the Central City District, on the east flank of the Front Range, Colorado, has been described in detail by Sims (1956) and Sims, Drake & Tooker (1963); significant geochemical aspects of the zoning have been reviewed by Sims & Barton (1961, 1962). Although the literature pertaining to the district is extensive, the essential features of the zoning are well described in these papers, from which the following brief summary has been prepared.

The ore deposits are mesothermal veins, genetically associated with early Tertiary (Laramide) hypabyssal intrusions into Precambrian gneisses and intrusive granitic rocks. Although the lodes contain lead, zinc, copper and uranium minerals, they were mined principally for gold and silver and in fact the zonal relationships were first described by Collins (1904) in terms of systematic variations in silver-gold ratios. Native gold and silver are rare; both occur mostly in the structures of sulphides and sulfo-salts.
22.

The ore minerals were deposited as structurally controlled shoots, in open space fillings located in discontinuous pre-ore faults. The wallrocks were uniformly altered, showing initial argillization grading into intense sericitization; there is no evidence, however, for any chemical control of ore deposition. There is no regional zoning in the mineralogy of the wallrock alteration, although the width of the alteration envelope decreases in the outer zones.

The hydrothermal zoning is manifested by gradual lateral changes in mineralogy, metal content, metal ratios and some minor-element distributions. Sims (1956) distinguished four concentrically disposed zones (Fig.6), with gradational boundaries, as follows:

1. **Central zone:** A NE-trending elliptical area, approximately 3 miles long and 1 mile wide, is characterised by quartz-pyrite veins which, near the outer margin of the zone, also contain copper minerals (chalcopyrite, tennantite, enargite), minor sphalerite, and much of the economically significant gold mineralization of the field. Silver-gold ratios are low. The quartz is dominantly a white to grey, coarsely crystalline, massive variety.

2. **Intermediate zone:** Quartz and pyrite, similar to those of the Central zone, persist over most of the intermediate zone, although pyrite declines rapidly in
abundance near the outer margins of the latter. Copper mineralization continues but rapidly becomes economically unimportant; tennantite shows a wider dispersion than chalcopyrite or enargite. Sphalerite and galena become abundant in the intermediate zone, generally associated with a massive crystalline quartz gangue but occasionally with small amounts of carbonate gangue. Gold values decline towards the outer margin of the zone, but silver values increase. The intermediate zone varies from 2000 to 5000 feet in outcrop width.

3. Peripheral zone: This zone ranges from 1000 to 4000 feet in outcrop width. Pyrite is relatively rare, and galena and sphalerite reach their maximum relative abundances in the inner part of the zone; thereafter they both decrease in abundance passing outwards. Quartz gangue is still abundant, but is chaledonic rather than massive crystalline; rhombohedral carbonates, and locally barite, become abundant. Gold values are low but silver values, although variable, generally increase passing outwards. The approximate coincidence of maximum silver grades with the first substantial zonal appearance of vein carbonates has also been observed at Zeehan, and, as indicated below, may have some geochemical significance.
4. Barren zone: Low grade veins containing galena in a gangue of Ca and Fe-Mn carbonates, cryptocrystalline quartz, and barite occur outside the Peripheral zone, but are seldom of economic grade (a few contain sporadic pockets of silver ore).

Paragenetically, the veins of the Central City district appear to have been formed during a single period of mineralization, broken into three distinct stages separated by recurrent, synchronous fault movements. A quartz-pyrite-pitchblende stage was followed successively by a quartz-pyrite stage and a base-metal sulphide stage. The paragenetic relationships have been studied in detail, and generally agree closely with the observed zonal sequence.

Sims & Barton (1961, 1962) attempted to use the sphalerite geothermometer to delineate the thermal gradient associated with the mineralization. Sphalerite is a common constituent of the base-metal mineralization phase in the Intermediate and Peripheral zones and was also observed in the Central and Barren zones; it varies markedly in colour from light grey or pale yellowish brown through to dark reddish brown. The darker varieties are in general characteristic of the inner zone, but much of the sphalerite is growth-zoned - adjacent growth-zones visible in thick sections were found by Sims & Barton to vary in iron content by as much as 14 mole per cent FeS. Growth-zoning is most pronounced in sphalerites from the Peripheral zone and the outer part of the
Intermediate zone.

The analyzed sphalerites were found to contain from 0.05 to 12 weight per cent iron, together with detectable amounts of several minor elements. At the time the Central City study was being undertaken, the concept of sphalerite geothermometry (Kullerud, 1953) was being revised to take account of the effect of sulphur fugacity on the substitution of Fe for Zn in the sphalerite structures. On the basis of the experimental data then available, and in the light of restrictions imposed on the possible range of sulphur fugacities by the presence of certain other sulphide minerals coexisting with the sphalerites, Sims & Barton concluded that the iron contents indicated that "the sphalerite was deposited in the Central City district over a temperature range from about 150°C at the margins to at least 620°C in the inner parts, with even larger variation possible".

Following further experimental studies in the system Fe-Zn-S (Barton & Toulmin, 1966), the equilibrium relationships between sphalerite composition, temperature and sulphur fugacity have been further revised. In particular it has been shown that the composition of sphalerite crystallizing in equilibrium with pyrrhotite is not independent of sulphur fugacity, as had previously been thought (Barton & Kullerud, 1958). The temperatures of crystallization quoted by Sims & Barton therefore require some modifications which are, however, not extensive, since none of the Central City assemblages lie in the drastically revised
pyrrhotite field and since fairly wide limits were quoted for many of the original estimations because of the possible range of sulphur fugacities. It appears probable, however, that the maximum figure of 620°C for sphalerites of the inner zone is a little high. The data of Barton & Toulmin (1966) show that the 20 mole per cent FeS sphalerite isopleth virtually coincides with the pyrite-pyrrhotite equilibrium curve on a T/fS2 plot between 450°C and 600°C. At higher or lower temperatures, sphalerite of this composition can crystallize only in equilibrium with pyrrhotite. Thus the inner zone sphalerites must have crystallized within this temperature range. The corresponding possible range in sulphur fugacities is 10⁻² atm. (600°C) to 10⁻⁶ atm. (450°C).

Slight adjustments are also suggested for crystallization temperatures in the intermediate and low temperature ores, and in several instances permit reconciliation with otherwise anomalous temperatures estimated from fluid inclusion filling data. Thus growth zones in a sphalerite crystal from the Carroll Mine were found to range in composition from 2.4 to 10.6 mole per cent FeS. The best estimate for the filling of fluid inclusions in the lightest zone was 230°C; the composition of the dark zones, however, was thought to indicate a minimum temperature of at least 400°C, despite the improbability of temperature fluctuations of this magnitude during the growth of a delicately zoned crystal. Although the extrapolations involved in the newer data of Barton & Toulmin are admittedly tenuous, they indicate a possible temperature...
range of approximately 220-700°C for the dark Carroll Mine sphalerite, and in fact they suggest that the growth zoning could have resulted entirely from fluctuations (of little more than an order of magnitude) in sulphur fugacity at a constant crystallization temperature of 230°C, as indicated by the fluid inclusion data.

Sims & Barton concluded that the Central City mineralization resulted from hypogene mineralizing solutions which "moved upward and outward from the region beneath the central zone. The solutions cooled rapidly in the vicinity of the intermediate and peripheral zones, first by a Joule-Thomson expansion through constrictions, and then by mixing with ground waters. The resulting hybrid solutions then moved outward (in a relative sense) to form the outlying deposits....details of the thermal pattern remain unknown....The S₂ activity also decreased outward, but to an extent such that more sulphur-rich assemblages, that is, enargite and iron-poor sphalerite (+ pyrite) could form marginally".

Sims & Barton noted that the temperature-sulphur fugacity trends differ somewhat from those deduced for the Butte ores by Sales & Meyer (1949), and might possibly be explained by shifts in equilibria within the ore fluids as they cooled, rather than by chemical fixation of sulphur by reaction with wallrocks. This observation is consistent with the "main-line" limitations on the composition of cooling hydrothermal fluids proposed by Holland (1965).
Interpretation of the trace element data of Sims & Barton (1961) and of Sims, Drake & Tooker, (1963) was hampered by the restricted number of samples analysed and the semi-quantitative nature of some of the analytical techniques employed. The following general relationships were observed:

1. The manganese content of Central City sphalerite varies widely, from 7 to 2800 ppm, and shows a positive correlation with iron content. Studies of the partition of manganese between sphalerite and pyrite were thwarted by the limited (surficial) equilibrium between these minerals; partition between sphalerite and carbonate gangue minerals was not considered.

2. Cadmium contents in sphalerites vary from 3000-7000 ppm, but are commonly close to 3000 ppm and show no correlation with iron content.

3. Indium is present in all sphalerites containing more than 0.5 per cent Fe.

4. Bismuth, molybdenum and mercury in sphalerites are erratic and generally sparse.

5. Bismuth, cadmium and antimony are present in most galena samples and possibly occur in the galena structure.

6. The dominant trace elements in pyrite are Ti, Mn, Bi, Co, Cr, Ni, Mo and Zr. Cd, Ga, In and V occur sparsely
in some samples.

In general, trace element data were inadequate to attempt to trace any systematic zonal patterns.

Central District, New Mexico, and Bingham District, Utah:

Although the zonal relationships in ore deposits from these districts differ in some respects from those of Zeehan and of the examples previously cited, brief descriptions are included here because of the studies of Rose (1961, 1967), which are among the few reasonably comprehensive attempts yet described to examine systematic trace element variations in zoned ore deposits, on a district scale.

In the Central District of New Mexico, metal zoning is well developed around a number of early Tertiary granodiorite to quartz monzonite porphyry stocks emplaced in Paleozoic to Cretaceous sediments overlying a Precambrian granite-gneiss-schist-greenstone basement. The zonal relationships are complicated by the spatial proximity of several of the stocks, with ensuing polymagmatic overlap of mineralization derived from the several centres.

At Santa Rita, chalcopyrite, pyrite and molybdenite were deposited within a granodiorite porphyry stock, and magnetite, pyrite and chalcopyrite in the contact zone, grading outwards to copper-zinc and finally zinc mineralization. On the south lobe of the Hanover stock, magnetite was deposited close to the contact, and grades outwards to zinc ores in which the proportion of lead
and silver (and copper in the vicinity of the Santa Rita stock) progressively increases. Similar zoning is evident at the north end of the Hanover stock and along the Barringer Fault (Rose, 1967). In general replacement processes appear to have been prominent during crystallization of the ore minerals, by contrast with the predominantly fissure-filling types previously described.

Rose used emission spectrographic techniques to examine the trace element contents of chalcopyrite and sphalerite, on single crystal, single polished section, single ore-body and district scales.

In the case of chalcopyrite, the district scale survey allowed subdivision of the samples studied into four groups which reflect geographic and host-rock controls but which, apart from a possible lateral decline in manganese contents away from the intrusives, show no clear zonal patterns.

In the Central District sphalerites, surveys of the iron contents (Rose, 1961) yielded FeS contents (wt. per cent?) ranging from 1.96 to 19.8. Most of the sphalerites analyzed occurred intergrown with pyrite; ten analyzed specimens were reported to contain pyrrhotite + pyrite, but in some instances the pyrrhotite occurred as "exsolution" blebs which reflect post-crystallization changes and do not imply buffered sulphur fugacity during the original deposition of the sphalerite. Rose interpreted these compositions as indicating sphalerite crystallization at minimum temperatures up to "slightly over 600°C", based on the data of
Barton & Kullerud (1958). Again the more recent data of Barton & Toulmin (1966) suggest that 600°C should be regarded as a maximum rather than a minimum for the high iron sphalerites (except possibly for rare samples, such as one from the Blackhawk Mine which was reported to be intergrown with pyrrhotite with no pyrite).

Regardless of theometric implications, a plot of sphalerite FeS contents against distance from the nearest stock shows a clear parallel to zonal changes in the Zn/Pb ratio (Rose, 1961, Figs. 3 and 6).

Although Rose noted that sphalerites coexisting with pyrrhotite and pyrite generally have higher iron contents than those with pyrite alone, it is also significant that compositions of the former range from 9.1 to 19.8 per cent FeS (quoted in the text) or 5.65 to approximately 20 per cent (listed in Rose's Table 2a). This variation is not expected from the experimental equilibrium data reported by Boorman (1967), and will be further discussed in a later chapter.

The data for cadmium in sphalerite show geographic groupings analogous to those described for chalcopyrite. Within individual groups, cadmium contents are apparently uniform and show no zonal variations parallel to the iron trends.

By contrast, cobalt contents in sphalerite show considerable variation, from less than 10 to 1000 ppm; part of this variation results from a lateral zoning away from the intrusives, with the
cobalt contents decreasing parallel to those of iron. Despite its statistical significance, the correlation is relatively poor, and Rose suggested that factors other than the zoning are involved in determining the cobalt content. "Vugginess", and the relative abundance of carbonate minerals, galena, euhedral quartz and chalcopyrite blebs all show an empirical correlation with low cobalt contents, but the true controlling factor is not apparent. There is a possibility that the low-cobalt sphalerite is paragenetically later than the high-cobalt varieties, and the difference may be due to polyascendant mineralization.

Indium, silver and bismuth contents are also variable, but not clearly related to zonal regularities. These elements appear to increase in the vicinity of abundant chalcopyrite blebs (even on a single polished section scale), in contrast with the opposite relationships displayed by cobalt.

Manganese, gallium and possibly tin and germanium are laterally zoned away from the stocks, with manganese decreasing and the other elements increasing outwards.

In the Bingham District, Utah, zoning is well developed around the central granite porphyry of the Bingham stock. Disseminated copper and molybdenum sulphides occur mostly within the stock, with chalcopyrite the main copper mineral, associated with hypogene chalcocite, digenite and bornite in the central part of the ore zone. Replacement copper deposits are associated with
calc-silicate alteration of limestones adjacent to the southwest contact of the stock; passing laterally outwards, the calc-silicates merge into white marble and then into black limestones. The change from marble to limestone closely parallels a change from pyritic copper ore to lead or lead-zinc ore.

Minor lead-zinc mineralization also occurs to the northeast of the Bingham stock. Although replacement orebodies again predominate, some lead-zinc ore occurs in veins or fissures transecting the limestone.

Paragenetic relationships are complicated, with chalcopyrite in particular showing variable age relationships, possibly due to polyascension (Rose, 1967).

Lateral zoning of some trace elements in Bingham chalcopyrite reflects in part some similarly zoned mineralogical features. Thus within the pit, the abundance of indium parallels the distribution of bornite, chalcocite and digenite in the central zone. The abundance of indium declines in the outer portions of the pit, but, however, increases again to a pronounced maximum in the peripheral lead-zinc areas. Manganese and silver show similar tendencies to abundance in the peripheral ores, and relative impoverishment in the inner zones. Bismuth, tin and possibly nickel also tend to be most abundant in chalcopyrite associated with chalcocite, digenite and bornite, but they do not appear to be enriched in the peripheral ores.

Bingham sphalerites were divided by Rose (1961) into two
groups, characterised by high and low iron contents respectively. All coexist with pyrite; although pyrrhotite has been reported from Bingham, none was observed in the samples examined by Rose. Systematic trends are difficult to define, although Rose reported a statistically significant tendency for sphalerites from one limestone horizon to increase in iron content with increasing depth in the mine.

The high-iron sphalerites are characterised by low gallium, and vice versa; germanium may show a similar distribution to gallium, but the trends are less clearly defined. There is some evidence for a lateral zoning of gallium contents.

Surprisingly, Rose (1967) observed no correlation between the iron and manganese contents of Bingham sphalerites; in fact, the highest manganese contents were reported from very low iron sphalerites.

Following the suggestions of Bethke & Barton (1959), Rose (1967) examined the partition of Ag, Bi, Cd, Co, In, Mn and Ni between sphalerite and chalcopyrite samples from both the Central and Bingham districts. Apart from suggestions that Ag, Mo and Sn generally tend to be concentrated in chalcopyrite rather than sphalerite, and that Cd, Co, In and Mn show the opposite tendency, no meaningful relationships appeared; certainly no systematic changes in measured partition coefficients which could be related to systematic variations in temperature and/or pressure of mineralization were observed. It appears that in most instances
the two minerals did not crystallize or remain in "trace element equilibrium".

Many other examples of zoned mineral deposits have been described, although relatively few have been subjected to quantitative mineralogical or chemical study. In some instances, it is clear to the critical eye that the evidence on which the postulated zoning is based is rather vague and uncertain. Thus Park (1955), in one of the most comprehensive reviews of zonal theory yet published, chose the Zeehan field as the first of four "classic" examples, despite the fact that no data more recent than those of Twelvetrees & Ward (1910) and Ward (1911) had been published concerning this field, and there were obvious inconsistencies in their descriptions and interpretations. Likewise Blanchard (1947), although recognising the probable existence of zoning in several districts, in summary expressed considerable dissatisfaction with the existing status of the zonal theory. He concluded: "in order that the hypothesis of mineral zoning may be suitably evaluated ....and more fully elucidated.... there is need for an earnest, judicial and far more detailed study of its expression than has been accorded it in the past; for a more liberal presentation.... (of)....pertinent results relating to the concept; and for an objective re-examination of the published literature to ascertain the degree to which assertions of zonal expressions have been based....upon adequate factual evidence on the one hand, and upon
incomplete observation, faulty evidence, or mere assumption on the other". Similarly Park (1955) noted that even the relatively recent descriptions of zoning in Cornwall-Devon "are almost entirely descriptive, and very few supporting chemical or physical data are given".

Despite these limitations, there is no doubt that the zonal theory has won general acceptance in most quarters, as exemplified by Park's (1955) conclusion that "Composition zoning is a fact. It is widely recognized and is generally accepted in many mining districts". On the other hand, the causes of zoning are still not clearly understood. Although Emmons believed temperature to be the most important controlling factor through its effect on mineral solubilities, it was soon shown that common zonal and paragenetic sequences do not coincide with those predicted from simple chemical solubilities. Suggestions that relative solubilities may in some cases be reversed at high temperatures (Magnée, 1932) have not been substantiated by laboratory studies, and in fact it has been convincingly demonstrated (e.g. Krauskopf, 1951) that aqueous solubilities of most minerals are too low to constitute feasible mechanisms of ore transport. Genetic significance has been attached to many other mineralogical properties, including melting points, boiling or sublimation points, hardnesses, cation ionization potentials, free energies and enthalpies of formation etc., but it is difficult to conceive of any of these as properties directly controlling sequential
precipitation. It is much more likely, as Barnes (1962) has suggested, that each of these properties is in fact a secondary consequence of one or more as yet unrecognized primary controlling parameters.

Whatever these parameters may be, it seems probable that zonal and paragenetic sequences reflect changes in the physico-chemical environments of ore deposition. In conjunction with laboratory investigations of mineral stabilities, detailed studies of zonal relationships should therefore assist in limiting the possible range of environments of hypogene mineralization, which at present remains one of the major problems of geology.

The hydrothermal environment

The present state of knowledge concerning the physico-chemical environment of ore deposition has been reviewed by Barton (1959) and Krauskopf (1967), and may be briefly summarised as follows:

1. **Composition:** The dissolved constituents of ore-forming solutions, apart from the metals and sulphur necessary to form the ore minerals, consist largely of silica, the cations $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{++}$, $\text{Mg}^{++}$, and the anions $\text{Cl}^-$, $\text{HCO}_3^-$ and $\text{SO}_4^{--}$. The most abundant ions are $\text{Na}^+$ and $\text{Cl}^-$, and studies of the compositions of fluid inclusions indicate that these may be highly concentrated. $\text{CO}_2$ may be several orders of magnitude more abundant than $\text{H}_2\text{S}$, but a dense $\text{CO}_2$-rich phase is
unlikely.

At elevated temperatures, the normal concepts of "acids" and "bases" are difficult to apply, and present data do not permit the pH's of hydrothermal fluids to be precisely defined. However, marked departures from neutrality are unlikely because of the buffering effects of the wallrocks; strongly acid solutions would be expected to react with silicates and carbonates, and strongly basic solutions would be neutralized by silica. Similarly, recurrent features in the mineralogy of many hydrothermal deposits have led Holland (1965) to conclude that the possible ranges of fugacities of $\mathrm{CO}_2$, $\mathrm{S}_2$ and $\mathrm{O}_2$ at any temperature are limited by chemical equilibria within the hydrothermal solutions and pH-controlling wallrock reactions.

2. **Temperature:** Much research has been devoted to the study of the temperatures of ore mineral deposition, and some aspects of sulphide geothermometry will be reviewed in more detail in later chapters. Although difficulties have been encountered with some of the approaches employed, there is fairly general agreement that most hydrothermal ore deposits were formed within the temperature range $50^\circ\mathrm{C}$ to $500^\circ\mathrm{C}$. It is generally assumed that minerals deposited early in zonal or paragenetic sequences were formed at higher temperatures.
than those which crystallized late, but this assumption often rests on purely intuitive foundations.

3. **Pressure**: Methods of directly estimating total pressure at the time of ore deposition are seldom available; instead geological reconstruction is commonly employed to guess at the depth of burial. Krauskopf (1967) has suggested an upper limit of approximately 2 kb. for the formation of vein deposits. Limiting partial pressures (fugacities) of some individual gas phases, up to moderate temperatures, have been calculated from thermochemical data (Barton, 1957; Holland, 1959, 1965; Barnes & Kullerud, 1961). Barton (in Roedder, 1965) has suggested that the effects of total pressure are relatively insignificant compared to those of other equilibrium-controlling variables.

4. **Mechanisms of ore-metal transport**: Many mechanisms have been proposed to explain the large-scale transport of ore minerals and the commonly observed zonal and paragenetic sequences; in recent years most attention has been concentrated upon the profound effects of complexing on sulphide solubilities. Thus Garrels (1941) showed that at 100°C, a 2M concentration of chloride ions complexes sufficient Pb to prevent precipitation of galena before sphalerite. Barnes (1962) used thermodynamically calculated stabilities
of covalently bonded complex ions to account for the observed mineralogical relationships. In the absence of any other satisfactory explanation of the natural phenomena, complexing is generally conceded a significant role in ore metal transport; however, the exact types of complexes involved are unknown. Those which have attracted the most attention include the following:

(a) **Sulphide complexes**: Some heavy metal sulphides, such as HgS, can readily be dissolved in alkaline sulphide solutions; accordingly it has been suggested that ore metals could be transported in hydrothermal solutions as complex sulphides (e.g. HgS$_2^{2-}$). However, appreciable concentrations of S$_2^{2-}$ are only stable in alkaline solutions such as are expected only in restricted geological environments, and extensive sulphide complexing in hydrothermal fluids is improbable.

(b) **Polysulphide complexes**: Similar considerations apply to polysulphide complexes, although Cloke (in Roedder, 1965) has suggested that the Eh-pH stability field of polysulphides might increase appreciably at high temperatures.

(c) **Bisulphide complexes**: Although Barnes (1960) has demonstrated enhanced solubility for ZnS in H$_2$S solutions up to 195°C, and Krauskopf (1967)
believes "hydrosulfide complexes are the most promising lead at present toward an explanation of how metals can be transported in sulfur-bearing solutions", some difficulty is encountered in explaining the high concentrations of $H_2S$ and $HS^-$ required to maintain their stability.

(d) Chloride complexes: The evidence for high concentrations of chloride ions in hydrothermal solutions has led to the suggestion that metals might be transported as chloride complexes; the case for chloride complexes has been most vigorously argued by Helgeson (1964). Helgeson's proposals have many attractive features, but it is evident that the stabilities of the complexes are governed by equilibria in reactions of the type

$$M_2S + 4Cl^- \rightarrow 2MCl_2^- + S^{2-}$$

and hence are dependent on the relative concentrations of $Cl^-$ and $S^{2-}$. Thus Barnes & Romberger (1962) found chloride complexes of zinc to be negligible contributors to sphalerite solubility at low temperatures (below 200°C) and high total dissolved sulphur (greater than 0.5N); however, Helgeson (p.87) argues that at higher temperatures and in lower sulphur environments, chloride complexes become more important. In the absence of high
temperature experimental data and detailed knowledge of the chemistry of the ore fluids such arguments can be pursued indefinitely.

(e) Other complexes: Hydroxide, carbonate, bicarbonate, sulphate, sulphide and thiosulphate complexes are all capable of increasing the solubility of one or more of the common ore metals under appropriate physical conditions, but in general not enough is known of their high temperature stability to assess their probable roles in ore transport.

Krauskopf (1967) has pointed out that "with present information, no one kind of complex can be picked out that will solve all the difficulties in the hydrothermal hypothesis. It seems likely, in fact, that different kinds of complexes will be found to play important roles for different metals". It is, however, obvious that any theory under consideration must be capable of explaining the systematic mineralogical and chemical variations observed in zoned ore deposits, and to that end it is worth analyzing the precise nature of these variations. Barton (1959) commented that "we need detailed geological information on...mineral relations (both from field and laboratory), fluid inclusion compositions, and temperatures and pressures of ore deposition from many types of mineral deposits".

The present study was planned to obtain some of this information from the ores of the Zeehan field. Initially the
nature and extent of the zoning was investigated by means of a compilation of all available records concerning the geology and mineralogy of approximately 60 mines which have operated, with varying degrees of economic success, in the area, and by means of detailed microscopic examinations of paragenetic relationships and systematic mineralogical variations in a suite of Zeehan ore samples.

Preliminary studies showed sphalerite to be widespread in the Zeehan ores, and suggested systematic variations in its chemical composition. In view of the possible thermometric implications, an extensive analytical programme was undertaken to trace variations in the iron and manganese contents of sphalerite and relate them to the mineralogical zoning; for various reasons (Williams, 1965) the use of electron microprobe techniques was favoured for this part of the work, which necessitated the development of satisfactory analytical procedures (Williams, 1967).

The literature abounds with suggested qualitative relations between the contents of trace elements in various minerals and their temperatures of formation - e.g. the often quoted belief that the cadmium content of sphalerite varies inversely with temperature of formation. Theoretically, the partition of trace elements between co-existing minerals also offers promise for geothermometric applications (Bethke & Barton, 1959). Accordingly, a study of trace element distribution in the principal ore and gangue minerals was undertaken. The results of these investigations are summarised in the following chapters.
CHAPTER IV: THE ZEEHAN FIELD

Communications, physiography and climate

The township of Zeehan lies about 8 miles inland from Trial Harbour, on the West Coast of Tasmania (Fig. 1). Although its population was over 5000 at the 1901 census, and may previously have been several thousand higher, by 1961 it had declined to 780 (Bureau of Census and Statistics, 1961 Census), many of whom were employed in the mines at Mt. Lyell (17 miles to the south-east), and Renison Bell and Rosebery (8 and 13 miles, respectively, to the north-east). Access to the field was originally by sea, via Macquarie, Trial, or Granville Harbours; these were notorious for their hazards, and the consequent high freight and insurance costs were another burden on a mining field already short of capital.

Completion of the Emu Bay Railway, which linked Zeehan (via Renison Bell, Rosebery, and Waratah) with Burnie, on the north-west coast, eased the difficulties, as did the rail link between Hobart and Queenstown. Zeehan is now connected by road with both Hobart and Burnie; following completion of the latter road in 1964, rail services to Zeehan ceased altogether in 1965.

From Zeehan, roads lead east to connect with the Queenstown-Renison Bell road (Murchison Highway), and west to Trial Harbour. A track north-west to Granville Harbour is accessible to four-wheel drive vehicles, as are the road beds of the former Zeehan-Strahan railway to the south and Zeehan-Renison Bell railway to the north-east. Within the field, access to many
of the workings can still be obtained on old nine tramways, of which the most important are the Zeehan-Comstock, Comstock-Tasmanian, Zeehan-North-east Dundas and Dunkley's tram. However, these are all deteriorating rapidly and will soon be of little utility.

The Zeehan region is generally mountainous, and reflects the influence of recent vigorous stream erosion on a complex geological terrain (Blissett, 1962). The presence of flat-lying Permian tillites is evidence of a pre-Permian erosional surface, which has been modified by Tertiary (post-Jurassic) block faulting and subsequent dissection.

Much of the Zeehan field itself lies in a swampy, relatively flat Tertiary surface (elevation 800-1200 ft. above sea level) between Mt. Dundas (3750 ft) to the east, the Heenskirk range (up to 2769 ft) 5 miles to the west, and Mt. Zeehan (2300 ft), a monadnock 3 miles to the south. To the north, the Tertiary surface is deeply dissected by tributaries of the Pieman River. In the Zeehan area, the Proterozoic rocks are characterised by a relief generally higher than that of the more deeply weathered Paleozoic rocks. Within both groups, however, lithology has exerted strong control over topography (Blissett, 1962); limestones are invariably weathered to low swampy flats; shales and sandstones form low, rounded ridges; quartzites are more resistant and tend towards steeper, hog-back ridges, and the silicified Ordovician Owen Conglomerate has produced the marked relief of Mt. Zeehan.
to the south and Misery Hill to the east.

The Heemskirk Range consists of a core of granite intruded into Proterozoic and Lower Paleozoic quartzites and slates; the drainage pattern is influenced by prominent joint or fault planes (Blissett, 1962). Cambrian ultrabasic intrusions also form a rugged surface modified in places by areas of extensive serpentinization, which tend to be characterized more by swampy flats.

The effects of structure and lithology on topography have been reviewed in more detail by Blissett (1962).

The West Coast region has a temperate, wet climate. Average annual rainfall at Zeehan is 97.1 inches, which tends to be concentrated in the April-November period; summers, however, may nevertheless feature prolonged periods of rain. Geological studies are often hampered by climatic conditions, deep weathering and consequent poor outcrop, and by the generally rugged terrain and dense vegetation. The heavy rainfall made de-watering a constant difficulty in mining; underground "bursts" were on occasion responsible for loss of life, and many mines were forced to close because of their inability to cope with the water problem. Most of the old underground workings are either full of water, or in the case of adit workings, have collapsed, preventing access to the best exposures.
History of the Zeehan Mining Field

Following the discovery of rich tin ore at Mt. Bischoff in 1871, and its subsequent successful exploitation, prospecting parties pushed south-west to the Pieman River and beyond. Gold diggings on the Pieman were short-lived, but reports arrived as early as 1872 (Somerset, 1958) of tin lodes to the south, and in 1876-77 two parties arrived in the vicinity of Mt. Heemskirk. Tin was found by a government prospecting party led overland from Waratah by Charles P. Sprent, and in the following summer the Meredith brothers sailed from Hobart to Macquarie Harbour and prospected north towards the Pieman. They pegged the St. Dizier lease on alluvial tin at North Heemskirk, and were followed the next year by several other parties (Blainey, 1962), but progress was slow and was not enhanced by the discovery that the first eight tons of tin concentrate shipped by the Great Western Company consisted entirely of worthless ilmenite.

In 1879 vein tin was discovered at South Heemskirk by Alex Tengdahl, and wild speculation broke out on the Hobart stock exchange. Many companies were floated, despite poor communications, difficult conditions and incompetent management. Following the well-known practice of installing the plant before testing the orebody, apparently to boost market confidence, at least ten companies built mills; none of them ever paid a dividend, and very few produced any ore. Not surprisingly, the investors rapidly lost confidence, and by 1884 the field had collapsed. Its chief
48.

contribution to the history of West Coast mining was the enthusiasm it engendered among prospectors, culminating in the discovery of richer fields such as Zeehan, Mount Lyell, and Rosebery.

In 1882, Frank Long, a member of Sprent’s 1876 expedition, discovered traces of gold and argentiferous galena in a small creek near the present Zeehan Post Office, and after further prospecting pegged the original Mount Zeehan lease. His companion, J. Healy, pegged the adjoining 80 acres for the Despatch Company. As so often has happened, these leases subsequently produced only relatively minor amounts of ore, and Long derived no financial benefit from his discovery. At this time, investment finance was already becoming difficult as a result of the Heemskirk and other fiascos. Although the Zeehan lodes were inherently more worthy of support, they required capital for development since, as a consequence of climatic and topographic factors, they generally lacked the rich oxidized capping which gave so many other fields their start.

In 1887, G. Bell discovered rich argentiferous galena near what was to become the Silver Queen Mine. At this time the Broken Hill companies had just begun to pay dividends and the great national mining boom of the first months of 1888 was about to begin. Capital for any Australian silver mine, regardless of its distance from Broken Hill, became freely available. The Zeehan-Trial Harbour road was completed in 1889, and by 1891 there were at least 159 syndicates at work on the field (Blissett,
1962, Blainey, 1963), bolstered by the confident opinion of G. Thureau, Government Geologist, that the bold gossanous outcrop of Manganese Hill was indicative of another Broken Hill lode at depth (Thureau, 1888). Two small smelters were constructed on the field - again prematurely, since insufficient ore was available locally, and the smelters were unable to work to capacity.

In 1891 the Bank of Van Dieman's Land crashed, which closed most of the mines and seriously hampered, through lack of capital, the development of the few remaining. Over 80,000 acres were pegged at this stage, and the capital available was insufficient to keep more than a few of the larger companies operating. The smelters closed, and it was necessary to ship concentrates to Europe or the mainland for treatment. However, total production was maintained at about 14,000 tons of ore per annum. In 1894 this was worth nearly £300,000, but as the price of silver fell, annual production steadied to a level of a little over £200,000 (Blainey, 1963).

In 1898, the German-backed Tasmanian Smelting Company erected new, large smelters intended to serve both the Zeehan field and the Hercules Mine at Mt. Read; the Huntington-Heberlein process was developed for treatment of the complex Hercules ore. Thenceforth, as Blissett (1962) has pointed out, the fortunes of Zeehan were closely linked to those of the smelters. A long strike at the Hercules Mine, from 1905 to 1907, imposed difficulties and the plant closed in 1909. It re-opened in 1911,
but the Zeehan mines were rapidly exhausting their shallow ore and had no resources to finance proper exploration. The outbreak of war in 1914 shut off the European markets for metal and concentrates, and the smelters closed again.

After the war attempts were made to merge the Tasmanian Smelting Co. with the Hercules mines and the Primrose Mine at Rosebery; construction of an electrolytic plant was also planned. Ultimately, however, the Mt. Read and Rosebery mines passed to the control of the Electrolytic Zinc Company of Australasia, which already had extensive treatment works at Risdon. Rosebery ore thereafter was treated at Risdon, and although the Zeehan smelters continued to treat small parcels of ore, they operated well below capacity and finally closed in 1948. Mining activity after 1918 was only sporadic with most production coming from tribute parties. The last significant producers in the field were the Montana Silver Lead Mine, which ceased operation in 1958, and the Oceana Mine, which closed in 1960.

Details of production of individual mines in the Zeehan field are given, where available, in Appendix I. Most of these figures are taken from Blissett (1962); they indicate a total production of approximately 200,000 tons of lead, 2,750 tons of zinc (in the early days, most of the zinc was rejected during sorting and milling or lost during smelting), 26.5 million ounces of silver, 945 tons of copper and 40 tons of cadmium.
Previous geological investigations

The earliest geological descriptions of the Zeehan field are to be found in the reports of Thureau (1885, 1888) and Montgomery (1890, 1891, 1893, 1895, 1896). These are generally limited to their scope, and the first comprehensive surveys of the field as a whole were those of Twelvetrees (1901) and Waller (1902, 1903, 1904). Waller (1904) first drew attention to zonal regularities in the distribution of ore and gangue minerals in the Zeehan and Heemskirk fields, which he cited as evidence for a genetic connection between mineralization and emplacement of the Heemskirk intrusion.

Waller's observations were repeated and amplified by Twelvetrees & Ward (1909, 1910) and by Ward (1911). With the decline in mining activity, the zonal concept was not investigated further, and succeeding geological investigations have generally been confined to a large number of reports, many unpublished, prepared for the Tasmanian Department of Mines or for private companies and mostly concerned with descriptions of individual mines or prospects. Reference is made to these reports in the appropriate sections of Appendix I.

In recent years, summary descriptions of the Zeehan ore deposits have been provided by Edwards (1953) and McAndrew (1965). The geology of the field and the surrounding region has been described by Blissett (1962) and, on a smaller scale, by Pitt (1962). However, apart from minor studies of restricted scope, such
as those of Stillwell (1950) and Edwards (1951), no detailed mineralogical studies were made prior to those of Both (1966) and the present study. Both's investigation was intended to establish the validity or otherwise of the zoning and to provide a framework for isotopic studies to be carried out in conjunction with M.L. Jensen, T.A. Rafter and M. Solomon; preliminary results of this work are expected to be published shortly.

Reviews which include the Zeehan ore deposits in the wider context of West Coast regional mineralization have been given by Hall & Solomon (1962) and Solomon (1965). The tectonic and stratigraphic evolution of the region and its associated mineralization have been discussed at length by Campana & King (1963). Further descriptions of the regional geology are to be found in Spry & Banks (1962) and in Brown, Campbell & Crook (1967).

**Regional tectonic and stratigraphic setting**

Most of the primary metalliferous deposits of Tasmania lie within an arcuate zone of Proterozoic and Lower Paleozoic rocks extending around the western, northern and eastern sides of the Central Highlands. These rocks were deposited during marine sedimentary and tectonic evolution of the early phases of the Tasman Geosyncline, one of the major tectonic units of the Australian continent. In Tasmania, the pre-Devonian rocks in particular were affected by several phases of deformation, culminating in the Devonian Tabberabberan Orogeny (Fig. 7, after Both, Rafter & Solomon, 1967).
### Fig. 7: Stratigraphic sequence at Zeehan (after R.A. Both, unpubl.).

<table>
<thead>
<tr>
<th>AGE</th>
<th>THICKNESS (feet)</th>
<th>SEDIMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permian</td>
<td>50 +</td>
<td>Tillite</td>
</tr>
<tr>
<td>Mid - Devonian to Silurian</td>
<td>5000 +</td>
<td>TABBERABBERAN OROGENY</td>
</tr>
<tr>
<td>Cambrian</td>
<td>1500</td>
<td>Sandstones, mudstones (Eldon Group)</td>
</tr>
<tr>
<td>Lower Ordovician</td>
<td>1500</td>
<td>Limestone, shales (Gordon Limestone)</td>
</tr>
<tr>
<td>Cambrian</td>
<td>1500 +</td>
<td>Sandstones, basal fanglomerate (Mt. Zeehan Conglomerate)</td>
</tr>
<tr>
<td>Younger Precambrian (Proterozoic)</td>
<td>5000 +</td>
<td>JUKESIAN OROGENY ?</td>
</tr>
<tr>
<td></td>
<td>Thickness unknown</td>
<td>Sandstones, dolomitic limestones, basaltic lavas, tuffs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>PENGUIN OROGENY ?</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Quartzites, mudstones (Onah Quartzite and Slate)</td>
</tr>
</tbody>
</table>
Fig. 8: Major Cambrian structural units.

Fig. 9: West Coast synclinoria and anticlinoria.
Rocks thought to be of older Precambrian age outcrop in the Central Highlands and parts of the north and west coast regions. They consist of relatively strongly deformed schists, quartzites, phyllites and amphibolites. Spry (1957, and in Solomon, 1962) believes them to be separated from a younger Precambrian group by an unconformity resulting from a phase of metamorphic and tectonic activity which he called the Frenchman Orogeny. Burns (in Solomon, 1962) agrees that there may be a distinction between an older and a younger group, but suggests that in at least some cases variations between Spry's groups may be explained by localized deformation in shear zones.

Carey (1953) suggested that the older and younger Precambrian groups (then called the Davey and Carbine Groups respectively) together formed a stable nucleus (the Tyennan Block) in the centre of Tasmania and a smaller block (the Rocky Cape Geanticline) to the north-west, and that succeeding Lower Paleozoic sedimentation took place in an arcuate eugeosynclinal belt between the two blocks. Further studies have slightly modified Carey's concepts; Solomon (1965) summarises present opinion as follows: "....in Younger Precambrian time the older Precambrian formed a geanticline (the Tyennan Geanticline) in the Central Highlands area and...the surrounding basin formed part of a large niogeosyncline that probably extended to the mainland of Australia. The margins of the geanticline have had a significant control over fold trends in succeeding orogenies" (Fig. 8).
Deposition was interrupted by the Penguin Orogeny, probably in the late Proterozoic (Solomon, 1965). The events immediately succeeding the orogeny are poorly understood, but it appears that several thousand feet of sandstones, siltstones, and dolomite were deposited over the younger Precambrian miogeosyncline and margins of the Tyennan Geanticline. These sediments included the Carbine Group at Dundas, the Success Creek Group (Taylor, 1954), and the upper parts of the Oonah Quartzite and Slate (Blissett, 1962; Solomon, 1965, uses the term "Oonah Formation"). These rocks are grouped by several writers as the loosely defined "Success Creek phase", but there is considerable uncertainty about correlations within the group. The Success Creek phase has been variously assigned to the late Proterozoic or the early Cambrian (Spry & Banks, eds., 1962; Campana & King, 1963; Brown, Campbell & Crook, 1967).

By the end of the Success Creek phase, a wider trough had developed, with considerable overlap on to the margins of the Tyennan Geanticline. At this stage a thick volcanic pile known as the Mt. Read Volcanic Arc developed around the north and west margins of the Tyennan Geanticline. Considerable metallogenetetic significance is attached elsewhere to these volcanics (Solomon, 1964), but at Zeehan they are possibly represented only by the keratophyric tuffs and flows in the upper part of the Oonah Quartzite and Slate. Here the Success Creek sediments are followed, apparently conformably, by the Crimson Creek Argillite (unfossiliferous).
and the Dundas Group (Lower Middle Cambrian to Upper Middle Cambrian). The Crimson Creek Argillite and Dundas Group, which were deposited in a narrow elongate basin known as the Dundas Trough, have been compared by Campana and King (1963) with the synorogenic flysch facies argillite and greywacke types respectively, although Solomon (1965) has indicated that this lithological comparison is not altogether convincing.

The Crimson Creek Argillite also contains keratophyric tuffs and spilitic lavas, with associated thin sills and plugs of dolerite and gabbro and relatively large, sheet-like bodies of serpentinite and serpentinized pyroxenite. The larger bodies are hosts for small deposits of copper-nickel sulphides, magnetite, chromite and osmiridium.

The Dundas Trough was possibly mildly deformed towards the end of the Early Cambrian, with the Dundas Group being deposited in part unconformably on the Crimson Creek Argillite (the Stichtan Unconformity). Dundas Group deposition was in turn terminated abruptly at the close of the Middle Cambrian or early in the Upper Cambrian by the onset of the Jukesian Orogeny (the "Tyennan" Orogeny of Browne, 1949; Brown, Campbell & Crook (1967) use both terms in various contexts). The sediments were gently folded on trends parallel to the margin of the Tyennan Geanticline; major faulting on similar trends uplifted the Tyennan and Rocky Cape Geanticlines and produced an intervening depression split by an axial ridge (the Porphyroid Anticlinorium of Carey, 1953,
or the Dundas Ridge of Bradley, 1954) into two elongate basins. Campana, Dickinson, King & Matheson (1958) interpreted the eastern, or Owen, basin as a rift valley, and suggested the rifting played a significant role in localization of mineralization. Some rifting may also have been involved in the formation of the western, or Zeehan, basin.

The Jukesian movements were followed by the deposition, in the two basins, of rocks of the Ordovician Junee Group, beginning in the eastern basin with the Jukes Breccia or Conglomerate, derived from the erosion of marginal portions of the Mt. Read Volcanics. This formation, which is absent from the Zeehan basin, was succeeded by the Owen Conglomerate, consisting of coarse, possibly fluviatile conglomerates grading upwards into finer conglomerates and sandstones. The initially rapid erosion was accompanied by lateral marine transgression; by the end of the Lower Ordovician, thin marine sandstones covered much of the axial ridge and parts of the geanticlines. With a progressive return to miogeosynclinal conditions, shales and limestones (e.g. the Gordon Limestone) were deposited over wide areas.

Minor movements towards the close of the Ordovician, possibly correlated with the Benambran Orogeny in Victoria, affected source areas and led to a change in sediment lithology. The Crotty Sandstone at the base of the Eldon Group is generally regarded as Silurian, but is possibly of late Ordovician age (Brown, Campbell & Crook, 1967); it is succeeded by a thick (3000 m.)
sequence of sandstones, mudstones and limestones extending into the Lower Devonian. Although there are possibly some disconformities within the Silurian part of the sequence, their magnitudes have not been determined, and it appears that the Bowning Orogeny in New South Wales is not significantly reflected in the Tasmanian sequence.

The Middle Devonian (see below) Tabberabberan Orogeny brought an end to geosynclinal sedimentation in Tasmania. Solomon (1962, 1965) has tentatively suggested that the deformation took place in two stages. In the first stage, differential vertical uplift formed arcuate synclinoria and anticlinoria on the previously established trends, controlled by the Tyennan and Rocky Cape Geanticlines (Fig. 9). In the second stage, the orogeny produced structures of approximately north-west trend, particularly in the Zeehan-Queenstown district. Superimposition on earlier folds produced local complications, notably marked changes of plunge. In some areas, north-west-trending folds are bent towards east-west trends, and these zones are characterised, again notably at Zeehan and Queenstown, by approximately east-west faults with pronounced vertical and transcurrent movements. This tendency is most strongly developed in the Precambrian to Lower Ordovician formations; in the shallower Devonian sediments the faults swing to north-easterly trends and display dominantly tensional characteristics (Fig. 14).

During the Tabberabberan Orogeny, several granitic stocks, all
with associated marginal mineralization, were intruded along large scale anticlinal structures (Carey, 1953). These stocks are post-folding but in some places have been faulted (e.g. at Heemskirk).

Rb-Sr determinations by Brooks & Compston (1965) suggest an age of 354 m.y. for the Heemskirk granite, and McDougall & Leggo (1965) report an age of 340±5 m.y., based on K-Ar determinations. These dates indicate, on the time scale of Kulp (1961), a late Devonian age for the Heemskirk granite; if the modification discussed by McDougall & Leggo (1965) and McDougall, Compston & Bofinger (1966) is adopted, then the Heemskirk granite should be regarded as early Carboniferous. McDougall & Leggo drew attention to two concentrations of measured ages of Tasmanian granites around 370 and 340 m.y. respectively, which lends support to the suggestion of Browne (1949) that there are two ages of granite in the region; Browne believed them to be Tabberabberan and Kanimbilan (Middle Carboniferous) respectively, with mineralization largely confined to the latter.

Post-Carboniferous sedimentation in the West Coast region was essentially superficial (e.g. Permian tillites north of Zeehan), and post-Permian tectonics were mainly tensional and epeirogenic. Again the Tabberabberan and earlier structures appear to have exerted considerable control over the younger movements. At Zeehan, for example, there is strong evidence for post-orogenic movement on major faults which pre-dated or were pene-contemporaneous with the mineralization (including both the east-west and north-
The stratigraphic succession

The Heemskirk-Zeehan district consists essentially of upper Proterozoic and Paleozoic sediments in the eastern half, and igneous rocks, chiefly the Heemskirk granite, in the west (Fig. 10). The sediments occupy the core and western flank of a belt of complex folding and faulting which Solomon (1965) called the Zeehan-Mt. Pearse Synclinorium; the granite appears to have been emplaced in a parallel anticlinal zone to the west, which also includes (to the north-east) the Meredith and Hampshire Hills granites (Fig. 9).

The local geology of the Zeehan area is summarised in Fig. 11; this map has been compiled from those of Blissett (1962), Pitt (1962) and Solomon (1964), supplemented by field observations made during this study. The latter did not extend to detailed mapping, but were confined to the attempted resolution of some confictions in the published data which were of significance to the study of the zonal relationships. As noted earlier, outcrop in the Zeehan area is generally poor, and some aspects of the interpretation offered in Fig. 11 remain contentious.

The oldest rocks in the Zeehan field are the alternating white and grey quartzites, micaceous quartzites and siltstones, and grey, green and black shales of the Oonah Quartzite and Slate formation. These are unfossiliferous (Blissett, 1962, was
Fig. 10: Geology of the Zeehan - Rosebery district (after Solomon, 1965).
Fig. 11.
Fig. 12: Zeehan mine localities.
unable to locate fossiliferous localities reported by Waller and Twelvetrees & Ward), but are accepted by most authors as being predominantly of Upper Proterozoic age, possibly ranging into the Lower Cambrian.

Spilitic lavas and tuffs interbedded with shales, sandstones and dolomites outcrop in a curved belt north and west of Zeehan (Fig. 11), and are particularly common in the vicinity of the No. 1 Montana, Oonah, and Queen Mines (for mine localities, see Fig. 12). The volcanic rocks have been described by Twelvetrees & Ward (1910) and King (1961); Hills & Carey (1949) called them the "Montana Melaphyre Volcanics", and Blissett (1962) considered them as interbedded in the upper portion of the Oonah Quartzite and Slate. Solomon (1965) correlated them with the Success Creek phase, implying a Lower Cambrian age. King (1961) noted that most of the production of the Zeehan field came from lodes within the volcanic sequence, and commented on the possible selective host-rock control of mineralization, a hypothesis which had earlier been rejected by Waller (1904).

Although unconformity as a consequence of the Penguin Orogeny has been noted elsewhere, at Zeehan the passage from the Oonah Quartzite and Slate into the Success Creek phase appears to be conformable and the boundary transitional. Hence in Fig. 11, the "Montana Melaphyre Volcanics" are shown as an upper phase, correlated with the Success Creek phase, of the Oonah Quartzite and Slate. This in agreement with the interpretation of Blissett (1962),
but differs from that of Solomon (1964, 1965); it should be noted that available data do not yet permit the difference to be resolved, and the relationships of Fig. 11 have been adopted largely for convenience. However, the present author disagrees with Solomon's (1964) mapping of the rocks in the Comstock-Britannia-Spray-Nubeena area as correlatives of the Success Creek Group. There appears to be little lithological evidence for this interpretation.

The Success Creek rocks are succeeded, possibly conformably, by a sequence of grey to reddish, fine-grained spilitic tuffs and interbedded brown, green or black slates which Twelvetrees & Ward (1910) termed the "Keratophyric Tuffs and Breccias" and which Blissett (1962) correlates with the Crimson Creek Argillite. Waller (1903) noted the low relief of the Y-shaped area whose arms extended from Manganese Hill north across the Argent Flat, west to the Sylvester Mine, and south-east along the Austral Valley; the rocks outcropping in this area are those mapped by Blissett (1962) as correlatives of the Crimson Creek Argillite.

The validity of the presumed conformity between Success Creek and Crimson Creek correlatives in the Zeehan district is open to some question. The two units are in contact in the vicinity of the Sylvester Mine, along the western side of the Austral Valley "arm", and along the western side of the Argent Flat "arm". In the first instance, outcrop is poor, and the general similarity in lithologies makes interpretation of the field evidence extremely
difficult; the possibility of a faulted contact cannot be dismissed. The Austral Valley contact is completely obscured by alluvial cover and/or deep weathering. Portion of the Argent Flat contact was mapped by Blissett (1962) as a conformable boundary, but Pitt (1962) interpreted most of it as a faulted contact, which is in better agreement with the structural and mineralogical interpretations of the ore zoning advanced in the present study. A conformable transition thus remains only a possibility which is not clearly established from field relationships in this area.

The occurrence of Diplagnostus sp. in Crimson Creek shales in the Summit Cutting of the Comstock Tramway correlates part of the Crimson Creek rocks in the Zeehan area with the Hodge Slate, several hundred feet above the base of the Dundas Group at Dundas (Opik, 1951). Again the lithologies are very similar, and the two units cannot be reliably distinguished in the Zeehan area.

The boundary between the Cambrian beds and the Ordovician Junee Group is also generally obscured in the Zeehan area by major faulting, apart from one isolated area on the north-west flank of Mt. Zeehan, about 2 miles west of the Oceana Mine. By analogy with a lithologically similar transition at Misery Hill, several miles to the east, Blissett (1962) suggests that the boundary is conformable or possibly disconformable. In view of the tectonic history, the latter alternative is more likely; the basal conglomerates of the Junee Group are thought to indicate an abrupt change in provenance as a consequence of Jukesian movements.
In the Zeehan area, the lowest unit of the Junee Group is the Mt. Zeehan Conglomerate of Blissett (1962), correlated with the Owen Conglomerate. This is succeeded conformably by the Caroline Creek Sandstone (the "Moina Sandstone" of Blissett) and the Gordon Limestone. The latter is rarely exposed, since it has weathered to black or grey clays forming swampy button-grass flats. Edwards (1953) suggested that the relative lack of known ore deposits in the Gordon Limestone is in part a consequence of the poor outcrop.

The Junee Group sediments are followed, probably disconformably, by the Silurian to Lower Devonian Eldon Group. The basal Crotty Quartzite is succeeded in turn by the Amber Slate, Keel Quartzite and Austral Creek Siltstone, all of Silurian age, and the Lower Devonian Florence Quartzite and Bell Shale. These occur in a strongly faulted, north-easterly trending zone on the western flank of the Zeehan Syncline; the outcropping core of the latter consists of Bell Shale to the east and south-east of Zeehan, and Florence Quartzite to the north-east.

As noted earlier, geosynclinal sedimentation in this region ceased with the onset of the Tabberabberan Orogeny in the Middle Devonian. Flat-lying Permian tillites occur in the Zeehan district, in the vicinities of the Montana Silver-Lead, Oonah, Tasmanian and Swansea mines.

**Intrusive igneous rocks:**

A large mass of hornblende gabbro outcrops on the Zeehan-Trial
Harbour road at McIvor Hill, about 6 miles west of Zeehan (Fig. 10). It consists essentially of hornblende and basic labradorite (Green, 1966), with crystals of both ranging from less than 1 mm. up to several cm. in size. To the south-west, a mass of serpentinised dunite outcrops near Trial Harbour, and contains minor nickel mineralisation consisting of disseminated pentlandite, heazlewoodite, millerite and minor shandite (Williams, 1958; Green, 1966).

The gabbro-serpentinised dunite association shows general similarities with basic-ultrabasic complexes elsewhere in Tasmania, notably the Bald Hill, Beaconsfield and Melba Flat - Ring River areas (Twelvetrees, 1913; Reid, 1923; Taylor, 1955; Green, 1959; Blissett, 1962; Green, 1966). Because of their overall similarities, these associations are considered to be genetically related to the same period of igneous activity. Their intrusive relations are confined to Cambrian or older rocks, and Upper Cambrian sediments at Adamsfield contain pebbles of serpentine (Solomon, 1965); they are therefore presumed to be of Middle to early Upper Cambrian age. Where their stratigraphic relationships can be observed, the basic-ultrabasic bodies tend to form concordant sheets along the Crimson Creek Argillite - Dundas Group boundary (Solomon, 1965).

Brooks (1966) determined, from Rb-Sr measurements, an age of 518 ± 133 m.y. for the McIvor Hill complex which, although generally sill-like in form, shows marked transgressive characteristics.

The northern part of the McIvor Hill gabbro has been partially
serpentinised and dolomitized, and contains massive bodies of magnetite (e.g. the Tenth Legion deposit). Minor sulphides were reported in these bodies in earlier literature, but more recent drilling (Hughes, 1958) located only traces of pyrite. The magnetite was originally presumed to have been derived from the same magmatic source as the lead-zinc mineralization (Waller, 1903), and Twelvetrees & Ward (1910) included a "contact metamorphic zone" in their zonal classification of the Heemskirk-Zeehan ores on the basis of the Tenth Legion and other smaller deposits of magnetite. However, Hughes (1958) suggested that the iron oxides are genetically related to the basic intrusives rather than the Heemskirk granite. In view of the basic-ultrabasic affiliations of similar iron ore deposits elsewhere in Tasmania (e.g. Savage River), Hughes' interpretation is considered the more reasonable.

Solomon (1965) has noted that gabbro-serpentinite bodies are typical of the ophiolite association in tectonically active eugeosynclinal belts.

The small Heemskirk granite pluton outcrops along the coast for approximately 6 miles north of Trial Harbour, and extends inland, with a total outcrop surface of nearly 50 square miles (Fig. 10). It was first described by Waterhouse (1916); because of its unusual petrographic features it has recently been subjected to more detailed studies, summarised by Brooks & Compston (1965), Green (1966) and Heier & Brooks (1966).

The granite forms an elongated stock or boss, emplaced in the
axial zone of an anticlinorium of Precambrian and overlying Paleozoic sediments. Although it is more or less conformable on a regional scale (Fig. 9), local contacts with the sediments are transgressive. To the north and east, Onnah Quartzite and Slate sediments are invaded, with only minor contact metamorphic effects. To the south, the contact aureole includes Paleozoic sediments ranging from Cambrian to Upper Silurian (Amber Slate) in age; here metamorphic effects are more pronounced, with the sediments having been converted to hornfelses (Green, 1966). The intrusive contacts are generally vertical or dip steeply outwards; the form of the contact has been somewhat disrupted by post-intrusive faulting.

Petrographically, the granite can be divided into two types, Red and White, based on the colour of the orthoclase feldspar (Brooks & Compston, 1965). The White type constitutes just over half of the outcrop, but 70 per cent of the granite-sediment contacts involve the Red variety (Fig. 13). Brooks & Compston further subdivide the White type into sub-types A and B, the former consisting of "normal" equigranular coarse white granites and the latter porphyritic varieties containing more biotite and altered xenoliths. The contact between Red and White granites is commonly irregular and diffuse, and the Red granite frequently develops a discontinuous rim of a grey variety (of similar composition) at intrusive contacts. Tourmaline (schorlite) is abundant, particularly in the central portions of both White and Red granites.
Fig. 13: Sub-types of the Heemskirk granite (after Brooks & Compton, 1965).
Detailed petrographic and chemical descriptions are given by Brooks & Compston (1965) and Heier & Brooks (1966). The granites are highly fractionated, typically high level calc-alkaline varieties, distinguished by anomalously high apparent initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios, which vary appreciably from 0.716 in the Red granite to 0.741 in the Type B White granite. Rb-Sr age measurements indicate that the Red and White A granites are indistinguishable at 354 m.y., but that White B could be up to several m.y. older. As noted earlier, this indicates either Late Devonian or Early Carboniferous age, depending on the time scale adopted.

$\text{Sr}^{87}/\text{Sr}^{86}$, Th/U and K/Rb ratios were interpreted by Heier & Brooks (1966) as indicating two major phases of intrusive activity involving a highly differentiated high level magma. In the first stage, the White granites were produced by reaction between initially emplaced and crystallized granite and a vapour phase from the parent magma. The presence of xenoliths in the White granite, the high initial $\text{Sr}^{87}/\text{Sr}^{86}$ ratios, and the low K/Rb and Th/U ratios all suggest incorporation of crustal material; this is further supported by sulphur isotope data obtained by Rafter and Both from mineralization within the granite (R.A. Both, pers. comm.).

The second phase, according to Heier & Brooks, was the intrusion of the parent magma into the White granite and surrounding sediments to form the Red granite.
The tin zone of Twelvetrees & Ward (see below) is concentrated in and immediately adjacent to the granite. The present author disagrees with the implication of Heier & Brooks (1966, p. 633) that tin and associated sulphide mineralization was concentrated in the White granites; rather field examination and literature surveys suggest that mineralization was found in both White and Red granites, with the largest deposits being associated with the Red granite or its marginal grey variant.

Several quartz porphyry and aplite dykes have been described by Waller (1904) and Twelvetrees & Ward (1910) - e.g. at the Sylvester Mine, west of the Western Mine, in the Summit Cutting of the Comstock Tran, and in the vicinity of Queen Hill. These are invariably heavily weathered, and little is known of their origin and distribution. Ward (1911) believed them to be "without doubt apophyses from the magma which produced the granite of Mt. Heenskirk".

**Structural Geology:**

The major structures of the Zeehan area were produced by folding and faulting in the Tabberabberan Orogeny, followed by post-Permian epirogenic block faulting. The ore veins occur on the western flank of a major synclinal structure (the Zeehan Syncline) whose axis follows the regional trend to the NNW; although some preliminary investigation suggested that a study of the minor folding might prove informative, it soon became apparent that it would be too lengthy to include in the present project, and little
is yet known of the minor fold geometry.

The distribution of the major faults is shown in Figs. 11 and 14, and that of the known veins in Fig. 14. Most of the information necessary to compile the latter was obtained from the maps and reports of Waller (1903, 1904); since these were prepared while many of the veins were exposed in underground workings, they provide much more comprehensive data than can currently be obtained by surface mapping. It is evident from Fig. 14 that the orientation of the veins, which are usually tensional fissure fillings, is closely related to the faulting. Two major sets of veins may be distinguished - one striking NNW and the other N to NNE. Veins of the first set occur throughout the field, but those of the second set are most abundant in the Proterozoic and Cambrian rocks outcropping in the vicinity of the NNE-striking faults in the Argent Flat - Queen Hill area. It is unfortunate that detailed information on the dips of veins is generally sparse, except where it can be deduced from mine plans, but it is known that they were mostly steep (60° or more).

In a brief, generalised tectonic analysis, Solomon (1965) has suggested that the effects of the Tabberabberan Orogeny can be explained in terms of a first stage of broad folding parallel to the pre-existing trends controlled by the Tyennan and Rocky Cape Geanticlines (i.e. N-S trends in the Zeehan area), followed by development of a new strain pattern dominated by NW folds and WNW to E-W transcurrent fractures which also show vertical movement.
ZEEHAN FIELD Fault and Vein Patterns

Vein Patterns

Fault Strikes

Vein Strikes

Fig. 14.
Fig. 15.

1. Compression
Conjugate shearing
Major fold axes

2. Release and/or radial jointing

3. Tension veins
Tension faults
Transcurrent shearing
The distribution of folds, faults and tension fractures in the Zeehan field is in general agreement with this model, and may have originated in the following way:

1. The first compression, along present ENE-WSW directions, produced major folds striking NNW; the dominant NW-NNW trending fissure veins were probably produced by this folding, either as a radial joint set formed during the folding, or as a release joint set (Billings, 1954; Badgley, 1965) formed on relaxation of the stress. (In the absence of information on vein attitudes, it is not possible to decide between the two alternatives).

2. Concurrently, a conjugate shear set (Fig. 15) was produced; a study of fault distribution (see rose diagram inset of Fig. 14) shows the two principal fault sets to strike approximately 60° apart, with each being about 30° from the presumed stress direction, in accordance with theoretical prediction. The amount of movement on the shears at this stage is not known, but was possibly not large.

3. Application of an approximately E-W oriented transcurrent shear stress (north side west) considerably accentuated north block west movement on the E-W shear set produced during the first compression (Fig. 15) and produced the major transcurrent faults (Tenth Legion, Comstock, Balstrup Faults) which dominate the Zeehan fault
pattern and are thought to be analogous to the Linda Fault Zone (Solomon, 1965).

Corresponding movement on the NE-striking conjugate shear set would not have been large, since this would have represented a direction of tensional rather than shearing stress. The subsidiary NE to NNE striking fissure veins were most probably formed as a consequence of this tensional stress.

The directions of the E-W transcurrent faults and the NNE to NE striking veins depart by up to 20° from those predicted to eventuate from the application of an E-W transcurrent shear stress to a homogeneous rock system; however in this case the earlier shear sets would have represented directions of weakness along which movement or tensional fissuring would be preferred.

4. Further movement may have taken place along any of these directions during post-Permian block faulting; it may well have favoured the N to NE trending directions left in tension after the transcurrent shearing.

In view of the general lack of data concerning fault and vein attitudes, it is not possible to produce a more detailed analysis of the structural evolution of the Zeehan field. The scheme postulated above agrees satisfactorily with the data available, and with previous analysis of the Linda Fault Zone, (Solomon, 1965). While a more comprehensive analysis is obviously essential
to any future prospecting activity, the principal interest in the present study of the ore zoning attaches largely to the possible extent of post-mineralization faulting.

Waller (1904) and Twelvetrees & Ward (1910) were emphatic in their belief that the ore minerals were deposited after the faulting, for the following reasons (Twelvetrees & Ward, 1910, pp. 81-83):

1. In some of the underground workings, ore was encountered within the fault zones; in at least some such cases the ore was reported to show no sign of brecciation.

2. Some veins (e.g. the "north carbonate lode" of the Oonah Mine) were reported to cross the faults without displacement.

3. "Frequently it is found that the lode as it approaches the ruschel (Fault zone) splits up into a number of stringers, which diverge as they approach the slide (fault), so that the lode, as seen in plan, spreads out like a fan, with narrow wedges of country rock between the stringers of lode matter......In some cases one of the stringers may be seen to bend round till it follows the course of the slide, while other stringers actually penetrate for a short distance into the ruschel itself".

The observations on which these arguments were based were made on relatively minor faults exposed within underground workings,
chiefly those of the Montana and Oonah Mines; they cannot be extended to the major faults of the Zeehan field. Even in the case of the minor faults, the descriptions given by Twelvetrees & Ward are frequently inconsistent, and their reasoning is difficult to follow. Thus on p.82 they state "In those cases in which intersections are visible the lode fissures are not broken by the slides", but on p.83, referring to the intersection of Nos. 2, 3 and 4 lodes with the main slide, "at some points the lode runs right up to the slide, and there ends abruptly", and on p.84 "In many cases it is apparent that a lode fissure on reaching a slide "dies out" or terminates abruptly". Furthermore, it is evident from a study of mine plans that the Oonah Fault clearly displaces the Oonah lodes, despite Twelvetrees and Ward's opinions to the contrary. In fact, close examination of the mine descriptions of Waller (1902, 1903, 1904) and Twelvetrees & Ward (1910) reveals abundant examples of post-mineralization lode displacement on various scales. Thus Waller (1902) noted that lodes in the Western Mine were cut off by "slides" and (1904) that orebodies are dislocated by faulting in the No. 2 Argent Mine. Twelvetrees (1901) described complex faulting of veins exposed in the main crosscut of the Mt. Zeehan Mine. Other similar post-mineralization displacements of ore veins were recorded in the Stonehenge, Tasmanian, Nubeena, South King and Crown Mines.

The Heemskirk Granite is generally regarded as "post-orogenic" (e.g. Brooks & Compston, 1965, p. 6251) and if the mineralization is
though to be related to granite emplacement, then there can be no doubt that the principal fault and vein patterns were established prior to ore deposition, as proposed above. However, there is also abundant evidence for post-mineralization faulting, summarized by Blissett (1962). The granite itself is displaced by the Tenth Legion Fault and by a N-S trending fault mapped by Brooks (Brooks & Compston, 1965). At the Montana Silver-Lead Mine, Campana & King (1958) showed that Proterozoic rocks have been thrust over Permian tillite along a NNW-striking fault with an easterly attitude of $45^\circ$; Solomon (1962) suggested that the dislocation may have been due to renewed movement along an older fault. The tillites lie unconformably on a Permian erosion surface; Edwards (1941) drew attention to their varying altitudes (e.g. a difference of over 400 feet between the Montana Silver-Lead Mine and Oonah Hill outcrops) and suggested post-Paleozoic fault movement as an explanation.

In view of this evidence, Blissett (1962, p. 85) concluded that "much of the complex disturbance of Proterozoic to Devonian rocks in the vicinity of Zeehan must be attributed to post-Permian, possibly Tertiary, faulting which was partly controlled by Tabberabberan structures and zones of weakness".

If post-mineralization movements were of substantial extent, then they might be expected to have disrupted any zonal patterns in the mineralization; it will be shown later than in fact the zonal relationships in the Zeehan field can only be established and
interpreted satisfactorily if such faulting is assumed.

CHAPTER V: MINERALOGY, PARAGENESIS AND ZONAL RELATIONSHIPS IN

THE ZEHEM ORE

Previous descriptions of the zonal relationships...

Waller (1904) observed that the fissure veins of the Zechen field differed considerably in their "mineral contents" and in the relative proportions of the different minerals present. He recognised the presence of three characteristic types of ore, which he described as follows:

1. "The Pyritic Formation" - lodes in which the gangue consists principally of pyrite with argentiferous galena and often much sphalerite; siderite is absent or present in only small proportions.

2. "The Sideritic Formation" - lodes in which the gangue is siderite associated with argentiferous galena and little or no sphalerite. Pyrite may be present in small amounts.

3. "The Stannite Formation" - lodes in which the gangue is principally pyrargyrite associated with "argentiferous stannite", chalcopyrite and small quantities of wolframite, bismuthinite, galena and siderite.

Waller noted that many veins could not be categorised as clearly as this classification might indicate, and in particular that many lodes were mineralogically intermediate between the pyritic and sideritic types. As examples, he cited the lodes of
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Waller noted that many veins could not be categorised as clearly as this classification might indicate, and in particular that many lodes were mineralogically intermediate between the pyritic and sideritic types. As examples, he cited the lodes of
the Oonah Mine ("Main Galena Lode"), No. 4 Queen, some Argent Valley lodes, Spray and Grubb's; these he reported to contain pyrite and siderite in more or less equal amounts, often with abundant sphalerite. He noted that the "antimony minerals, especially jamesonite (sic), appear to be more abundant in the intermediate formations than in either of the extremes", and also that the silver grade of the galena, although subject to the effects of secondary enrichment, was generally low in the pyritic ores and high in the sideritic; intermediate types carried intermediate values.

Although Waller did not specifically discuss the zonal distribution of the ore types which he described, he drew attention to certain similarities between the ores of Zeehan and those of Freiberg (e.g. the gradational change from pyritic to sideritic ores, the change in silver grade of the galena with changing gangue type, the relative abundance of sphalerite in the pyritic ores etc) and he presented, without further comment, a diagram (Fig. 16) showing the distributions of magnetite, pyrite, siderite, galena, silver in galena, sphalerite, antimonial ores, cassiterite and stannite in terms of three "zones", which he called the "contact or magnetite", "pyrite" and "siderite" zones respectively.

Waller gave no indication of the geographical distribution of these zones, apart from incomplete lists in the text of examples of the pyritic and sideritic types. The intermediate types mentioned
Fig. 17: The zoning according to Twelvetrees & Ward; the square encloses the area of the present study.
Twelvetrees & Ward (1910) amplified Waller's observations and extended them to include the Heenskirk tin field. They suggested that the ores showed a zonal relationships to the Heenskirk Granite (Fig.17) and, while again recognising the presence of intermediate varieties indicative of transition rather than abrupt zonation, they suggested that the lodes could be grouped in the following zones:

1. **The Granite Zone**: Within and immediately adjacent to the borders of the Heenskirk Granite occur a number of orebodies in which cassiterite is associated with pyrite and minor wolframite, bismuth, bismuthinite and molybdenite.

2. **The Contact Metamorphic Zone**: As noted earlier, this zone was defined to include the magnetite lenses in the area between the Comstock mines and the eastern outcrop boundary of the Heenskirk Granite.

3. **The "Transmetamorphic Zone"**: This was subdivided into pyritic and sideritic belts, merging in transitional types:
   
   (a) **The Pyrite Belt**: These were described as consisting essentially of pyrite-sphalerite-galena or pyrite-galena; the pyrite-stannite-chalcopryite and pyrite-stannite-galena ores of the Oonah - Queen Hill district were considered to be a special variant making a marked
incursion into the sideritic belt.

(b) The Sideritic Belt: These included the lodes of the eastern portion of the field, characterised by abundant siderite, rare pyrite and variable sphalerite.

Twelvetrees & Ward distinguished two vein types in this zone, viz., siderite-galena and nickel-silver types (the latter confined to one occurrence).

An enlarged version of Waller's diagram, including the Granite Zone, was presented. The zoning was ascribed to "the effect of differing physical conditions in causing the precipitation of different assemblages of minerals from the same metalliferous solutions according to the distance from the magmatic hearth"; this constitutes one of the earliest clear statements of the zonal theory of hydrothermal ore deposition.

Despite the undeniable overall change in vein mineralogy from west to east in the Heemskirk and Zeehan fields, many anomalies in the simple zonal pattern proposed by Waller and Twelvetrees & Ward are apparent, apart from those due to gradual transition from one zone to the next. For example the pyrite-stannite-cassiterite deposits of the Oonah - Queen Hill area are more or less surrounded by sideritic types, and no stannite zone is present in the southern part of the field. Ward (1917) proposed mineralization derived from multiple intrusive centres beneath the Zeehan field and implied that the source of the Oonah ores was chemically different from the others; his reasoning, however, is
generally vague and does not account satisfactorily for the
previously observed regularities, or for the absence of stannite
from the pyrite-cassiterite ores of the Heemskirk field.

In the southern portion of the field, the ores of the Swansea
Mine contain far less pyrite than do those of the Tasmanian and
Grubb's Mines, short distances to the north-west and north-east
respectively. In the Argent Flat - Queen Hill - Oonah area, the
relative proportions of pyrite and siderite vary considerably and
with no clear geographic relationship. In the workings of the No. 2
Montana (Silver Queen) Mine, distinctively different pyritic and
sideritic lodes were exposed within several hundred feet of each
other. To the north-east, the ores of the Despatch Mine contained
significant proportions of pyrite, while those of the Montana and
Western Mines, to the west, contained very little.

Both (1966), on the basis of a mineralogical study,
concluded that the Zeehan ores are in fact epigenetic, derived from
the Heemskirk granite, and are generally zoned in accordance with
the concepts of Twelvetrees & Ward. He suggested that "the more
obvious horizontal component of the zoning was complicated by a
vertical component, possibly due to a cupola-type development of
granite underlying the Oonah - Queen Hill part of the field";
the anomalous mineralogy of the ores of this area, however, was
not explained.

Both modified the zones proposed by Waller and Twelvetrees
& Ward to eliminate the Contact Metamorphic Zone. He preferred a
threefold division into tin, pyritic and sideritic zones, based on the following mineralogical changes (from west to east):

1. A general decrease in the ratio \((\text{pyrite} + \text{sphalerite}) : (\text{galena} + \text{siderite})\).

2. An increase in the abundance of boulangerite and bournonite, with a pronounced maximum in the Swansea - Spray - Queen Hill belt.

3. A general increase in the silver content of the galena.

4. A general decrease in the iron content of the sphalerite (subject to several marked exceptions).

5. Decreasing abundance of "exsolution" bodies of chalcopyrite and pyrrhotite in sphalerite.

6. Initial increase in the abundance of arsenopyrite, followed by a general decrease.

7. Increase in the cation : anion (weight per cent) ratio.

The present study

Considerable attention was paid during the present study to detailed microscopic studies of the ore and principal gangue minerals. The following observations summarise the relationships observed in approximately 400 polished and polished thin sections; thin sections were employed to resolve some details of gangue mineralogy and to examine wallrocks, but in general the emphasis was concentrated heavily on the opaque minerals. Although the significance of wallrock alteration was recognised, it is not generally
prominent in the Zeehan field and its study is severely hampered by pronounced weathering and, because of the inaccessibility of most mine workings, the lack of suitable sample material. Similarly, the carbonate gangue minerals are worthy of more comprehensive attention than could be given them within the framework of the present investigation.

The microscopic work was undertaken to establish the validity or otherwise of the zonal relationships postulated in earlier descriptions and to provide a framework for subsequent geochemical studies. The following discussion summarizes data on the distribution of the primary ore and gangue minerals in the veins of the Zeehan field, and their mutual textural relationships. The samples studied came from 57 individual deposits within the field; specimens were collected from the dumps (or, in some cases, outcrop or accessible workings) of 47 of these, and museum specimens were used for the remainder. Most of these deposits were dignified with names (often reflecting the optimism of the discoverer rather than the extent of the ore) and these names have been retained for convenient reference in the present discussion; the locations to which they refer are shown in Fig. 12. In some cases some considerable confusion in nomenclature exists (e.g. the "Silver Queen", "No. 1 Queen" and "No. 2 Montana" were all applied, at various times, to the same workings); in such cases the usage represented in Fig. 12 has been adopted throughout the present study.

In this discussion, textural and paragenetic relationships are
emphasized, and the data are grouped accordingly. For many purposes it is also convenient to group together the data for individual deposits. To avoid undesirable repetition in the text, the geology, mineralogy, and production details of individual deposits are described separately in Appendix I, where the deposits are listed alphabetically for ease of reference.

Paragenetic Relationships

Introduction.

Abundant evidence, such as crustification and cockade textures (Edwards, 1954), exists to suggest that all of the minerals in certain types of ore deposits did not crystallize contemporaneously. In such cases, the sequence of formation of the various minerals is often termed the "paragenetic sequence"; the term "paragenesis" is often used more or less synonymously (e.g. Edwards, p. 131), although as noted earlier, in much European literature the latter is widely used in the sense of "assemblage". Reference has already been made to the relationship between paragenetic and zonal sequences, and it is evident that any study of zonal relationships must also include an examination of the time sequence of mineral deposition, so far as it can be determined.

The general concept of paragenetic sequences in mineral deposits has been discussed by many authors, and summarized by Bastin (1950) and Edwards (1954), who both presented extensive descriptions of textural criteria which could be employed to
determine the sequence in a particular mineral deposit. For many years it has been conventional to present complicated histories of ore deposits, deduced from intergranular textural relationships by applying these criteria, often rather more indiscriminately than the original authors intended.

As previously noted, authors (e.g. Lindgren, 1937; Edwards, 1954) have commented on the overall similarity of the paragenetic sequences thus determined for a wide variety of mineral deposits; the "general" paragenetic sequence has been variously related to physical or chemical properties such as hardness, melting points, free energies of formation, crystal structures, aqueous solubilities, cation:anion ratios etc. For a long period relatively little attention was paid to the reliability of the textural criteria employed, despite several warnings such as those of Schouten (1934), who produced synthetic replacement textures in the laboratory and commented (p.655) "The results....may resemble natural intergrowths of the bladed, zonal, graded, lattice, mottled, colloform, graphic, exsolution or transection type. They may closely simulate the formation of mutual boundaries, of so-called "inter-crystallized minerals", structures with crystallographic orientation, apparent inclusions, and vein or vugh filling. Hardly one of the known textures or structures in ore specimens, considered separately, is a safe criterion against metasomatism (replacement)." On the other hand, Edwards (1954, p.129) pointed out that "caries" textures, generally thought to have resulted from
replacement, might well have been produced by simultaneous crystallization of one mineral in the granular interstices of another.

In recent years several authors have voiced a fresh disquiet concerning the validity of several conventional textural interpretations. Thus Stanton (1964) critically reviewed the textures characteristic of some stratiform ores, and showed convincingly that in many cases the "paragenetic sequence" is most probably a crystalloblastic sequence analogous with those commonly displayed by silicate minerals in metamorphosed assemblages; in other words, the textural relationships of the minerals concerned stem from physical properties which need not show any relationship to time sequences of crystallization. Basing his reasoning partly on observed grain boundary configurations and partly on metallurgical principles, Stanton suggested that at least some "replacement textures" simply represent approaches to intergranular configurations of minimum interfacial free energy, and that they can be produced by the mutual interaction of grains growing in the solid state - e.g. during the annealing of microcrystalline aggregates.

Brett (1964), in a study of sub-solidus phase relationships in the system Cu - Fe - S, observed relationships directly opposite to those noted by Schouten; he described exsolution textures closely resembling vein, mutual boundary, and several other textures conventionally thought to be due to replacement.
Barton & Toulmin (1966) noted, from experimentally determined phase relationships in the system Fe - Zn - S, that blebs and lamellae of pyrrhotite in sphalerite, fulfilling all the classical textural criteria of exsolution intergrowths, cannot in fact be produced by simple unmixing of a ZnS-FeS solid solution (see also the discussion in Chapter VI).

It is thus apparent that the use of textural criteria to determine paragenetic sequences must be approached with some caution; nevertheless, it should be stressed that most of the objections which have been raised to date have not been directed at the concept of paragenetic sequences in general, and furthermore that there remain many textures which appear to be capable of unequivocal interpretation. Throughout the present study the hazards of textural interpretation have been clearly recognised; nevertheless, the author is firmly of the opinion that much valuable information can be gained from observations of the physical relationships between the ore and gangue minerals, and that evaluation of this information is essential to an understanding of the zonal and geochemical characteristics of the Zeehan ores.

While it was clearly impossible to establish paragenetic relationships for every pair of minerals present in the ores, in general several distinctive stages of mineralization were apparent, as follows:

1. Early: Cassiterite, wolframite, magnetite, bismuthinite (?), pyrite, pyrrhotite, arsenopyrite, quartz.

3. Late: Galena, tetrahedrite, stannite, boulangerite bournonite, pyrargyrite, argentite, chalcopyrite, pyrrhotite, pyrite, marcasite, arsenopyrite, quartz.

Recognition of these stages does not necessarily imply actual discontinuities in the supply of mineralising solutions or in the crystallization of ore and gangue minerals. In particular, there are no reliable criteria for making a sharp distinction between the first two stages; however, textural and geochemical data both strongly suggest a paragenetic distinction between the last two, suggestive of polyascendant relationships (Kutina, 1965). No paragenetic significance is attached to the order of minerals within any of these groups.

In the following discussion, minerals are described in two groups. The first includes the relatively abundant minerals, which are treated in the order indicated in this generalised paragenetic sequence. Minerals occurring more than once in the proposed paragenetic sequence are discussed fully within the first group in which they appear. Very rare minerals, or those for which paragenetic relationships could not be established, are then described, in alphabetical order, in a subsequent group. Only primary ore and gangue minerals are discussed; Both (1966) has provided a comprehensive list of secondary minerals which have been observed in oxidised lode cappings.
Early Stage

Cassiterite:

Although cassiterite was the major ore mineral of the few producing mines in the tin zone within and adjacent to the margins of the Heemskirk Granite, it has not been observed in the ores of the Zeehan field, except in the Oonah - Queen Hill area. Here cassiterite was found in samples from the Oonah, Stormsdown and Clarke's Lode (No. 4 Queen) workings. Many specimens of the Stormsdown ore contain abundant, small cassiterite crystals, up to 30 microns in diameter. Most are enclosed in sphalerite (Fig. 18), but a few occur in pyrite and siderite, or in galena where it has replaced sphalerite. The crystals are generally anhedral and are distributed more or less randomly through the enclosing minerals; thus the textural relationships provide no information concerning the age of the cassiterite, although its dominant occurrence in (high iron) sphalerite may indicate approximately contemporaneity.

Samples of ore from the Stormsdown mine have been reported (Blissett, 1962) to assay between 0.58 and 4.13% Sn. No other tin minerals were observed in this ore.

Edwards (1951) described two types of cassiterite in samples from the Oonah Mine. One consists of isolated, corroded crystals or clusters of crystals, enclosed in stannite but often separated from it by an irregular, narrow sheath of chalcopyrite which appears to have unmixed from solid solution in the stannite.
Fig. 18: Inclusions of cassiterite (dark grey) in sphalerite (light grey) which is partly replaced by galena (white). Stormsdown Mine. X400

Fig. 19: Subhedral inclusions of primary cassiterite (black) in a vein of chalcopyrite (white) traversing stannite (grey). Stannite Lode, Oonah Mine. X500
Fig. 20: "Needle tin" - stannite (light grey) enclosing fine inclusions of cassiterite (dark grey) with a narrow sheath of chalcopyrite (white). Stannite Lode, Oonah Mine. X700

Fig. 21: Brecciated pyrite "healed" by a quartz matrix. Junction Mine X200
and coalesced around the cassiterite inclusions (Fig. 19). Similar subhedral crystals occur in pyrite and arsenopyrite, or enclosed in quartz; again age relationships are not conclusive, but Edwards thought this cassiterite, together with wolframite, pyrite, arsenopyrite and quartz, to belong to "the early stage of mineralization".

The second form consists of minute acicular or anhedral grains (Fig. 20) forming irregular and impersistent seams traversing stannite, and invariably enclosed by a sheath of chalcopyrite whose width is directly proportional to the grainsize and abundance of the included cassiterite (though many chalcopyrite seams contain no cassiterite). Occasionally acicular or radial aggregates of cassiterite occur in quartz gangue adjacent to areas of stannite; in such cases the chalcopyrite sheath is absent.

The chalcopyrite seams which contain the cassiterite generally appear to be fracture fillings rather than segregation veinlets, although Edwards observed that occasionally the chalcopyrite sheath is contiguous with exsolution bodies of chalcopyrite in the enclosing stannite; these in turn contain small, ovoid bodies of stannite.

Acicular cassiterite of this type is commonly known as "needle tin" and has been observed elsewhere. For example, Randohr (1950) has described identical occurrences in ore from Hunan, China, and interpreted them as resulting from the breakdown
of stannite. Edwards agreed with this interpretation, suggesting (in accordance with Frueh's observations on the low pressure dissociation of stannite) that fracturing and pressure release while the ore was still at a relatively high temperature would cause partial dissociation of stannite, with the tin being re-precipitated as fine-grained cassiterite and the copper and iron as chalcopyrite. Both (1966) has described a sample of brecciated stannite in a matrix of sphalerite; the whole breccia is transected by continuous veinlets of chalcopyrite containing needle tin. Formation of the latter, therefore, clearly post-dates (or is possibly a consequence of) at least one period of post-stannite fracturing.

Twelvetrees & Ward (1910) reported a small lode outcropping east of the Oonah shaft and carrying grey cassiterite and pyrite encased in black slate.

Rare "needle tin" was also observed in chalcopyrite veinlets in stannite from Clarke's Lode.

Wolframite:

Although wolframite accompanies cassiterite in the Heemskirk tin ores, it is rare in the Zeehan field, and has not been observed during the present study. Its presence has been recorded in ore from the Oonah Stannite Lode by Twelvetrees & Ward (1910), Edwards (1951) and Both (1966); it occurs as rare subhedral crystals, up to 1 mm wide, associated with pyrite and quartz.
Bismuthinite:

Bismuthinite is also associated with cassiterite in the Heemskirk tin ores, and is rare in the Zeehan field. Small amounts were reported by Both (1966) in ores from the Oonah Stannite Lode and Clarke's Lode on the Zeehan Queen leases. The bismuthinite forms aggregates of bladed crystals, up to 1.5 cm. long and 3 mm. wide, intergrown with pyrite, arsenopyrite, stannite and chalcopyrite. Although Both believed the bismuthinite to have partially replaced most of the minerals with which it is associated, he noted that most of the textural relationships are inconclusive, so that its paragenetic relationships are obscure.

Both (1966) also reported small clusters of acicular bismuthinite crystals in ore from the Zeehan Bell Mine.

The only bismuthinite observed during the present study consisted of a few small bladed or acicular inclusions in stannite, chalcopyrite, sphalerite and galena from the Oonah Stannite Lode. These generally match Both's descriptions, but are much finer grained.

Magnetite:

With the exception of the Tenth Legion and similar deposits, which are thought to be genetically related to the Cambrian McIvor Hill Gabbro, the distribution of magnetite is confined to the western pyritic ores. Magnetite is an abundant constituent of ore from the Silver Stream Mine, and rare magnetite inclusions were observed in polished sections from the Stonehenge and Tasmanian Mines.
Twelvetrees & Ward (1910) and Waller (1903) reported the presence of magnetite intergrown with pyrite, sphalerite, chalcopyrite and galena in the "Copper Lode" of the Silver Stream workings, and intergrown with sphalerite on a section known as Sligo's lease, south of the Tenth Legion Mine. Sligo's workings could not be located, but several samples from the Silver Stream Mine were found to contain abundant magnetite occurring as irregular aggregates and rounded grains, up to 100 microns wide, enclosed in sphalerite. Much of the common pyrrhotite in the Silver Stream sphalerite occurs as irregular rims moulded around magnetite inclusions, which apparently provided nuclei around which the separating pyrrhotite coalesced.

In the Stonehenge ore, magnetite occurs as rounded inclusions in sphalerite and occasionally in segregation patches of chalcopyrite. It is rare in the Tasmanian Mine samples, being observed only as isolated rounded inclusions, or occasionally larger aggregates (up to 0.5 mm. wide) extensively replaced by siderite.

Pyrite:

As noted in earlier descriptions, pyrite is common in the lodes of the western part of the Zeehan field, and its abundance (particularly relative to siderite) decreases passing eastwards. It is rare in ores of the eastern and south-eastern parts of the field, but is seldom completely absent. There is a marked reversal of the general zonal trend of pyrite distribution in the Queen Hill area.
Under the microscope, several varieties of pyrite can be distinguished, as follows:

1. The most common, and by far the most abundant, variety is that typical of ores of the pyritic type, in which most of the pyrite occurs as seams or granular aggregates of subhedral and euhedral grains of pyrite; individual grains commonly range from 0.1 to 1 mm. in diameter, with the aggregates ranging up to several centimetres in width.

Pyrite of this type is usually intergrown with quartz. In some cases euhedral pyrite crystals are enclosed in a matrix of quartz (e.g. at the Boss Mine); in others (Fig. 21) the pyrite has been brecciated and "healed" by a quartz matrix (Junction Mine). Less commonly, the pyrite itself contains rounded or subhedral inclusions of quartz (Britannia Mine); these are often distributed in a crudely zonal fashion.

In crustified ore from the Comstock Mine, the veins are lined with coarse grained pyrite and are succeeded by zones of younger sulphides; there is little doubt that this pyrite is paragenetically early.

Veins in fractured pyrite and pyrite-quartz intergrowths are commonly filled with sphalerite, siderite, galena and, in some instances, minor sulphides such as tetrahedrite or boulangerite. In most cases, the pyrite has been
partially replaced by the younger minerals. All stages of the replacement can be seen, from sharp fracture fillings with parallel walls and very little replacement through to scattered, heavily corroded residuals of pyrite, disseminated throughout the replacing sulphides or carbonate. In some aggregates, the replacement has proceeded along grain boundaries of the pyrite rather than from fractures.

Sometimes coarse granular pyrite is strongly zoned, with the zoning arising from regular bands of pits up to 5 microns in diameter (No. 2 Argent and Boss Mines, Fig. 22). High magnification optical and electron microprobe examination of these pits revealed no identifiable inclusions; it is possible that material may have been plucked from them during polishing, despite considerable care in the treatment of the sections. Their origin and significance remain uncertain, although the possible former presence of fluid inclusions cannot be discounted.

Much of the general paragenetic sequence proposed above is based on veining and replacement relationships between pyrite and other minerals. For example, samples from the Nubeena Mine contain massive aggregates of pyrite, extensively veined and partly replaced by sphalerite and siderite. These intergrowths have been further
Fig. 22: Zonally distributed pits in pyrite -
(a) Boss Mine, X200
(b) No. 2 Argent Mine, X500.

Fig. 23: Platy habit of pyrite, possibly pseudomorphous after pyrrhotite.
Spray Mine. X250
Fig. 24: Zoned and platy pyrite (white) partly replaced by galena (very light grey) and sphalerite (mid-grey).
Oceana Mine.
X300

Fig. 25: "Reaction rims" of pyrite -
(a) at galena-siderite interfaces, Tasmanian Mine
X250
(b) at galena-sphalerite interfaces (note also blebs of pyrrhotite in sphalerite).
T.L.E. Mine.
X250
Fig. 26: Seams of "dusty" pyrite in grain boundaries of sphalerite, which also contains bleb-like inclusions of chalcopyrite and/or pyrrhotite - (a) Silver Stream Mine, X500, (b) Montana Mine, X250.

Fig. 27: Oriented inclusions of pyrrhotite in sphalerite. Silver Stream Mine. X600
brecciated, with fractures subsequently filled with arsenopyrite and galena. Few departures from this general sequence have been noted, except that late veins of arsenopyrite (q.v) are not common.

Euhedral pyrite crystals are not confined to the vein fillings, but are also disseminated throughout fragments of slaty wallrocks enclosed in the ore and in some cases in the wallrocks themselves. While some of this pyrite may have formed by wallrock alteration during the mineralisation, some also grades into Type (2) (see below) and probably formed by recrystallization during diagenesis.

Pyritic ores often show a crude banding which occasionally results from crustification, but which more frequently resembles short, discontinuous veins of pyrite within sphalerite and/or galena; these irregular veinlets often show sub-parallel or roughly en echelon relationships, or poorly developed "swirling" textures. Under the microscope, the vein-like appearance is seen to be deceptive; the pyrite "veins" consist of elongated irregular aggregates of euhedral to subhedral crystals of pyrite, commonly between 10 and 500 microns wide, extensively replaced by the enclosing sulphides. The latter show evidence of strong deformation - sphalerite is fine-grained and heavily twinned, and galena shows bent
cleavages and frequently weak anomalous anisotropism. These textures are interpreted as "deformation banding" (Edwards, 1954, p.35), and the younger age of pyrite which they superficially appear to indicate is fallacious.

2. Fine-grained microspherular or frambooidal pyrite aggregates, usually less than 20 microns in diameter, are common in fragments of wallrock enclosed in the ore, and in some of the wallrocks themselves. These aggregates closely resemble the microspherular pyrite described by Love & Zimmerman (1961) from the Proterozoic Mt. Isa Shale and considered by them to be syngenetic. Similar pyrite has been described from numerous localities - e.g. the Mansfeld Kupferschiefer (Schneiderhöhn, 1923), Rio Tinto in Spain (Schouten, 1946), Tilkerode in the Harz Mountains (Ramdohr, 1955), and Branch Creek, near Port Sorell in northern Tasmania (Baker, 1960) - not all of which are associated with epigenetic ore formation. While some controversy exists concerning the precise mode or origin of the minute spheres, particularly in relation to the possible role of micro-organisms, there seems little doubt that they are not epigenetic features and in the present instance they are most probably not directly related to the mineralization.
3. Several polished sections from the Oceana and Spray Mines contain, within seams of galena, inclusions of pyrite displaying an unusual platy habit (Fig. 23); in some instances aggregates contain cores of platy pyrite surrounded by outer areas displaying a more conventional zoning, parallel to crystal faces and accentuated by preferential replacement by the enclosing galena (Fig. 24). The platy habit is more typical of pyrrhotite or marcasite than of pyrite, and suggests that the aggregates may be at least partly pseudomorphous after one or both of the former.

It is unlikely that simple monotropic inversion of marcasite to pyrite has been involved, since Kullerud (1967) has shown that marcasite is stable to over 400°C, even at pressures exceeding 2 kb.; the preservation of the lamellar habit under these conditions is improbable, and strain effects in the surrounding galena of the Oceana specimens would probably have been removed by annealing at temperatures of this order, although experimental evidence is lacking.

The breakdown of pyrrhotite to lamellar marcasite and minor pyrite has been observed in samples from the Comstock Mine. Edwards (1954, p. 123) notes that the formation of marcasite under these circumstances is dependent on the acidity of the environment, and in cases
where "the environment is not sufficiently acid for marcasite to form" pyrite is produced instead. Kullerud (1967), reporting preliminary work in the system Fe-S-O-H, noted that marcasite formed only in Fe-S-O-H experiments, whereas pyrite could be synthesised in both Fe-S-O and Fe-S-O-H runs; he suggested that marcasite might be stabilised by H-S bonds. These matters will be further discussed below when the distribution of marcasite in the Zeehan ores is reviewed; for the present it is proposed that the lamellar pyrite formed by pseudomorphous alteration of pyrrhotite, under relatively alkaline conditions. Although this type of pyrite is rare, the possible indication of alkaline conditions within the sideritic zone at the time of deposition of galena is of some significance to the interpretation of chemical changes in the ore fluids (see Chapter VIII).

4. Thin, discontinuous seams of pyrite and/or marcasite are frequently observed along boundaries between siderite and sphalerite, siderite and galena, and sphalerite and galena (Fig. 25). These commonly appear to be "reaction rims" at replacement boundaries; they usually consist of stringers of euhedral or subhedral crystals which are individually between 10 and 100 microns wide. Under these circumstances pyrite grains
often show "atoll" textures (Edwards, 1954, p.118) which might have arisen from partial replacement of the pyrite, as proposed by Edwards, but which might equally well have been formed during growth in the solid state, as a consequence of the strong crystalloblastic tendencies of pyrite. It is significant that these "atoll" textures are particularly abundant in the vicinity of replacement boundaries between these mineral pairs, and are relatively rare elsewhere. In polished sections of ore from the Tasmanian Mine, for instance, there is a pronounced difference in texture between residual anhedral pyrite grains of Type (1), enclosed within sphalerite and corroded around their external margins, and "atoll"-type pyrite at galena-sphalerite and galena-siderite replacement boundaries.

It is believed that pyrite of this type was formed by reaction between iron set free during the replacement and sulphur introduced in the hydrothermal fluids. Independent evidence (see Chapter VI) suggests that sulphur fugacities may have been relatively high during the crystallization of the galena, in agreement with this proposal. The alternative possibility of reaction between introduced iron and sulphur set free by replacement of sphalerite is not favoured, since it would not account for the formation of pyrite at galena-
siderite replacement boundaries.

Again the formation of pyrite or marcasite or intergrowths of both is believed to be a function of the pH of the hydrothermal fluids at the time of the replacement. In general, marcasite of this type is more common, but by no means ubiquitous, in ores of the pyritic types (e.g. Doric and Tasmanian Mines, and pyritic ores of the Queen Hill area). Nowhere, however, does marcasite occur to the exclusion of pyrite which suggests, from the preliminary data of Kullerud (1967), that the ore solutions varied from alkaline to no more than slightly acidic (see below).

5. Closely related to Type (4), in both distribution and probable origin, are narrow, impersistent seams of fine-grained "dusty" pyrite (Fig. 26), which are frequently observed in sphalerite in the immediate vicinity of galena replacement boundaries. These seams, consisting of aggregates of small, subhedral to euhedral crystals, transect areas of sphalerite or, more commonly, occupy grain or twin boundaries. In many cases (e.g. in specimens from the T.L.E. Mine) there is a marked correlation between the intensity of the replacement and the abundance of these minute pyrite inclusions.

Bleb-like inclusions of pyrrhotite and chalcopyrite
frequently show a similar concentration in sphalerite zones adjacent to replacement interfaces; the geochemical significance of these assemblages is discussed elsewhere.

It is thus possible to distinguish between several generations of pyrite in the Zeehan ores, viz:

(i) the framboidal pyrite, which is probably syngenetic or diagenetic and unrelated to the mineralization;

(ii) the granular pyrite which formed early in the paragenetic and zonal sequences and which is characteristically brecciated, "healed", and partly replaced by sphalerite, siderite and galena; and

(iii) the "reaction rims" and fine, dusty pyrite, which are closely associated with replacement boundaries involving younger minerals (particularly galena).

(iv) "Bladed" pyrite which appears to have in some instances by the breakdown of pyrrhotite; marcasite has more commonly been produced under these circumstances.

Pyrrhotite:

Pyrrhotite is never a major constituent of any of the Zeehan ores, but small proportions, generally only detectable in polished sections, are present in many of the veins. It is rather more abundant in the western pyritic lodes than in those to the east.
By far the greater part of the pyrrhotite occurs as small bleb-like inclusions, generally between 3 and 50 microns in diameter, enclosed within sphalerite. Rarely they show a crude crystallographic control in their orientation within the sphalerite (Fig. 27). They range from abundances so extreme that it is very difficult to find areas sufficiently clear for microprobe analysis (e.g. Doric Mine) down to a few scattered, minute inclusions which are easy to overlook (Grubb's Mine, Argent Flat mines). They are frequently associated with similar emuloid or bleb-like inclusions of chalcopyrite (although composite pyrrhotite-chalcopyrite inclusions are rare); generally chalcopyrite is rather more abundant than pyrrhotite, but several occurrences of pyrrhotite alone were noted.

Both chalcopyrite and pyrrhotite display a feature already noted in the case of fine-grained, "dusty" second-generation pyrite - they are not uniformly distributed through their sphalerite hosts, but show a marked concentration in the vicinity of boundaries between sphalerite and other minerals, the latter being paragenetically either older or younger than the sphalerite. Thus in crustified ore from the Comstock Mine, marginal pyrite and pyrite-pyrrhotite (see below) layers often give way abruptly to an inner crust of dark, iron-rich sphalerite. Narrow bands, up to 100 microns wide, in the sphalerite and immediately adjacent to the older pyrite contain scattered blebs and rod-like inclusions of pyrrhotite (Fig. 28).
Much more commonly, pyrrhotite inclusions in sphalerite are concentrated in the vicinity of boundaries between the host sphalerite and replacing galena, quartz or, rarely, siderite (Fig. 29). As already noted, such replacement boundaries are commonly lined with irregular, discontinuous "reaction rims" of pyrite and/or marcasite, and the narrow bordering zones, again up to 100 microns wide, in which the pyrrhotite is abundant may also contain chalcopyrite and fine-grained pyrite; the latter two minerals may also be present, together or singly, in the absence of pyrrhotite.

The experimental studies of Barton & Toulmin (1966) have demonstrated that pyrrhotite of this type, although it fulfills most of the classical textural criteria of exsolution origin, cannot have been produced by the isochemical unmixing of a sphalerite solid solution. The closely related distributions of pyrite and chalcopyrite, together with chemical data on the compositions of the host sphalerite zones, provide keys to an interpretation of the origin of the pyrrhotite, which is discussed in more detail in a later section (Chapter VI). The formation of pyrite-pyrrhotite-sphalerite assemblages of this type has considerable geothermometric significance which will also be reviewed later.

In cases where the galena replacement has advanced to the point where sphalerite occurs only as scattered rounded residuals in a galena matrix, pyrrhotite occurs as slightly larger blebs in
Fig. 28: Fine bleb-like inclusions of pyrrhotite in sphalerite, concentrated in narrow zones adjacent to pyrite interfaces. Comstock Mine. X250

Fig. 29: Inclusions of pyrrhotite in sphalerite, adjacent to contact with replacing siderite. Note also inclusions of pyrite in siderite. Comstock Mine. X250
Fig. 30: Coarse pyrrhotite partially rimming sphalerite which has been extensively replaced by galena; some fine blebs of chalcopyrite and pyrrhotite in the sphalerite residuals. Silver Stream Mine. X 350

Fig. 31: Coarse pyrrhotite and chalcopyrite similar to those of Fig. 30; fine blebs of chalcopyrite and pyrrhotite somewhat less abundant. Doric Mine. X 250
Fig. 32: Alteration of pyrrhotite to marcasite, crudely symmetrical about thin veinlets of carbonate (black). Comstock Mine. X250

Fig. 33: Quartz (white) and sphalerite (stippled); a "mutual boundaries" texture probably indicative of contemporaneity. High relief inclusions are arsenopyrite. Spray Mine. X50
the sphalerite, and as considerably larger patches, up to 200 microns wide, in the galena; chalcopyrite shows similar relationships. Both pyrrhotite and chalcopyrite often form partial rims on the unreplaced sphalerite (Fig. 30). It appears in such instances that both pyrrhotite and chalcopyrite have resisted replacement and, as the sphalerite matrix has been progressively removed, they have coalesced into larger aggregates, some of which contain both minerals. Some specimens (notably several from the Silver Stream Mine) represent the virtual culmination of this process – they consist of massive, relatively coarse-grained intergrowths of galena, chalcopyrite and pyrrhotite, with extensively corroded residuals of pyrite and sphalerite (Fig. 31).

By contrast, in several instances where pyrrhotite inclusions in sphalerite are particularly abundant (e.g. Doric Mine), the inclusions have been preferentially replaced by the galena. Replacement of the pyrrhotite is complete near the sphalerite–galena boundaries, partial up to 30 or 50 microns away, and not observed at all more than 200 microns from the "contact". These variations in the nature of preferential replacement probably reflect different chemical environments during the replacement.

In several samples, electron microprobe analyses demonstrate clear correlations between the degree of replacement, the abundance of pyrrhotite, chalcopyrite, and pyrite inclusions, and the iron and manganese contents of the sphalerite. The chemical
data are discussed in more detail in Chapter VI; an example is provided by ores of the T.L.E. Mine, which show a strong variation in sphalerite geochemistry. Unreplaced sphalerite, free of inclusions, contains from 0.9 to 2.3 weight per cent FeS and less than 0.1 weight per cent MnS. Moderately replaced sphalerite, transected by narrow seams of galena and containing a few scattered inclusions of chalcopyrite, pyrrhotite and minor pyrite, contains from 3.0 to 5.8 per cent FeS and 0.2 to 0.3 per cent MnS. Extensively replaced sphalerite residuals in seams of galena, with abundant inclusions of chalcopyrite, pyrrhotite and pyrite, range from 8.5 to 9.5 per cent FeS and 0.5 to 0.6 per cent MnS.

In rare instances, such as in the Comstock Mine ore, pyrrhotite occurs in coarsely crystalline granular intergrowths with early pyrite; in such cases the original pyrrhotite has frequently been altered to lamellar intergrowths of marcasite (q.v) and minor pyrite, with intimately intergrown carbonate inclusions (Fig. 32). As reported above, these pyrite-pyrrhotite intergrowths were observed in crustified sequences, where they were followed by layers of sphalerite. These represent the only cases in the Zeehan ores where sulphur fugacity during crystallization of the sphalerite might possibly have been fixed by the co-existence of pyrite and pyrrhotite, so that the composition of the sphalerite might be indicative of its temperature of crystallization.
Marcasite:

Small amounts of marcasite were observed in many polished sections of the Zeehan ores. Both (1966) noted that marcasite is frequently associated with pyrite, and therefore is more abundant in ores from the western part of the field; the present study supports the latter conclusion, but not the reasoning on which it was based. Recent experimental data on the stability of marcasite suggest that it is more likely that its limited distribution is a function of temperature and changing chemistry of the hydrothermal fluids.

Several texturally distinctive types of marcasite can be distinguished, as follows:

1. A relatively coarse grained variety, usually intimately intergrown with pyrite and/or arsenopyrite aggregates (Silver Stream, No. 5 Argent, Grubb's, Nubeena Mines, and the Oonah Stannite Lode). The marcasite grains generally occupy the interstices between euhedral pyrite or arsenopyrite crystals; they often show well-developed polysynthetic twinning.

2. Lacy networks of fine, anhedral crystals in cleavages and fractures in siderite and in both galena and siderite adjacent to galena-siderite replacement boundaries (galena replacing siderite). In the latter case, seams in galena are extensions of veinlets in siderite; the marcasite is evidently younger than the siderite, but its age
relationships with the galena are less clear. Where pyrite occurs in the vicinity of these contacts, it is often intimately intergrown with marcasite; the intergrowths can be distinguished from Type (1) marcasite only by their evident spatial relationship with the replacement boundaries and their relatively fine grain size. In the eastern part of the field, pyrite occurs alone in this environment; to the west and in the Queen Hill area (e.g. Oonah Galena Lode) marcasite increases in relative abundance, but never to the complete exclusion of pyrite.

3. Closely related to Type (2) are the "reaction rims" of pyrite and minor marcasite which are observed at galena-siderite replacement boundaries and which have already been described. Again marcasite is absent from these "reaction rims" in the eastern part of the field and is more abundant to the west (e.g. Tasmanian and T.L.E. Mines), but is always accompanied by pyrite.

4. Similarly related to (2) and (3) are fine, dusty inclusions and small euhedral crystals of marcasite in grain boundaries of sphalerite, adjacent to galena-sphalerite replacement boundaries. Marcasite of this type is much less abundant than similar pyrite, having been observed in appreciable proportions only in ore from the Doric Mine.

5. Samples from the No. 5 Argent, Comstock and Stonehenge Mines contain distinctive marcasite characterised by a marked lamellar
texture; it is usually accompanied by residuals of pyrrhotite, which it clearly pseudomorphs, and by small inclusions or narrow seams of carbonate gangue (which, in the particular case of Comstock ore, are rare elsewhere). The alteration of the pyrrhotite is often crudely symmetrical about narrow carbonate veinlets (Fig. 32) and appears to have proceeded outwards from these veins.

Similar textures resulting from the breakdown of pyrrhotite, usually in the presence of carbonate gangue, have previously been observed in a variety of hypogene ore deposits (e.g. Buseck, 1967), and have been described as hypogene textures by Edwards (1954), who states "... a change in the acidity and temperature of the residual mineralizing solutions renders the pyrrhotite unstable, so that it dissolves spontaneously. The iron and sulphur set free are reprecipitated almost immediately as marcasite, which is stable under the new conditions. This change coincides with the appearance of hypogene carbonate deposition, and commonly the fine-grained marcasite forms composite parallel or radiating lamellae, which are intimately intergrown with the carbonate mineral, in which the excess iron of the pyrrhotite is accommodated. Occasionally the excess iron is deposited as magnetite.... In other cases the environment is not sufficiently acid for marcasite to form, and the pyrrhotite is replaced by equally
fine-grained intergrowths of pyrite and carbonate or pyrite and magnetite".

Similar breakdown of magmatic pyrrhotite to marcasite has been noted by Wager, Vincent & Smales (1957) in rocks of the Skaergaard intrusion, and has been attributed by them to "the elimination of some iron, sulphur remaining constant" (p. 869).

The textural and zonal relationships of marcasite in the Zeehan ores have several implications:

(a) Kullerud (1967) has shown that marcasite inverts to pyrite at temperatures ranging from $432 \pm 3^\circ C$ at 1 atmosphere to $423 \pm 2^\circ C$ at 2 kb. total pressure. Pyrite, however, does not revert to marcasite below these temperatures. The presence of marcasite, of any textural type, therefore places upper limits of temperature on the ores at the time the marcasite formed and during their subsequent history.

The coarse, granular (Type 1) marcasite intergrown with massive pyrite is rare or absent in the strongly pyritic ores of the western part of the field, but becomes relatively common in the Grubb's - Spray - Argent Flat belt. This distribution, which contrasts with those of the paragenetically younger types, is suggestive of a temperature control.

(b) When further experimental studies have been made to define the stabilities of marcasite and pyrite in terms of pH, the
coexistence of pyrite and marcasite in many of the Zeehan ores will assist in defining the pH of the hydrothermal fluids, providing independent estimates of temperature are available. It will be shown later than a reasonable basis exists in several cases for estimation of the temperature of galena-sphalerite replacement, with which pyrite-marcasite reaction rims are associated. In the meantime, the relative abundance of marcasite of this type in the western pyritic ores and its absence from the eastern sideritic ores qualitatively suggest a gradual west-to-east change in the hydrothermal fluids from "acid" to "alkaline". Even in the pyritic zones, however, extremely "acid" conditions are improbable, since marcasite invariably coexists with pyrite.

The early crystallization of pyrite and pyrrhotite in some ores, the subsequent breakdown of the pyrrhotite to marcasite and carbonates, and then the further production of a second generation of pyrite and pyrrhotite (q.v) indicates fluctuations in the chemistry of the ore-forming fluids, lending strength to the concept of a paragenetic sequence.

Calculations of the limiting chemical environment for the breakdown of pyrrhotite, according to the reaction:
are presently hampered by inadequacies in the available thermochemical data (e.g. Holland, 1965, has drawn attention to some inconsistencies in the published data for the decomposition of siderite) and by a lack of knowledge of the temperature at which the breakdown took place. An upper limit of approximately 430°C is imposed by Kullerud's (1967) data on the stability of marcasite, but there is no way of estimating a reliable lower limit.

At 400°C, the calculations of Holland (1965) show that marcasite and siderite can co-exist, in equilibrium, only if \( f_{CO_2} \geq 10^2 \) atmospheres and \( f_{S_2} \geq 10^{-7.3} \) atmospheres. Under lower \( CO_2 \) fugacities, pyrrhotite oxidises instead to magnetite or \( FeS_2 + \) magnetite, depending on sulphur fugacity (cf. Edwards, 1954, quoted above), and under lower \( S_2 \) fugacities, pyrrhotite oxidises to siderite or magnetite, depending on \( CO_2 \) fugacity.

At 250°C, Holland's data indicate that marcasite and siderite can co-exist stably under much lower \( CO_2 \) fugacities (\( > 1 \) atmosphere), although near the lower end of this range, the marcasite-siderite equilibrium boundary barely lies within the "main-line" \( f_{S_2} - f_{O_2} \) field as defined by other common hydrothermal assemblages, and it seems probable that 10 atmospheres would be a more realistic minimum for \( f_{CO_2} \).

\[ 2FeS\text{*} + CO_2 + \frac{1}{2}O_2 \rightleftharpoons FeCO_3 + FeS_2 \]

* Approximate composition
At 400°C, pyrrhotite is stable over an appreciable portion of the "main-line" \( \frac{f_{S_2}}{f_{O_2}} \) field, even under high \( CO_2 \) fugacities (10^2 atmospheres); at 250°C, however, the stability field of pyrrhotite barely encroaches on the "main-line" field when \( f_{CO_2} < 10^{-2} \) atmospheres.

While it is therefore possible that the breakdown of pyrrhotite to marcasite + siderite can result simply from re-equilibration during "main-line" cooling, the subsequent formation of a second generation of pyrrhotite poses some problems. Either the temperature must have increased again or, more probably, the breakdown resulted from a temporary effective increase in \( f_{CO_2} \) at some temperature higher than 250°C but below 430°C.

Formation of the second generation of pyrrhotite accompanied the deposition of galena and quartz during a paragenetic stage which is believed, from textural evidence, to be distinct from the early pyrite-pyrrhotite-sphalerite-siderite mineralization. Thus it is also possible that the breakdown of the first generation of pyrrhotite resulted from re-equilibration during limited cooling under high \( CO_2 \) fugacities associated with the first phase of mineralization, and that \( CO_2 \) fugacities during the later stage were much lower, allowing the formation of more pyrrhotite. This interpretation, which is consistent with both textural and thermochemical evidence, thus implies that \( CO_2 \) fugacities were of the order of 10^2 atmospheres (depending somewhat on temperature and
sulphur fugacities) during the early to middle stages of the paragenesis, but were much lower - of the order of $10^{-2}$ atmospheres - during the late stages.

**Arsenopyrite:**

Arsenopyrite is a minor constituent of many of the Zeehan ores; however, it was not observed in sideritic ore from the eastern and south-eastern group of mines or the strongly pyritic deposits of the Comstock - Silver Stream area. In the sections examined, it was found to be most abundant in samples from moderately pyritic to intermediate sidero-pyritic ore types from the Sylvester, Britannia, North Tasmanian and Spray Mines and the Oonah Stannite Lode.

Texturally, several different types of arsenopyrite can be distinguished, and these appear to indicate its deposition, in various parts of the field, virtually throughout the paragenetic sequence.

In many of the ores containing the early, granular type of pyrite, euhedral and subhedral crystals of arseno-pyrite are intimately intergrown in the pyrite aggregates, sometimes occupying the interstices between euhedral pyrite crystals, and sometimes occurring as characteristically rhomboid crystals enclosed within pyrite. Individual arsenopyrite crystals are commonly up to 500 microns wide; coarser grained crystals and crystalline aggregates up to several millimetres wide were observed in samples from the Oonah Stannite Lode.
Pyrite-arsenopyrite intergrowths are commonly enclosed within a quartz matrix; many are brecciated and have been "healed", with varying degrees of replacement, by sphalerite, siderite, chalcopyrite and galena. In several instances the arsenopyrite in these intergrowths appears to have been preferentially replaced, particularly by siderite (Despatch Mine).

In many other cases, arsenopyrite occurs as smaller, euhedral crystals, usually less than 100 microns wide, disseminated throughout siderite and showing no sign of replacement (Zeehan, Grubb's, No. 1 Montana, No. 2 Queen Mines) or varying degrees of apparent corrosion by the siderite (Western, Big Ben, Nike Mines). The apparent corrosion may be deceptive, and may simply have resulted from strong crystalloblastic effects during simultaneous crystallization of the two minerals.

Rarely, arsenopyrite occurs as ill-defined "stringers" of small, euhedral crystals showing a tendency to concentrate near galena-sphalerite boundaries (No. 3 Queen, North Tasmanian Mines). This apparent concentration is much less well-defined than those of pyrrhotite, chalcopyrite etc. which have been discussed above.

Small euhedral crystals of arsenopyrite are also common in late veinlets of galena, quartz and/or tetrahedrite transecting intergrowths of pyrite, sphalerite and siderite (Argent Flat, Nubeena Mines). In some cases (Nubeena Mine) sharply defined veinlets containing arsenopyrite alone transect areas of pyrite and sphalerite.
Crudely crustified veinlets from the No. 1 Argent Mine show a sequence from early intergrowths of pyrite and arsenopyrite through siderite to late quartz and arsenopyrite.

In several cases euhedral crystals of arsenopyrite, up to 1 mm wide, are disseminated (along with pyrite crystals of similar size) through fragments of black, slaty host-rocks enclosed within the ore (Montana Silver-Lead Mine, Oonah Galena Lode).

Arsenopyrite is consistently partly replaced by galena (except in the late galena-quartz-arsenopyrite veins) and frequently by sphalerite. It appears to have been extensively replaced by tetrahedrite, boulangerite and bournonite in the unusual ores of the Spray Mine, but again many of the resulting textures are open to alternative interpretations.

In experimental studies of the system Fe-As-S, Clark (1960) has shown that the assemblage pyrite + arsenopyrite is stable only up to $491^\circ \pm 12^\circ$C, under the vapour pressure of the system; above this temperature the assemblage is destroyed by the reaction:

$$\text{pyrite} + \text{arsenopyrite} \rightarrow \text{pyrrhotite} + \text{liquid or vapour}.$$  

Under confining pressures of 2.07 kilobars, Clark found that pyrite and arsenopyrite could coexist up to $528^\circ \pm 10^\circ$C.

The absence or rarity of arsenopyrite from the pyritic ores of the Silver Stream - Comstock area, contrasted with its abundance in the pyritic ores of the Britannia and Sylvester Mines, short distances to the east, may thus have thermometric significance. It is possible that crystallization temperatures
in the early paragenetic stages of the Silver Stream - Comstock mineralization were above the arsenopyrite-pyrite stability limit, but declined below it in the Britannia - Sylvester region as a consequence of the thermal gradient outward from the Heemskirk Granite or, more probably, its subsurface continuation beneath the Zeehan field.

Since 1 to 2 kb. is not an unreasonable estimate of the confining pressure in the aureole of a high level granite intrusion, this reasoning would indicate possible temperature ranges of approximately 500°C or more for the Comstock - Silver Stream ores (at the time of pyrite deposition), and 500°C or slightly less for the Britannia and Sylvester ores. These estimates will be compared with those obtained from other mineralogical and geochemical parameters in Chapter VI.

Quartz:

Although little reference is made in earlier descriptions to the distribution of quartz, the present study has shown it to be almost ubiquitous, albeit frequently in minor amounts, in the Zeehan ores. It is the principal non-metallic gangue mineral in the western pyritic ores, but further east is generally subordinate to siderite.

Paragenetically, quartz shows a wide range of crystallization affiliations. Most of the early granular pyrite aggregates are enclosed in a matrix of quartz; in many instances (e.g. Boss Mine) the pyrite occurs in areas of quartz which are
in turn enclosed in sphalerite or siderite. Occasionally pyrite grains are studded with crudely zonally distributed inclusions of quartz (Britannia and Comstock Mines). Samples from the Junction Mine contain pyrite which has been brecciated and "healed" by quartz; the resulting pyrite-quartz intergrowth is veined, and the pyrite is extensively replaced, by massive, coarsely crystalline siderite.

In some cases, intergrown pyrite and sphalerite have been brecciated, and the resulting fractures are filled with younger quartz (Britannia Mine). The ores of the Silver Duke Mine, southeast from the Swansea section, were reported to consist of fragments of ore sulphides loosely cemented by siderite and quartz. The gangue of the Swansea veins consists principally of siderite, irregularly intergrown with patches of quartz which show no decisive textural relationships with the siderite, and probably crystallized at the same time. Similar textural relationships between quartz and sphalerite in the Spray ores are correspondingly difficult to interpret (Fig.33), and also probably indicate approximate contemporaneity.

Both (1966) has described samples of "chopped" or "hacked" quartz from the Sunshine Mine (Tramway Formation), and has suggested that the angular impressions in the massive quartz have been produced by preferential leaching of siderite or another carbonate mineral.

In crudely banded ore samples from the Nike Mine, seams of
late galena are separated from enclosing siderite by bands of quartz, up to several millimetres wide. Similarly, quartz occasionally forms impersistent rims in galena veins transecting sphalerite in samples from the Western Mine. Quartz, galena and, in some cases, tetrahedrite are intimately intergrown in late veinlets transecting pyrite, sphalerite and siderite from many deposits (Argent Flat, King, No. 1 Montana, Nike, Oceana, T.L.E., and Tasmanian Mines). Euhedral, acicular crystals of boulangerite from the Spray Mine are commonly enclosed in a matrix of younger quartz.

Finally, late quartz veins transecting galena, and occasionally filling galena cleavages, have been observed in several deposits (Grubb's, Beauty Mines).

Quartz therefore ranges in age through the whole paragenetic sequence, from approximate contemporaneity with the early, granular pyrite to the galena stage and later. Particular interest attaches to the younger phases which occur as narrow veinlets transecting areas of sphalerite; thin sections frequently show the sphalerite to be markedly darker in colour adjacent to these veinlets, (Fig. 34) and electron microprobe analytical profiles across the dark zones (Fig. 35) reveal that the dark colour is a reflection of increasing iron content in the sphalerite. The significance of these relationships is discussed more fully elsewhere (Chapter VI); it is believed that they result from mineralogical adjustments in the sphalerite consequent
upon changes in the chemical environment between the stages of sphalerite and quartz crystallization.

As an approximate generalization, paragenetically early quartz is more abundant in the western pyritic ores than in the eastern sideritic types, and the later quartz shows an opposite distribution. There are, however, several exceptions to both trends.

Sphalerite whose abundance is comparable with that of pyrite and greatly exceeds that of galena, but in the Austral Valley deposits, for example, most of the sphalerite occurs as fine-grained, extensively corroded residuals in a predominantly galena-siderite matrix.

Paragenetically, there is little doubt that most sphalerite is younger than the coarse granular pyrite, and is in turn distinctly older than the galena and associated sulphosalts. Sphalerite frequently fills fractures in pyrite, with varying degrees of replacement, and, in the pyritic ores, corroded subhedral crystals of pyrite enclosed in sphalerite are common. On the other hand, veinlets of galena, chalcopyrite, tetrahedrite and quartz transecting sphalerite are common throughout the field; mineralogical and chemical changes in the sphalerite adjacent to these veins (see below and Chapter VI) strongly suggest that there is a paragenetic discontinuity between the crystallization of the sphalerite and the veinlet minerals.

The relationships between sphalerite and siderite are less decisive. In some instances sphalerite appears to be older, at
Intermediate phase

Sphalerite:

Sphalerite occurs in almost all of the deposits examined, but is significantly more abundant in the western part of the field compared to the eastern and south-eastern deposits. In the pyritic ores of the Comstock district, it is a major constituent whose abundance is comparable with that of pyrite and greatly exceeds that of galena, but in the Austral Valley deposits, for example, most of the sphalerite occurs as fine-grained, extensively corroded residuals in a predominantly galena-siderite matrix.

Paragenetically, there is little doubt that most sphalerite is younger than the coarse granular pyrite, and is in turn distinctly older than the galena and associated sulphosalts. Sphalerite frequently fills fractures in pyrite, with varying degrees of replacement, and, in the pyritic ores, corroded subhedral crystals of pyrite enclosed in sphalerite are common. On the other hand, veinlets of galena, chalcopyrite, tetrahedrite and quartz transecting sphalerite are common throughout the field; mineralogical and chemical changes in the sphalerite adjacent to these veins (see below and Chapter VI) strongly suggest that there is a paragenetic discontinuity between the crystallization of the sphalerite and the veinlet minerals.

The relationships between sphalerite and siderite are less decisive. In some instances sphalerite appears to be older; it
occurs as irregular, "shredded" inclusions in siderite, or grain boundaries in massive sphalerite aggregates are penetrated by narrow seams of siderite. "Reaction rims" of pyrite and/or marcasite are not uncommon at sphalerite-siderite interfaces, but they usually give no indication of the direction of replacement. On the other hand, the reverse relationships of siderite inclusions within sphalerite, or areas of siderite transected by sphalerite veinlets, are equally common. In some cases (Boundary, No. 1 Montana, Montana Silver-Lead, No. 3 Queen Mines), crustified ore consists of alternating bands of sphalerite and siderite. It is concluded that the two minerals were deposited more or less contemporaneously, possibly with some local exceptions. It is not uncommon for a series of polished sections of ore from a single deposit to show completely conflicting relationships, which can only be interpreted as almost complete paragenetic overlap.

Zeehan sphalerites vary considerably in colour; Table 3 shows the correlation between general colour and the range of FeS contents determined by electron microprobe analysis for a group of typical examples. It is apparent that there is a general darkening of colour with increasing iron content, but that there are some discrepancies; the inadvisability of using colour as a reliable guide to composition of sphalerites has previously been discussed (Williams, 1965).

There is a general decrease in iron content of sphalerite,
### TABLE 3.

Relation between colour and iron content of sphalerite

<table>
<thead>
<tr>
<th>Deposit</th>
<th>Sphalerite colour (hand specimen)</th>
<th>Range in FeS contents (wt. per cent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austral</td>
<td>Pale to mid-brown</td>
<td>0.1 - 1.4</td>
</tr>
<tr>
<td>King</td>
<td>Pale beige to mid-brown</td>
<td>0.1 - 1.5</td>
</tr>
<tr>
<td>Swansea</td>
<td>Pale beige to honey brown</td>
<td>0.1 - 1.2</td>
</tr>
<tr>
<td>Oonah</td>
<td>Mid-brown</td>
<td>1.3 - 5.2</td>
</tr>
<tr>
<td>Big Ben</td>
<td>Mid-brown resinous</td>
<td>0.1 - 3.7</td>
</tr>
<tr>
<td>No. 2 Queen</td>
<td>Dark brown</td>
<td>0.3 - 4.2</td>
</tr>
<tr>
<td>Stonehenge</td>
<td>Pale to resinous brown to black</td>
<td>1.4 - 14.4</td>
</tr>
<tr>
<td>Sunshine</td>
<td>Resinous brown</td>
<td>0.1 - 8.8</td>
</tr>
<tr>
<td>Grubb's</td>
<td>Orange red to dark brown</td>
<td>0.1 - 11.1</td>
</tr>
<tr>
<td>No. 4 Queen</td>
<td>Mid-brown to black</td>
<td>2.7 - 16.8</td>
</tr>
<tr>
<td>Boss</td>
<td>Dark reddish brown</td>
<td>6.4 - 9.4</td>
</tr>
<tr>
<td>Comstock</td>
<td>Very dark red-brown</td>
<td>5.0 - 16.3</td>
</tr>
<tr>
<td>Doric</td>
<td>Dark brown</td>
<td>10.0 - 20.5</td>
</tr>
<tr>
<td>Sylvester</td>
<td>Dark brown</td>
<td>0.3 - 17.7</td>
</tr>
<tr>
<td>Silver Steam</td>
<td>Dark brown to black</td>
<td>10.3 - 20.0</td>
</tr>
</tbody>
</table>
Fig. 34: Electron microprobe FeKα scan of a dark zone in sphalerite adjacent to a quartz vein (black area at right).
Stonehenge Mine. X150

Fig. 35: Profile of iron content of sphalerite across mid-line of Fig. 34.
Fig. 36: Growth zoning in sphalerite enclosed in siderite (thin section). Austral Valley. X60

Fig. 37: Abrupt compositional discontinuities in sphalerite due to "microfaulting" of originally inhomogeneous aggregates. Figures are FeS contents (wt. per cent) determined by microprobe analysis. Swansea Mine. X100
Fig. 38: Irregular compositional variations in sphalerite (thin section).
Stonehenge Mine. X200
with a parallel decrease in manganese content, from the pyritic ores in the west to the sideritic ores in the east, with a marked reversal in the Queen Hill area. These trends have been subjected to detailed examination based on some hundreds of microprobe analyses, the results of which are summarised and discussed in detail in Chapter VI.

Thin section examination of sphalerites, coupled with the results of the microprobe analyses, show the Zeehan sphalerites to be generally chemically inhomogeneous. Only rarely does the inhomogeneity stem from well defined growth zoning, as is common in many sphalerites from other localities (e.g. Barton, Bethke and Toulmin, 1963). Zoning of this type has occasionally been observed in some of the low iron sphalerites from the sideritic ores (Fig. 36). More commonly, however, the "zoning" is irregular and patchy, with ill-defined, gradational margins which cannot be related to any crystallographic boundaries.

In low iron sphalerites, chemical variation is apparent in polished sections as a consequence of pronounced changes in internal reflection; the theoretical changes in reflectivity as a consequence of changing refractive indices and absorption coefficients are, however, generally too slight to be detectable, even when immersion objectives are used. High iron sphalerites are sensibly opaque in thin section and do not show internal reflection from polished surfaces; detailed microprobe examination is required to trace variations in composition.
It is theoretically probable that accurate measurements of reflectivity would be useful to trace compositional variations in high iron sphalerites. Suitably accurate measuring equipment was not available during this investigation, and a suite of analyzed sphalerites was therefore submitted to Dr. D. Murchison, of the University of Newcastle, U.K., for examination on high sensitivity microphotometers developed for coal maceral studies. Unfortunately, the results of Dr. Murchison's investigation were not available at the time of writing.

It is clear from Table 3 that sphalerites from some localities are more or less uniformly dark in hand specimen colour, despite analyses which range down to relatively low iron contents (e.g. Sylvester). This is because the presence of relatively small proportions of dark sphalerite are sufficient to impart a dark colour, and an apparent opacity, to the hand specimen as a whole; this further stresses the futility of compositional estimates based on hand specimen colours.

Several types of inhomogeneity, apart from the rare growth zoning, can be distinguished in the Zeehan sphalerites, as follows:

(a) Abrupt discontinuities are often due to "microfaulting" of originally inhomogeneous sphalerite aggregates (Fig. 37).

(b) More commonly, the variations are irregular and patchy, as noted above (Fig. 38).

(c) A persistent feature is the presence of dark, iron-rich zones adjacent to transecting quartz veinlets, galena replacement boundaries, siderite-sphalerite boundaries, and
rarely pyrite-siderite boundaries. In some cases, the dark zones are present on either side of fractures in the sphalerite which contain no actual "filling"; again microprobe profiles show the dark zones to be due to increasing iron content (cf. Fig. 35). Frequently, but not invariably, these zones are characterised by abundant bleb- or lath-like inclusions of chalcopyrite and/or pyrrhotite, and sometimes fine-grained "dusty" pyrite or marcasite (Figs. 25, 26 and 29). The distribution of these inclusions has been reviewed above, and their origin and significance are discussed in Chapter VI. The width of the dark zones and the abundance of the inclusions within them are frequently directly related to the intensity of replacement or the reticulate density of the transecting veins.

A polished section of crustified siderite and sphalerite from the Boundary Mine revealed some interesting relationships between the siderite-sphalerite boundaries and the distribution of inclusions within the sphalerite. The siderite frequently occurs as euhedral crystals on which the succeeding layer of sphalerite has been moulded; the time sequence in the layers is thus apparent. The sphalerite is homogeneous and free of inclusions near its contacts with older carbonate layers. Where younger siderite is coated on sphalerite, however, the latter contains scattered blebs of chalcopyrite, together with semi-regular cloudy zones, more or less parallel to the siderite contact (Fig. 39).
Some of the cloudy zones exhibit a weak anisotropism, but most are sensibly isotropic. Textural detail could not be resolved under high magnifications, and the cloudiness was interpreted as incipient exsolution of stannite or tetrahedrite. Positive identification as stannite was made by electron microprobe analysis; Fig. 40 shows an SnKα scan of portion of an area similar to that of Fig. 39, clearly showing the concentration of tin in the cloudy zones. Similar areas of extremely fine grained exsolution stannite were also observed in samples from the No. 1 Montana, Montana Silver-Lead and No. 3 Queen Mines, although not always showing such clear spatial relationship to younger minerals.

Of the "exsolved" inclusions in sphalerite, those of chalcopyrite are the most common. It should be stressed that while these are often concentrated in the zones adjacent to galena, quartz or siderite boundaries, as described above, they are also often observed elsewhere. In some granular sphalerite aggregates (e.g. from the No. 1 Montana Mine) they are actually concentrated in the cores of sphalerite grains; the outer zones of these grains are free of inclusions, but the grain boundaries contain segregation veinlets of chalcopyrite which evidently have been produced by coalescence and migration. On the other hand, pyrrhotite does not show this distribution; except in the few cases (Silver Stream, Doric Mines) where it is sufficiently abundant to be studded throughout the sphalerite, it is almost
Fig. 39: Blebs of chalcopyrite and cloudy zones of incipient stannite exsolution in sphalerite adjacent to younger siderite (black). (cf. Fig. 40). Boundary Mine. X500

(a) (b)

Fig. 40: Electron microprobe scans of portion of Fig. 39 (note image is reversed) -
(a) electron back scatter scan, showing distribution of heavy elements (white areas);
(b) SnLα scan - white areas show distribution of tin.
Fig. 41: Galena (white) penetrating cleavages of siderite (black).
(a) No. 5 Argent Mine, X250;
(b) Montana Silver-Lead Mine, X250.

Fig. 42: Brecciated fragments of stannite enclosed in sphalerite.
Larger white areas are pyrite, and the smaller blebs are chalcopyrite, which also partially rims some stannite fragments.
Stannite Lode, Oonah Mine. X250
invariably concentrated in the bordering, high-iron "alteration" zones.

**Siderite:**

Paragenetically, siderite is closely related to sphalerite, as has already been noted; the correlation does not entirely extend however, to their respective zonal distributions. Whereas sphalerite is most common in the western and central parts of the field, siderite is rare in the west, and becomes progressively more abundant passing eastwards.

Early pyrite-arsenopyrite-quartz assemblages are clearly veined, and in some instances, partly replaced by siderite; siderite in turn is veined and partly replaced by galena, quartz and tetrahedrite. In many cases the siderite has been shattered, and the later sulphides fill the interstices between rhombohedral carbonate cleavage fragments (Fig. 41). This texture is not necessarily a reliable indication of relative age relationships, since similar textures could conceivably result from deformation of siderite-galena intergrowths, with the sulphide "flowing" into the interstices of the shattered carbonate grains. However, in many cases the siderite is in addition partly replaced by the younger sulphides, frequently with the development of irregular pyrite or marcasite "reaction rims" along corroded contacts.

Less commonly, extensive cleavage-controlled replacement has led to the formation of pseudo-myrmekitic intergrowths of galena and siderite (Florence Mine).
While siderite-sphalerite textural relationships are generally inconclusive from a paragenetic viewpoint, and several examples of crustified alternations of the two minerals have been described, several instances of sharply defined veinlets of siderite and quartz transecting earlier sphalerite-siderite intergrowths were also noted (e.g. No. 1 Montana Mine). Although similar veinlets of sphalerite crossing siderite have also been observed, they are comparatively rare. Hence it has been concluded that the two minerals show considerable paragenetic overlap, but perhaps with the siderite being slightly younger at some localities.

The crystallization of siderite in conjunction with the alteration of pyrrhotite to marcasite in samples from the Comstock Mine has already been described, and it has been noted that the formation of siderite under these conditions requires \( \text{CO}_2 \) fugacities of the order of \( 10^2 \) atmospheres. Thermochemical calculations show that these gas fugacities correspond, at 300°C and neutral pH, to carbonate anion activities in the hydrothermal solutions of the order of \( 10^{-4} \text{M} \), which are comparable with the anion activities calculated by Barton (1957, 1959) for hypothetical ore fluids at somewhat lower temperatures.

The present calculations were based on the simple \( \text{FeCO}_3 \) composition of siderite. The partial substitution of other elements, notably Mn, Ca and Mg, in the siderite structure should also be considered; free energy and enthalpy data suggest that the
presence of manganese would not seriously affect the calculations, but that the differences become more appreciable for calcite, dolomite and magnesite. The chemistry of the vein carbonates should therefore be studied if detailed conclusions concerning the chemistry of the hydrothermal fluids are to be drawn from their presence.

Apart from a limited study of the manganese contents of Zeehan siderites (see Chapter VI), this has not been possible in the present study because of the nature of the dump samples which provided most of the specimen material. In general the carbonates show pronounced weathering effects - notably the formation of limonite and related manganese oxides in cleavage-controlled replacement zones - and detailed chemical studies would be futile. In similar cases where fresh underground material is available, study of the carbonates could prove very informative.

The limited data available show that the Zeehan "siderites" contain between 1 and 33 weight per cent manganese; semi-quantitative electron microprobe analyses showed that the contents of calcium and magnesium are generally low - of the order of 5 per cent (combined) or less. Small amounts of calcite (q.v.) have been observed in some veins, but no dolomite or magnesite have been identified.

In view of the close paragenetic relationships between sphalerite and siderite, and the general similarity which is to be
expected between paragenetic and zonal sequences, the absence of siderite in the western pyritic ores is curious. It appears most probable that the physico-chemical conditions in this region in the intermediate stage of the paragenesis permitted the crystallization of sphalerite, but prevented the formation of siderite. Of the many possible limiting factors, pH, temperature and pressure are most likely to be of significance, but their evaluation is severely hampered by the lack of experimental and thermodynamic data applicable at the relatively high temperatures and pressures involved.

The thermal stability of siderite has been studied by French & Rosenberg (1965), who found that it decomposes to magnetite and graphite at $465^\circ C$ and 2 kb. $P_{CO_2} + P_{CO}$. Some recent studies in the Stanford University laboratories (O.F. Tuttle, pers. comm.) have suggested that French & Rosenberg's results may be in error, and that siderite breaks down to magnetite and graphite at $560^\circ C$ under 2 kb. total pressure, and $497^\circ C$ under 0.5 kb. (both temperatures $\pm 10^\circ C$). These temperatures are in the approximate range estimated for the pyritic zone at the time of sphalerite crystallization (see Chapter VI), and hence it appears possible that the absence of siderite in this zone may have been due to high temperatures. In this connection it is significant that magnetite is confined to siderite-free deposits from this zone (with the exception of the Tasmanian Mine, in which magnetite is rare).
In a study of the system CaCO$_3$-CO$_2$-H$_2$O, Holland & Borcsic (1965) showed that isothermal sections reveal an increasing solubility of calcite with increasing P$_{CO_2}$ up to 300°C, and confirmed the decreasing solubility of calcite with isobarically increasing temperature up to the same limit. Hence calcite cannot be precipitated from aqueous solution by isobaric cooling alone; it may be produced by heating or by isothermal release of P$_{CO_2}$. Under cooling conditions the release in P$_{CO_2}$ would have to be pronounced to outweigh the effect of falling temperature; Holland & Borcsic suggested that these conditions would be met in most geological environments only if the fall in P$_{CO_2}$ was unusually abrupt (as in boiling) or if the P$_{CO_2}$ were small.

There is insufficient experimental data to indicate the extent to which these results might be applied to siderite or siderite-rhodocrosite systems, or to systems at higher temperatures. It remains possible, however, that high partial pressures of CO$_2$ in the pyritic zone may have played some part in inhibiting crystallization of siderite.

Holland & Borcsic also noted that reduction of SO$_4^{2-}$ to S$_2^{2-}$ will increase pH, and this is capable of precipitating calcite under certain conditions. Likewise, reactions of hydrothermal fluids with wallrock feldspars or micas involve exchange of H$^+$ ions with alkali metal cations, thus increasing pH and possibly causing calcite precipitation.

Hence it is possible that temperature, pressure and pH may
all have played some part in limiting the inner zonal distribution of siderite. While evaluation of their respective roles must remain speculative, it is believed, in view of the antipathetic distributions of siderite and magnetite, that temperature was probably the most significant.

**Chalcopyrite:**

Chalcopyrite is a minor but almost ubiquitous constituent of the Zeehan ores. It is seldom sufficiently abundant to be visible in hand specimens (except in samples from the Silver Stream Mine, the Oonah Stannite Lode, and Clarke's Lode on the Queen leases); however few polished sections are free of minute chalcopyrite inclusions in sphalerite and/or galena. These are rather more abundant in ores from the western part of the field, but are by no means rare elsewhere.

Paragenetically, most of the chalcopyrite appears to belong to the late rather than the intermediate phase. However, much of the coarse-grained chalcopyrite of the Silver Stream Mine is intergrown with sphalerite in "mutual boundaries" textures which may indicate contemporaneity, and in the Oonah Stannite and Clarke's Lodes, chalcopyrite, stannite, sphalerite and minor tetrahedrite are closely related in paragenesis and distribution, each mineral showing complex exsolution relationships with the others. Stannite and chalcopyrite are the most abundant; generally stannite forms the host for abundant exsolved blebs and anastomosing segregation veinlets of chalcopyrite, which in turn
contain small blebs of stannite, apparently also of exsolution origin. A sample from the Oonah Stannite Lode, described by Both (1966) and kindly made available by him for further examination, consists of brecciated fragments of stannite enclosed in a sphalerite matrix (Fig.42); the stannite contains blebs and segregation veinlets of chalcopyrite which terminate abruptly at the margins of the stannite fragments, suggesting that segregation took place prior to brecciation. Early-segregation chalcopyrite of this type is commonly irregularly moulded around primary cassiterite (q.v.) inclusions.

Polished sections from this sample also reveal a second type of chalcopyrite, which occurs as long narrow veinlets transecting the whole breccia, without regard for stannite fragment boundaries. These veinlets contain the fine, secondary acicular cassiterite (or "needle tin"); as described earlier, Edwards (1951) and Ramedohr (1950) both considered them to have resulted from the breakdown of stannite, and the textural relationships observed in the Oonah specimens indicate that the breakdown must have been a relatively late stage (at least post-brecciation) process.

There is no indication, however, of the nature of the changes which caused instability of the stannite, nor does any of the massive stannite show signs of incipient alteration.

The most common occurrence of chalcopyrite in Zeehan ores is as minute blebs or lamellae, mostly less than 20 microns wide, in sphalerite. Occasionally these are oriented or aligned along
favoured crystallographic directions or twin boundaries in the sphalerite host, but more commonly they form cloudy aggregates with an overall emulsoid texture (Fig. 43); where they are abundant the sphalerite is darkened in hand specimen colour, independently of iron content. In some cases the small chalcopyrite inclusions are concentrated in the cores of sphalerite grains (No. 1 Montana Mine); larger areas of chalcopyrite in the grain boundaries suggest the outer "rims" of the sphalerite grains have been drained of chalcopyrite by diffusion in the early stages of unmixing. In other cases (generally more common) the chalcopyrite blebs are concentrated in marginal zones in the sphalerite, usually independently of grain boundaries, and adjacent to galena-sphalerite or siderite-sphalerite replacement boundaries. The latter instances coincide with similar concentrations, already described, of pyrrhotite and second-generation pyrite.

Thus in samples from the Silver Stream Mine, for example, large unreplaced areas of sphalerite are virtually devoid of inclusions of either chalcopyrite or pyrrhotite, but near galena boundaries bleb-like inclusions of chalcopyrite and pyrrhotite become abundant. As the evident replacement of sphalerite by galena becomes more intense, the pyrrhotite and chalcopyrite inclusions become more abundant and coarser-grained; some specimens consist of massive intergrowths of chalcopyrite, pyrrhotite and galena, with only minor, corroded sphalerite
Fig. 43: Fine emulsoid blebs of chalcopyrite in sphalerite. The coarser white blebs in the centres of the grains are pyrrhotite. Silver Stream Mine. X500

Fig. 44: Penetration of galena along grain boundaries of sphalerite; this texture might also be produced by simultaneous crystallization of the two minerals. Swansea Mine. X400
residuals.

Similar relationships have been observed elsewhere; for example, Lawrence (1962, 1967), in descriptions of lead-zinc ores from Emmaville and Thackaringa, N.S.W., has observed that large areas of massive sphalerite contain very few inclusions of other sulphides, but that chalcopyrite and fine-grained pyrite are much more abundant in small areas of sphalerite "intimately intergrown with other sulphide minerals". In the Thackaringa ores, Lawrence noted that "the most striking feature of the Thackaringa sphalerite is the extent to which it has accommodated chalcopyrite in solid solution, and the profusion of the resulting exsolution. It is estimated that, in places, the chalcopyrite derived by unmixing from the sphalerite reaches some 25 per cent by volume - and yet the large areas of sphalerite are virtually free of exsolution bodies" (1967, p.88).

Lawrence's descriptions are typical of the classical interpretation of a simple exsolution origin for inclusions of this type, However, while unmixing of solid solutions may have been responsible for some of the Zeehan chalcopyrite, there exist good grounds for suspecting that other processes may also have been operative. While it is possible that the concentrations of "unmixed" chalcopyrite adjacent to galena replacement boundaries may have been produced by annealing effects during the replacement, the sympathetic distributions of pyrrhotite and pyrite cannot be explained by this simple mechanism. As has
already been observed, Barton & Toulmin (1966) have suggested that pyrrhotite cannot be produced by isochemical unmixing of a sphalerite solid solution, and pyrite obviously cannot. Possible mechanisms which also take into account changes in the composition of the associated sphalerites are reviewed in Chapter VI.

Some of the Zeehan chalcopyrite is directly associated with galena and tetrahedrite rather than sphalerite. Thus galena from the Tasmanian Mine contains patches of chalcopyrite ranging up to 5 mm. in diameter. Both (1966) has observed that these occasionally contain "stars" of exsolved sphalerite. Similar chalcopyrite inclusions in galena from the Oceana Mine display "mutual boundaries" textures which are difficult to interpret with confidence; however, both galena and chalcopyrite fill fractures in siderite, with some associated replacement, and there is no evidence to suggest that they were not formed contemporaneously. In samples from the Junction and Florence Mines, chalcopyrite is intimately intergrown with galena and tetrahedrite, penetrating and partly replacing siderite, and some graphic or pseudo-myrmekitic intergrowths with galena have been observed. In some cases, rims of chalcopyrite have formed at interfaces between siderite and replacing tetrahedrite; these do not appear to be reaction rims, but rather in most cases seem to represent coalesced segregations from solid solution within the tetrahedrite; again, however, the textural relationships are
not unequivocal.

Finally, some chalcopyrite occurs, intergrown with quartz and tetrahedrite, in narrow veinlets filling galena cleavages and transecting galena-sphalerite-siderite intergrowths (Big Ben, Florence Mines).

In summary, it appears that some chalcopyrite formed contemporaneously with sphalerite (possibly as solid solutions which subsequently unmixed), particularly in ores from the Silver Stream and Queen Hill areas. Further chalcopyrite formed in sphalerite over most of the field as a consequence of partial replacement of the latter by galena. Some minor chalcopyrite crystallized together with the galena, and there is evidence to suggest that in a few cases a little chalcopyrite formed after the deposition of galena had ceased.

**Stannite:**

The distribution of stannite represents one of the major anomalies in the zonal schemes of Waller and Twelvetrees & Ward, since it shows no relationship to the Heemskirk Granite or to other general zonal variations in gangue mineralogy. Instead, stannite appears to be largely confined to a small area centred around the Oonah - Queen Hill region. It has not been described from the tin zone within and adjacent to the Heemskirk Granite, or from the pyritic ores of the Silver Stream - Comstock area; in the Oonah - Queen Hill lodes, however, it occurs in pyritic veins which are intermingled with sideritic types (e.g. the Stannite and Galena Lodes of the Oonah Mine, which are of markedly
different mineralogy). Both's (1966) proposal that the Queen Hill pyritic "incursion" is a consequence of an irregular sub-surface granite profile, with a cupola developed below Queen Hill, does not account for the predominant occurrence of tin as stannite rather than cassiterite. A modified interpretation which explains these anomalies is presented in Chapter VII.

The limited areal distribution of stannite, and its virtual confinement to the mineralogically distinctive ores of the Queen Hill area, mean that it is difficult to relate it paragenetically to the more widespread minerals of the Zeehan lodes. In Clarke's Lode and the Oonah Stannite Lode, seams of stannite transect pyrite-arsenopyrite-quartz aggregates, and show complex exsolution relationships with sphalerite, tetrahedrite and chalcopyrite. Reference has already been made to the cloudy zones of exsolution stannite in sphalerite from the Boundary, No. 3 Queen and Montana Silver-Lead Mines and from several of the Argent flat Mines, and to the fine, chalcopyrite-rimmed inclusions in tetrahedrite veins transecting siderite from the Argent Flat area. These relationships suggest stannite crystallization contemporaneous with sphalerite, perhaps overlapping into the galena stage. However, the unusual nature of the Queen Hill lodes precludes paragenetic correlation of their pyrite, sphalerite etc. with the same minerals elsewhere in the Zeehan ores; instead it will be proposed in Chapter VII that they represent a second phase of mineralization subsequent to that which produced the bulk of the
Zeehan ore minerals.

On the other hand, the minor stannite which is occasionally observed as exsolution intergrowths with sphalerite (Boundary Mine etc.) presumably belongs to the intermediate stage of the main paragenesis.

The stannite of the Oonah Stannite and Clarke's Lodes occurs as coarsely crystalline areas, up to 10 cm. or more in width, and as networks of narrow veinlets transecting pyrite and arsenopyrite aggregates. In some cases the stannite and pyrite show a crude banding, with individual bands up to 1 cm. wide; under the microscope each band is seen to contain considerable proportions of the other. The stannite invariably shows fine lattice twinning, on which a relatively coarse lamellar or "parquet" twinning is superimposed. The fine lattice twinning is possibly indicative of inversion from the high temperature cubic to the low temperature tetragonal structure (Ramdohr, 1950; Frueh, 1950).

As described earlier, some of the stannite is believed to have broken down to form veinlets of chalcopyrite enclosing aggregates of "needle tin".

Many assays have been quoted to suggest that the Oonah and Clarke's Lode stannites carry appreciable silver, ranging from 30 to 120 oz./ton. Where adequate information is available, it is clear that the assays have usually been made on grossly impure material - indeed the visible microtextures of the stannite ores suggest it would be virtually impossible to obtain...
pure samples. When the assay data are examined in detail - for example the group of assays quoted by Waller (1904, p.56), reproduced in part in Table 4 - it is often seen that the silver values are more closely related to copper than to tin, and in fact the highest silver contents were found in samples containing no tin. This suggests that most of the silver actually occurs in either chalcopyrite or, more probably, tetrahedrite, as proposed by Edwards (1951). On the other hand, the analysis by J.H. Levings (Table 4) shows a higher silver content than can reasonably be assigned to the relatively small amount of impurities. The possibility of some silver in stannite therefore remains open.

Petterd (1910) reported Clarke's Lode stannite to assay 3 dwt. Au/ton.

**Calcite:**

*Calcite is a rare gangue constituent of the Zeehan Lodes.*

It was observed as occasional thin layers in a crustified sphalerite-siderite sequence in samples from the Boundary Mine, where it forms thin, discontinuous layers separating euhedral siderite crystals from younger coatings of sphalerite. Narrow veins and irregular patches of calcite occur intergrown with siderite in ore from the Oceana Mine.
Table 4.

Assays of ore samples from the Stannite Lode, Oonah Mine. (Waller, 1904).

<table>
<thead>
<tr>
<th>Parcel No.</th>
<th>( \text{Ag} ) (oz./ton)</th>
<th>*Cu (%)</th>
<th>*Sn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>84</td>
<td>11.5</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>50</td>
<td>10.3</td>
<td>16.0</td>
</tr>
<tr>
<td>10</td>
<td>63</td>
<td>13.8</td>
<td>-</td>
</tr>
<tr>
<td>16</td>
<td>59.6</td>
<td>12.0</td>
<td>9.73</td>
</tr>
<tr>
<td>17</td>
<td>75.5</td>
<td>13.5</td>
<td>-</td>
</tr>
<tr>
<td>29</td>
<td>60.5</td>
<td>12.25</td>
<td>8.7</td>
</tr>
<tr>
<td>30</td>
<td>68.0</td>
<td>11.5</td>
<td>9.0</td>
</tr>
</tbody>
</table>

* Pure stannite \((\text{Cu}_2\text{FeSnS}_4)\) contains 27.6% Sn and 29.6% Cu

Table 4B

*Composition of Oonah stannite

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>26.77%</td>
</tr>
<tr>
<td>Sn</td>
<td>23.91%</td>
</tr>
<tr>
<td>Fe</td>
<td>12.11%</td>
</tr>
<tr>
<td>Bi</td>
<td>2.27%</td>
</tr>
<tr>
<td>Sb</td>
<td>0.505%</td>
</tr>
<tr>
<td>Zn</td>
<td>0.475%</td>
</tr>
<tr>
<td>S</td>
<td>32.1%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.4%</td>
</tr>
<tr>
<td>Ag</td>
<td>97.3 oz/ton</td>
</tr>
</tbody>
</table>

Late Phase.

Galena:

Economic proportions of galena were mined from veins over the whole of the Zeehan field, but it is clear that the relative abundance of galena increased from west to east. Twelvetrees & Ward (1910) criticised the then prevalent opinion that massive siderite in depth necessarily coincided with bottoming of the ore shoots, and pointed out that in fact the richest lead ores of the district occurred in veins with sideritic gangue. Their opinion has been substantiated by production figures; the seven leading producers of lead concentrates (No. 1 Montana, Spray, Western, Queen, Oceana, Oonah and Florence Mines) were all characterised by sideritic or sidero-pyritic gangue, and between them accounted for 88 per cent of the total production of lead and 92 per cent of the total silver.

The galena occurs in thin, ramifying veinlets transecting the wallrocks and earlier hydrothermal minerals; occasional larger seams and patches up to 10 cm. across are not uncommon, but mineable veins exceeding a metre in thickness appear to have been rare. The distribution of galena within the lodes was generally found to be capricious, which accounts for the shallow nature of most of the workings.

Paragenetically, there can be little doubt of the relatively late age of the galena. Pyrite, sphalerite and siderite are all extensively veined and partly replaced by galena; all three are
frequently brecciated, and the fractures have been "healed" by intergrowths of galena and late quartz. Extensively corroded residuals of early, coarse-grained pyrite in galena are common. Galena often invades the cleavages of siderite to form networks with distinctive rhombohedral patterns; as observed earlier, partial replacement of the siderite is frequently accompanied by the formation of "reaction rims" of pyrite and/or marcasite (with the latter being largely confined to occurrences in the western, or pyritic types of ore).

Veinlets of galena transecting areas of sphalerite are common, and are usually accompanied by some degree of partial replacement; etching of polished sections shows that the replacement is initially localised along grain boundaries, so that the galena-sphalerite boundaries often have a cuspate form. Incipient replacement is often revealed by minute, discontinuous blebs of galena in the sphalerite grain boundaries (Fig. 44); as the replacement proceeds, these "coalesce" into continuous grain boundary penetrations, and ultimately only rounded residuals of sphalerite remain within a matrix of galena.

Stanton (1964) has pointed out that these textures are not necessarily indicative of replacement, but might under some circumstances be produced during simultaneous solid state crystallization of the two phases, as a result of tendencies towards equilibrium configurations of minimum "interfacial free energy". It follows that replacement boundaries might well tend
towards the same configurations, so that it appears impossible to employ these relationships alone as criteria of relative age. In the present instance, however, the independent evidence for a sphalerite-galena discontinuity is so conclusive that there can be no doubt of their replacement origin.

Crustified ore samples invariably show a sequence pyrite-arsenopyrite-pyrrhotite→sphalerite-siderite→galena, with the galena occurring in the centre of the veins. More commonly, the younger age of the galena can readily be confirmed on a megascopic scale from the ramifying nature of the galena veinlets, which randomly transect areas of pyrite, siderite and sphalerite alike.

The best evidence for the younger age of the galena is probably provided by the mineralogical and chemical alterations which have been induced in sphalerite adjacent to galena boundaries. Several references have already been made to these alteration zones, whose significance is discussed more fully in Chapter VI.

The galena is commonly intergrown with quartz, and also forms the host for most of the tetrahedrite, boulangerite and bournonite (q.v). Where the sulphosalts inclusions are particularly abundant, graphic or myrmekitic intergrowths with the galena are occasionally observed; "mutual boundaries" textures are, however, more typical. Contemporaneity of the galena and sulphosalts is assumed more as a consequence of their closely related distributions than because of any particular textural
The silver content of galena, which was one of the parameters used by Twelvetrees & Ward (1910) to define the zoning of the Zeehan ores, is examined in detail in Chapter VI. In summary, it may be briefly stated here that it is clear that (a) most of the silver is present in tetrahedrite rather than galena (although the two minerals are so closely related spatially and paragenetically that there is little practical difference); and (b) tetrahedrite is most abundant, and silver assays are highest, in the intermediate or sidero-pyritic ores, rather than in the sideritic ores as postulated by Twelvetrees & Ward.

Inclusions of pyrargyrite or argentite may have contributed locally to high silver assays, but these minerals are generally rare. In some cases it appears that near-surface enrichment processes have been operative. Thus galena from the upper levels of Fahey's Tribute, on the southern extension of the King Lode, assayed over 100 oz. Ag/ton, but declined rapidly to 45 oz./ton at 92 feet (Waller, 1904); ore from the King Mine, on the northern portion of the same lode, did not assay higher than 45 oz./ton.

Waller (1903) described two classes of galena in the pyritic ores of the Susannite (or Britannia Extended) Mine: (i) a dense, fine-grained type carrying 0.5 oz. Ag/unit Pb, and (ii) a pure, cubical crystallized variety, carrying more than 1.0 oz. Ag/unit Pb.
Waller (1904) further describes "rich secondary ore" from the Susannite Mine, and Twelvetrees & Ward (1910) refer to "high returns of silver" from "the secondary ore"; there seems little doubt that these latter references are to the crystallized galena.

Much of the galena has undergone deformation, some at least as a consequence of post-crystallization fault movements. Bent cleavages are common, and sometimes the deformation has been sufficiently severe to induce a weak anomalous anisotropism. In some cases the deformation has produced extensive kinking, with sub-parallel kink band boundaries; in a brief discussion of the origin of mechanical twinning in galena, Lyall (1966) figured an excellent example of kinked galena from the Oceana Mine. (Lyall's caption "from the Zeehan fault zone" is misleading; see Appendix I, p.A77).

**Tetrahedrite:**

Tetrahedrite is a common, but generally a minor constituent of the Zeehan ores. It is rarely visible in hand specimens, although occasional occurrences of massive tetrahedrite have been recorded (e.g. in ore from the Sunrise Mine; Twelvetrees & Ward, 1910); however, it has been identified in polished sections from two-thirds of the deposits examined during this study. Within individual deposits the distribution of tetrahedrite is highly variable - even in cases where it is known to have been a major lode constituent, occasional polished
sections may fail to reveal its presence. In general, however, it is clear that it is a rare constituent of the western pyritic ores, becomes most abundant in the intermediate belt extending more or less directly southwards from the Montana Silver-Lead Mine to the Nubeena-Swansea area, and is significantly less abundant (but usually present in very small proportions) in the eastern and south-eastern lodes.

It appears clear that tetrahedrite accounts for most of the silver of the Zeehan ores. Early reports drew attention to high silver grades in ore containing visible "fahl-ore", and the massive (but probably impure) tetrahedrite of the Sunrise Mine was reported by Twelvetrees & Ward to assay 404 oz. Ag/ton. The capricious distribution of tetrahedrite in most lodes thus partly accounts for the marked variation in reported silver assays. This aspect is reviewed in more detail in Chapter VI, where it is shown that there is a strong positive correlation between the Sb and Ag contents of galenas from various deposits; the form of the correlation curve suggests that up to 0.08 per cent silver can, however, be accommodated in the galena structure.

In several cases where tetrahedrite is reasonably common (notably the King and Bell Mines), silver assays are surprisingly low, which suggests that the silver content of tetrahedrite is not constant, but declines markedly in the eastern part of the field. A possible similar decline in the western pyritic ores is less clearly defined because of poor sampling.
Paragenetically, a small proportion of the tetrahedrite shows exsolution relationships with sphalerite, stannite and chalcopyrite, notably in samples from the Oonah Stannite Lode and Clarke's Lode, and in these relatively rare instances the four minerals appear to be more or less contemporaneous. By far the greater part of the tetrahedrite, however, is intimately intergrown with galena, and these two minerals are so closely related in their distributions and textural relationships as to leave little doubt of their close paragenetic affiliations. Together with quartz and minor chalcopyrite, galena and tetrahedrite commonly occur interstitially or as fracture fillings in early pyrite-arsenopyrite aggregates, and as late veinlets transecting siderite and sphalerite. Galena-tetrahedrite cleavage fracture fillings in siderite are frequently observed.

Where the tetrahedrite is not abundant, it usually occurs as minute, ovoid inclusions in galena, frequently only a few microns in diameter. As its relative abundance increases, so to some extent do the grain sizes of the inclusions, which also become more irregular in shape. The larger inclusions, which occasionally range up to several millimetres in diameter (King Mine), usually show mutual boundaries relationships with the enclosing galena and occasionally with chalcopyrite; rarely graphic or myrmekitic intergrowths of tetrahedrite and galena or tetrahedrite and chalcopyrite are observed (Junction Mine). In general the tetrahedrite inclusions show no crystallographic control
over their distribution in the galena host; there appears to be little textural evidence to support Both's (1966) suggestion that the tetrahedrite has exsolved from the galena. It is not uncommon, however, for inclusions of tetrahedrite in galena to be partially surrounded by irregular rims of sphalerite, or to contain small sphalerite blebs; these may well have exsolved from the tetrahedrite.

Whether tetrahedrite is rare or abundant, a constantly recurring feature is its marked tendency to be concentrated in the vicinity of siderite inclusions or galena-siderite boundaries. Thus in the Comstock ores, galena is substantially free of inclusions, except in the vicinity of rare carbonate seams, which it partly replaces. In these areas, small blebs of tetrahedrite and boulangerite are almost invariably observed, and are often abundant. In the sideritic ores of the Oceana Mine, large patches and seams of galena are again free of inclusions, except for scattered, partly replaced residuals of pyrite and sphalerite. In the vicinity of siderite patches, however, the galena is crowded with small rounded inclusions of tetrahedrite with minor bournonite and boulangerite (or composite inclusions of all three). In specimens from the Swansea Mine, veinlets of galena traversing siderite are often lined with tetrahedrite, and in larger areas of galena, tetrahedrite commonly occurs as large patches, up to 1 mm. wide, completely or partially surrounding inclusions of siderite. The abundant tetrahedrite of the Florence Mine shows pronounced concentration along galena-siderite contacts; although
it occurs within the galena, it frequently appears to be "moulded" on the siderite.

These relationships are supported by the general observation that the highest silver grades in the Zeehan ores coincide with the first appearance of major siderite in the west-to-east zonal sequence. It thus appears highly probable that the siderite has exerted some controlling influence on the precipitation of copper, silver and antimony present in the hydrothermal solutions at the time of galena deposition; it will be shown in Chapter VI that other elements also show similar distributions, and their significance will there be discussed in more detail.

Where tetrahedrite occurs immediately adjacent to siderite, the two are commonly separated by a thin, discontinuous film of chalcopyrite. Inclusions and narrow veinlets of chalcopyrite are also common within many of the larger inclusions of tetrahedrite. Their paragenetic relationships are uncertain, but they may have unmixed from solid solution in the tetrahedrite.

**Boulangerite:**

Most of the early descriptions of Zeehan mineralogy (Waller, 1904; Twelvetrees & Ward, 1910; Petterd, 1910 etc.) refer to the presence of "jamesonite" in ores from the Spray Mine and the Argent Flat group of mines. Stillwell (1947) tentatively identified jamesonite in material from the Spray lodes; his identification was based on microscopic and microchemical
examinations, and he suggested that the mineral in question
might be boulangerite. In a brief review of the Zeehan deposits,
Edwards (1953) referred non-committally to "antimonial lead
minerals", but later, in a survey of sulphur-selenium ratios in
various Australian ore minerals, Edwards & Carlos (1954) quote,
without comment, a low ratio for "a specimen of boulangerite
from the Spray Mine, Zeehan, where boulangerite is an important
constituent of the ore". Both (1966) obtained x-ray data
confirming this identification, and the present author has obtained
supporting evidence for specimens from this and other Zeehan
localities. Diffraction patterns of Spray and Argent Flat
material are identical with those of boulangerite from Rosebery
(Williams, 1960). Neither Both nor the present author has
identified any jamesonite in the Zeehan ores, and there is little
doubt that the early identifications were in error.

Like tetrahedrite, boulangerite is most abundant in the
sidero-pyritic ores, but its "dispersion" is somewhat smaller.
It is abundant in samples from the Montana-Western, Argent Flat,
Spray and Nubeena-Grubb's-Tasmanian areas, but is rare in the
Comstock pyritic ores, the pyrite-stannite ores of the Queen Hill
area, and the strongly sideritic ores to the east and south-east.
The most remarkable feature of its geographic distribution is its
extreme abundance in the Spray lodes, in which it appears to have
been the dominant metallic mineral.
In the Spray ores, boulangerite occurs as massive seams and patches, up to several centimetres wide, veining and partly replacing pyrite, arsenopyrite, quartz, sphalerite and siderite. Paragenetically, it appears to be clearly younger than all of these minerals, with the exception of siderite, much of which contains abundant acicular inclusions of boulangerite, up to 50 microns thick and 500 microns long. In such cases, the siderite appears to have crystallized in the interstices of felted aggregates of boulangerite crystals, indicating a probable overlap in the deposition of these two minerals.

Some of the more massive patches of boulangerite consist of similar felted aggregates of tiny crystals down to 3 microns wide and 15 microns long. The interstices between the boulangerite "needles" are often filled with tetrahedrite or galena. The high silver assays of material variously described as "jamesonite" or "antimonial ore" (Twelvetrees & Ward, 1910) are probably due to interstitial tetrahedrite. It is unlikely that "antimonial ore" referred to tetrahedrite alone, since it was not reported as a significant constituent of the Spray ore.

An atomic absorption analysis of an impure concentrate of boulangerite from the Spray Mine (containing an estimated 10 per cent each of galena and sphalerite) showed 1100 ppm silver, most of which can be attributed safely to the impurities. The silver content of the boulangerite is evidently low.

The antimony content of the Spray ore was reported to
decrease with increasing depth in the workings.

Elsewhere the abundance of boulangerite is less spectacular, and it commonly occurs in similar fashion to tetrahedrite, with which it is often intimately associated. Minor proportions of boulangerite occur as ovoid blebs or acicular inclusions in galena, sometimes crudely oriented. These seldom exceed 15 microns in maximum width, but occasional patches up to several hundred microns in diameter were observed in Argent Flat and Nubeena ore. Boulangerite commonly shows the same close spatial relationship with siderite as has been noted for tetrahedrite.

**Bournonite:**

Bournonite is also a common minor constituent of the Zeehan ores; its distribution and textural relationships generally parallel those of tetrahedrite and boulangerite. Like boulangerite, its "dispersion" is somewhat more restricted than that of tetrahedrite; it is more common than boulangerite in the northern and south-eastern parts of the field, but is a relatively minor constituent of the Spray and Argent Flat ores. It is rare in the pyrite-stannite lodes of the Queen Hill area, and has not been observed in the Comstock-Doric-Silver Stream region.

Although relatively rare in the Spray lodes, bournonite is unusually abundant in many samples from the Swansea Mine, where it occurs as seams, up to several centimetres wide, transecting sphalerite and siderite. It is closely associated with
galena - there is a complete gradation from veins of galena with small inclusions of bournonite to veins of bournonite with small inclusions of galena. While tetrahedrite is found in both extreme types, the association between bournonite and siderite is much less well defined than that between tetrahedrite and siderite.

Much of the bournonite is coarse-grained and shows beautiful cross-lamellar or "parquet" twinning; extensive patches, however, show all stages from incipient to complete recrystallization to equigranular, allotriomorphic aggregates in which individual grains are polysynthetically twinned. Galena and bournonite are often intergrown in sub-graphic or myrmekitic textures.

Elsewhere, bournonite occurs more commonly as small, rounded inclusions in galena, similar to those of tetrahedrite and boulangerite. Again these seldom exceed 15 to 20 microns in diameter; the microscopic distinction between bournonite and boulangerite in particular requires some experience. Composite bournonite-boulangerite and bournonite-tetrahedrite inclusions are not uncommon.

The bournonite inclusions show little tendency towards regular orientation in the galena. Lawrence (1962) has described bournonite from Rivertree, N.S.W., occurring as lamellar inclusions oriented in the (100) planes of enclosing galena, and suggested that the bournonite had unmixed from solid solution in the galena. On the basis of a similar texture in a sample from the Tranway Formation (Surshine Mine), Both (1966) proposed a similar
origin for the Zeehan bournonite. The textural evidence, however, is not compelling and the present author, while not rejecting the possibility of exsolution, prefers to regard galena and bournonite simply as having crystallized contemporaneously.

Chemical analyses of Zeehan boulangerite and bournonite have been published by Twelvetrees (1901) and Petterd (1910). These analyses agree poorly with data from other localities, almost certainly because of severe contamination; they are of little value.
Minerals of doubtful paragenetic association.

Argentite:

Argentite is a rare constituent of the Zeehan ores. One section of ore from the Junction Mine contained several small inclusions, up to 20 microns wide, of argentite in pyrite; this is possibly analogous with the rich shoot of pyrite, argentite and pyrargyrite reported by Waller (1904) from the Hanrahan's Adit or "Gossan Tunnel" workings on the southern extension of the Junction Lode. Both (1966) described argentite in galena in a single specimen of ore from Hanrahan's adit which did not, however, generally match Waller's description. The rich pyritic shoot is reported to have been worked out, and it seems unlikely that further samples of this unusual assemblage can be obtained.

Petterd (1910) described "flakes of practically pure argentite... on siderite and other veinstones", and Both (1966) confirmed this description of Specimen X235 in the Petterd Collection of the Tasmanian Museum; thin films of argentite were observed on siderite, associated with small proportions of galena, covellite and pyrite. However, no argentite was observed in any of the Spray sections examined during the present study.

Thus the few grains of argentite observed to date are variously associated with pyrite, siderite and galena, in each case showing inconclusive textural relationships. Although argentite is generally thought to form late in typical paragenetic
sequences, the evidence available from the Zeehan specimens is not adequate to allow any firm conclusions to be drawn in this respect.

**Breithauptite:**

Several small (up to 5 microns) inclusions of a bright orange-pink, strongly anisotropic mineral were observed within galena or, in one instance, intergrown with pyrrhotite enclosed in sphalerite from the Tasmanian Mine. This mineral was tentatively identified, on the basis of optical properties alone, as breithauptite.

**Barite:**

Several occurrences of barite in the Zeehan lodes have been reported. Twelvetrees & Ward (1910) recorded a "barytic quartz formation" from the No. 4 level of the Grubb's Mine, and noted the presence of "bunches" of barite in the lodes of the Silver Stream Mine. Montgomery (1890) reported barite in the gangue of the No. 2 Lode of the Mt. Zeehan Mine.

No barite was observed during the present study, but Both (1966) confirmed the presence of barite in Tasmanian Museum Specimen X3048, from Grubb's Mine.

**Fluorite:**

Rare fluorite has been recorded from the Oonah Stannite Lode (Both, 1966). None was observed in the present study, and its paragenetic affiliations are unknown.
Gold:

Gold has been reported several times in the Zeehan ores; Frank Long, the discoverer of the field, is supposed to have found traces of gold with galena in Zeehan Creek (Tilley, 1891), and small amounts of alluvial gold occurred in the vicinity of the Tenth Legion magnetite deposits (Waller, 1903).

Twelvetrees & Ward (1910) reported appreciable recoveries of gold from some galena from the Comstock district, and Both (1966) observed several small particles of gold, up to 10 microns in diameter, in siliceous gangue from the Nubeena Mine.

No gold was observed during the present study.

Proustite:

Petterd (1910) reported proustite in the ores of several of the Zeehan mines, and notably those of the Spray Mine. The only occurrence noted during the present investigation was that of a few minute inclusions in galena associated with the unusual nickeliferous ores of the Central Balstrup Mine (see below; also cf. Both, 1966).

Pyrargyrite:

Small, ovoid inclusions of pyrargyrite in galena have been observed in specimens from the Grubb's, Nubeena and Mt. Zeehan Mines. Both (1966) also reported pyrargyrite from the No. 2 Argent, Hanrahan's Adit and Western Mines. Petterd (1910) recorded pyrargyrite from the Oonah and Spray Mines.

Twelvetrees & Ward (1910) refer to the presence of "ruby silver
ores" in the nickel ores of the Central Balstrup Mine; the occurrence of proustite in these ores is noted above, and it is possible that some pyrargyrite may also have been present.

Rammelsbergite and/or Pararammelsbergite:

Both (1966) identified rammelsbergite in the Central Balstrup ores, but did not observe it elsewhere in the Zeehan ores. During the present study, several small inclusions, up to 30 microns maximum diameter, of a white, highly reflecting mineral enclosed in galena were noted in ores from the Austral, Tasmanian and North Tasmanian Mines. This mineral has a polishing hardness similar to that of pyrite, and is strongly anisotropic; it resembles arsenopyrite, but its grey to brown polarization colours are unfamiliar. It was tentatively identified as rammelsbergite or para-rammelsbergite on the basis of optical and microchemical studies; its rarity and the small size of the inclusions suggested that more detailed studies were unwarranted.

Stibnite:

In view of Petterd's (1910) description of "Native Antimony" from Zeehan, Both (1966) examined a specimen so described, in the Petterd Collection of the Tasmanian Museum (No. X47), and found it to consist of stibnite. Petterd's description referred to the Spray Mine, and it is possible that the stibnite specimen was obtained from this locality. No other stibnite has been observed.
Ullmannite:

The present author (1958) identified gersdorffite in the Central Balstrup ores, and Both (1966) showed that additional samples from this locality contained intermediate members of the gersdorffite-ullmannite (NiAsS - NiSbS) series.

During the present study, several sections of ore from the Sylvester Mine were observed to contain isolated, small inclusions of a hard, white, isotropic mineral resembling pyrite but with a somewhat higher reflectivity. These inclusions are rounded in shape and seldom exceed 20 microns in diameter; they were identified by electron microprobe analysis as ullmannite. By contrast with the Central Balstrup occurrence, they were found to be remarkably pure in composition; no significant proportions of any elements other than Ni, Sb, S, and traces of Fe were detected. Arsenic could be present but masked by interference of the PbLα and AsKα lines (the grains were too small to prevent contamination from the surrounding galena); however, the possible As content is limited to trace proportions by the absence of detectable AsKβ emission.

Due to its fine grainsize and close resemblance to pyrite, ullmannite is difficult to identify with certainty, and is possibly more abundant in the Zeehan ores than the present description indicates. It may account for occasional high trace nickel contents (see Chapter VIII).

The textural relationships of the ullmannite inclusions
provide no information of paragenetic significance. They may represent replacement residuals, but they may equally well have been produced by crystallization contemporaneous with that of the enclosing galena.

During the course of some experimental studies of phase relationships in the system Ni-Sb-S, undertaken in 1967 in the Geophysical Laboratory of the Carnegie Institution of Washington, ullmannite was found to be stable under its own vapour pressure up to a congruent melting point at 752° + 10°C. The presence of ullmannite in the Zeehan ores, therefore, provides little useful information concerning the physical conditions of ore deposition.

Nickel Minerals from the Central Balstrup Mine:

The occurrence of niccolite, maucherite, rammelsbergite, gersdorffite-ullmannite, marcasite, chalcopyrite, galena, tetrahedrite and proustite, in specimens from the Central Balstrup Mine has previously been described, (Williams, 1958) and Both (1966), and is summarised in Appendix I, pp. A31-A34. This assemblage is unique within the Zeehan field, although nickel mineralization has been described from the serpentinite at Trial Harbour and from a group of dolerite sills or dykes in the Cuni field, several miles north-east of Zeehan (Williams, 1958); Waller (1904) reported a small deposit of "nickeliferous and cupriferous pyrites" close to a serpentine dyke on the southern bank of the Summit tunnel, near the Spray Mine. Waller concluded that the Summit tunnel occurrence resulted from the intersection
of Lode fissures with earlier serpentine dykes, and it seems most probable that the Central Balstrup ores originated in the same way. Their distribution is thus not a consequence of systematic zonal changes, and no significance attaches to their paragenetic relationships with the lead-zinc ores.

A zonal sequence, as can be established by reference to Fig. 72, which shows the nine localities. However, on the assumption that post-mineralisation faulting can be expected to have disturbed any zonal pattern, the deposits have been grouped into "blocks" which are separated from each other by major faults; in addition, the mineralogically anomalous ores of the Osah - Queen Hill area have been grouped together. The relative abundances of the principal gangue minerals pyrite and siderite are shown in Fig. 49, superimposed on the major fault pattern.

The indicated abundances in Table 5 are based on mapping of dump mineralogy, study of polished sections, and review of published reports. The scale adopted is intended only to be relative within each mineral group; i.e. "abundant" sphalerite is not quantitatively comparable with "abundant" houmanite. The symbols employed have the following approximate meanings:

++++ = abundant, +++ = moderately abundant, + = rare,
+ = very rare. Parentheses ( ) indicate reported occurrences not substantiated by the present investigation.
Zonal Relationships

The areal distributions of the principal ore and gangue minerals, together with variations in some geochemical parameters, are summarised in Table 5 and Fig. 45. The individual deposits have been listed in Table 5 in an approximate west to east zonal sequence, as can be established by reference to Fig. 12, which shows the mine localities. However, on the assumption that post-mineralization faulting can be expected to have disturbed any zonal pattern, the deposits have been grouped into "blocks" which are separated from each other by major faults; in addition, the mineralogically anomalous ores of the Oonah - Queen Hill area have been grouped together. The relative abundances of the principal gangue minerals pyrite and siderite are shown in Fig. 45, superimposed on the major fault pattern.

* The indicated abundances in Table 5 are based on mapping of dump mineralogy, study of polished sections, and review of published reports. The scale adopted is intended only to be relative within each mineral group; i.e. "abundant" sphalerite is not quantitatively comparable with "abundant" bournonite. The symbols employed have the following approximate meanings:

"++++" = abundant, "+++" = moderately abundant, "++" = rare, "+" = very rare. Parentheses ( ) indicate reported occurrences not substantiated by the present investigation.
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**Table 5:**
ZONING OF GANGUE MINERALOGY

LEGEND

△ Pyrite » Siderite
△ Pyrite > Siderite
○ Pyrite ≈ Siderite
□ Pyrite < Siderite
■ Pyrite » Siderite

⇒ First phase gradient
→ Second phase gradient

Fig. 45.
Zonally distributed regularities which are apparent from Table 5, Fig. 45, and from the previous discussion may be summarised as follows:

1. Magnetite is abundant only at one western locality, with minor proportions observed in two other western lodes.

2. Pyrite is generally more abundant in the western deposits, and within each block tends to be more abundant in the west than in the east. Some exceptions in the Queen Hill area can be noted.

3. Sphalerite is slightly more abundant in the western deposits.

4. Siderite is absent or rare in the western deposits, but, passing eastwards, rapidly becomes and remains abundant. Siderite and pyrite are by no means mutually exclusive or even approximately so, as implied in some previous descriptions. There is, however, abundant textural evidence to suggest that siderite is paragenetically distinct from the bulk of the pyrite - i.e. that although the two minerals may occur together, they did not crystallize together and do not necessarily constitute an equilibrium pair.

5. Tetrahedrite is most abundant in a broad, north-south trending central zone, and is relatively rare in the extreme western pyritic and eastern sideritic ores (although its overlap into the sideritic zone is more pronounced than that into the pyritic zone).

7. Bourononite and boulangerite are distributed in similar fashion
to tetrahedrite, but with somewhat narrower "dispersions". They are both rare in the extreme pyritic and sideritic types, and are most abundant in the intermediate sidero-pyritic ores.

8. Stannite is abundant in the Oonah - Queen Hill area, rare in the sidero-pyritic ores, and absent from the western pyritic and eastern sideritic types. The distribution of stannite is clearly centred around the Queen Hill region.

9. Cassiterite is observed only in the Oonah - Queen Hill area.

10. Chalcopyrite shows no clear zonal relationships, except that it is rather more abundant in the Silver Stream and Oonah - Queen Hill ores than elsewhere.

11. Arsenopyrite is rare in the western pyritic ores, rapidly becomes abundant passing eastwards, and then declines again to relative rarity in the sideritic lodes.

12. Quartz gangue shows no clear zonal distribution, but is more or less ubiquitous.

13. The FeS content of sphalerite shows a general decline from west to east, with a marked reversal in the Queen Hill area; MnS contents show a similar distribution, except that the Queen Hill reversal is very poorly defined. These data are discussed in more detail in Chapter VI.

14. The silver contents of the galena are low in the western pyritic zone, increase in the sidero-pyritic ores, and decline
to low values again in the eastern sideritic types. Table 5 shows both assay data compiled from the literature and the results of atomic absorption analyses performed during the present investigation; considering the sampling problems involved, the agreement in cases of duplication is considered to be reasonably good. These data are also further discussed in Chapter VI.

15. The suggestion that most of the silver is actually contained in tetrahedrite rather than galena is generally supported by the Sb contents of the galena samples analysed for silver. The moderately good Sb/Ag correlation ($r = +0.77$) is discussed in Chapter VI.

16. Pyrrhotite occurs mostly as "exsolution" bleb-like inclusions in sphalerite, generally in dark, high-iron zones adjacent to late siderite, galena and/or quartz veinlets or narrow fractures transecting the sphalerite. These zones also commonly contain similar small inclusions of chalcopyrite, and may also include fine-grained pyrite ore, rarely, stannite. In some instances, inclusions of pyrite and pyrrhotite can be observed in sphalerite zones depleted in iron.

17. Coarse-grained pyrrhotite, contemporaneous with pyrite, is confined to the western pyritic ores.

18. Marcasite and pyrite formed either by breakdown of pyrrhotite or by reaction between siderite and sphalerite, siderite and galena, or sphalerite and galena, occur only in
the pyritic ores or in the western portion of the intermediate or sidero-pyritic zone. In the eastern sideritic lodes, similar reactions have produced pyrite alone.

It is concluded that the zonal relationships originally postulated by Waller (1904) and Twelvetrees & Ward (1910) can be substantiated, providing due allowance is made for the effects of post-mineralization faulting and for the presence of marked overlap rather than a sharp demarcation between the pyritic and sideritic zones. As Ward (1911) implied, the vertical component of the zoning (i.e. zoning upwards from the subsurface continuation of the Heenskirk granite) is possibly more significant than the horizontal zoning around the present outcrop of the granite.

In this connection, the limited geophysical data presently available concerning sub-surface trends of the Heenskirk Granite contain internal conflicts which are difficult to resolve. Unpublished gravity surveys carried out in 1947 by the Bureau of Mineral Resources, in the vicinity of Zeehan township, have been interpreted (W.J. Langdon, pers. comm.) as indicating a subsurface granite profile rising gently towards the east, which suggests that the Heenskirk Granite extends laterally at depth beneath the Zeehan field. However, a recent regional gravity survey (Johnson, 1967) suggests that "the granite contact dips gently under the surrounding rocks to the south and east for at
least 1.5 km., before dipping steeply" (present author's emphasis). Johnson noted that "much more data is (sic) needed before a detailed interpretation of the shape and size of the granite can be attempted". Pending further study, the first interpretation is preferred as being in better accord with the occurrence of granitic dykes in the Zeehan township area and with geochemical and mineralogical evidence (see below) for a "hot-spot", or local reversal of the zoning, in the Oonah - Queen Hill area. The anomalous ores of this area cannot be satisfactorily explained by a simple zonal theory; interpretations of their origin will be discussed following a review of pertinent geochemical data.

Because of the transitional nature of the mineralogical zoning, the precise definition of the zones is necessarily somewhat arbitrary. Ores containing significant proportions of both siderite and pyrite are numerically more abundant than those of either the pyritic or sideritic extremes, and interpretation of the geochemical data is simplified by assumption of the following zonal classification:

(1) Cassiterite Zone: This includes the tin deposits within and adjacent to the margins of the Heems Kirk Granite; these deposits were not studied during the present investigation. The term "Cassiterite Zone" is preferred to the "Tin Zone" of Both (1966) to distinguish these ores from the stannite (with only minor cassiterite) lodes
of the Oonah - Queen Hill area.

(2) Pyritic Zone: This zone includes the strongly pyritic ores of the Silver Stream - Comstock area and several deposits in the Queen Hill area. Pyrite is the predominant ferriferous gangue mineral; siderite is relatively rare or, in some cases, absent.

(3) Intermediate (Pyrite-Sideritic Zone): The Pyritic Zone grades, with increasing abundance of siderite, into a zone in which pyrite and siderite are of comparable abundance. These ores are distinguished also by a relative abundance of lead sulpho-salts and, as a consequence of the distribution of tetrahedrite, by high silver grades.

(4) Sideritic Zone: The trends observed between the Pyritic and Intermediate Zones continue, passing eastwards, into a zone in which siderite becomes the principal ferriferous gangue mineral and pyrite becomes relatively rare.

The distribution of these zones within the Zeehan field is shown in plan in Fig. 46, and the probable effect of the vertical component is demonstrated schematically in Fig. 47. Because of their transitional nature, the zone boundaries in both diagrams are subjectively assigned, and are intended only to show the general regional trends. In particular, the fault-bound pyritic block shown north of the Swansea Mine should perhaps be included in the intermediate zone. The only ore deposit in this block is
Fig. 46.
Fig. 47.
the Sunshine Mine (Tramway Formation), which contains pyrite but no visible siderite. Geochemically, however, the Sunshine sphalerite is more closely related to the intermediate ores of Grubb's Mine (to the south) and Spray Mine (to the north-east) than to those of the Pyritic Zone. Because of sampling difficulties, some minor anomalies of this type are to be expected.

The geochemical studies can be divided, for convenience, into two complementary parts:

1. The principal minor elements in sphalerite, viz., iron and manganese, were studied by means of an extensive programme of electron microprobe analyses. Some of the reasons favouring this technique for this particular problem have been described earlier (Williams, 1965) and the analytical problems inherent in the technique, together with a convenient method for overcoming them, have also
CHAPTER VI. GEOCHEMICAL STUDIES

Introduction

Although the mineralogical relationships described in Chapter V substantiate the general concept of zoning as outlined by Twelvetrees & Ward, it is apparent that the simple mineralogical criteria are considerably more diffuse than had previously been supposed. Accordingly, a detailed investigation of the minor- and trace-element geochemistry of the principal ore and gangue minerals was undertaken, with the intention of establishing quantitative parameters which might assist in the more precise definition of the zonal relationships. Since most theories of hydrothermal zoning imply that it originated from progressive changes in the physico-chemical environment of ore deposition, it might be expected that these would be reflected in compositional differences in phases crystallizing in different zones.

The geochemical studies can be divided, for convenience, into two complementary parts:

1. The principal minor elements in sphalerite, viz., iron and manganese, were studied by means of an extensive programme of electron microprobe analyses. Some of the reasons favouring this technique for this particular problem have been described earlier (Williams, 1965) and the analytical problems inherent in the technique, together with a convenient method for overcoming them, have also
been discussed (Williams, 1967). From a practical viewpoint, the microprobe was particularly suited to this investigation because of the small amount of sample material required - accurate analyses could be made on ore samples which contained only microscopic amounts of sphalerite, without any need for preliminary concentration. This was particularly important in the many cases where little or no sample material other than museum specimens or low grade dump samples was available.

Some interesting results were obtained from microprobe studies of compositional heterogeneity in sphalerites; in previous investigations of this type (e.g. Sims & Barton, 1961) only limited attention could be paid to this problem because of the difficulties of extracting sufficient sample material for the available macro-analytical techniques.

2. Selected trace elements in sphalerite, galena, pyrite and siderite were determined by atomic absorption spectrophotometry. This had the disadvantage of requiring much larger samples (at least 200 mg. was preferred for each sample, to allow duplicate determinations for each of eight elements), and therefore coverage was much less comprehensive. The analysis samples had to be separated and purified, and severe contamination (e.g. by sulpho-salts in galena, siderite in high-iron sphalerite and
vice versa, etc.) could not always be avoided. Some difficulties in chemical dissolution of the samples were encountered, and a critical evaluation of the atomic absorption technique showed it to be more prone to interference effects than the current literature generally suggests (see Appendix II). Despite these problems, some interesting trends were observed, and the data obtained are thought to be more accurate than could have been obtained from optical emission spectrography (the source of most of the limited data on sulphide trace elements currently available). There is no doubt that the electron microprobe is inherently more satisfactory for this type of investigation; it was not employed in the present study because most of the trace elements are present in concentrations below the current microprobe limits of detection, but in view of the considerable advances which are being made in instrumental design leading to greatly improved stability, it seems certain that the microprobe will soon find extensive applications in similar studies. The dissolution problems can also be avoided by using X-ray fluorescence techniques, which offer high sensitivities relative to those of the microprobe but require larger samples and are of limited value for the study of compositional heterogeneities.
Minor elements in sphalerite

Distribution and zonal relationships

The FeS and MnS contents (weight per cent, as determined by microprobe analyses) of sphalerites from the various lodes of the Zeehan field are shown in Fig. 48 and 49. The figures shown are the arithmetic means of between 3 and 22 analyses for each point, the exact number of analyses depending on sample availability and degree of inhomogeneity. Analyses obtained from pyrite-, pyrrhotite- and chalcopyrite-bearing alteration zones adjacent to galena and quartz replacement boundaries (see below) have, as far as possible, been excluded from Fig. 48; in some cases, however, (e.g. Silver Stream Mine) no inclusion-free sphalerites were available for analysis, and hence it was occasionally necessary to analyse sphalerites which contained inclusions (particularly of chalcopyrite), providing they showed, in polished section, no obvious relation to replacement boundaries or alteration zones. The data of Figs. 48 and 49 are therefore presumed in nearly all cases to reflect variations in the original compositions of the sphalerites, possibly modified by re-equilibration during cooling, but not by the limited alteration accompanying deposition of galena and quartz. The compositions of the altered zones are further discussed below.

No geochemical significance is attached to the arithmetic means; they simply represent a convenient way of portraying the overall differences from one lode to another. The variation at
SPHALERITE
IRON CONTENT
(MEAN WEIGHT PER CENT FeS)

Fig. 48.
Fig. 49.
Fig. 50.
Fe/Mn correlation in sphalerite

I Pyritic ore

FeS (wt per cent) vs Fe/Mn correlation

II Sideritic ore

FeS (wt per cent) vs Fe/Mn correlation

Fe/Mn correlations

III Pyrite - Sideritic ore

FeS (wt per cent) vs Fe/Mn correlation

Fig. 51.
each locality is difficult to show graphically, but is summarised in Table 6. For any pair of localities or locality groups, the significance of apparent differences in the arithmetic means must be evaluated statistically by variance analysis; this has been done for the combined pyritic, intermediate and sideritic groups (see below).

The averaged FeS data generally show the expected decline from west to east, with some anomalies which correlate with those observed in lode mineralogies. Thus the FeS values are generally high in the western, or Comstock, area and low in the south-eastern portion of the field. Their rapid decline between the Comstock and Swansea Mines is unexpected from the simple zonal theory, and matches the corresponding relatively abrupt transition from pyritic to sideritic mineralogy along the same line. Reference to Figs. 11 and 14, however, indicates that both trends are probably accentuated by the effects of post-mineralization faulting which, in the plane of the present topographic surface, has "dropped" blocks of Paleozoic host rocks into juxtaposition with older sediments which were, at the time of mineralization, closer to the parent intrusive. The high iron contents of the Tasmanian Mine sphalerites (by comparison with those of the North Tasmanian Mine, to the north-west, and the Swansea Mine, to the south-east) correlate with a relative abundance of pyrite.

The general west-to-east decline in FeS contents shows a marked reversal in the Queen Hill area, again in accord with
Table 6

Fol Contents of Zeehan Sphalerite

<table>
<thead>
<tr>
<th></th>
<th>Unaltered</th>
<th>Altered</th>
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<tr>
<td></td>
<td>Mean (wt. per cent)</td>
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<td>Susanite</td>
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<td>T.L. R.</td>
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<td>Crown</td>
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<td>Montana</td>
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<td>Ring</td>
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<tr>
<td>Bell</td>
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<td>0.3</td>
</tr>
<tr>
<td>Sunrise</td>
<td>10</td>
<td>0.4</td>
</tr>
<tr>
<td>Oceanus</td>
<td>13</td>
<td>1.8</td>
</tr>
</tbody>
</table>

* No coexisting pyrite
** Parentheses indicate no pyrrhotite in alteration zones analyzed
mineralogical observations.

It is tempting to contour the FeS data and to assign them a zonal significance on this basis. However, in view of the apparent disruption of the original zonal patterns by post-mineralization faulting, such contouring would be meaningless except to emphasise the discontinuities. Instead, Fig. 50 presents three histograms showing the distribution of FeS analyses as a function of ore types; variance analysis shows the obvious differences to be statistically significant at the 99% confidence level. There can be no reasonable doubt that the iron content of sphalerite declines progressively from the pyritic through the intermediate to the sideritic types; the decline appears to be more rapid between pyritic and intermediate than between intermediate and sideritic.

The MnS contents of Zeehan sphalerites also show a progressive decline from west to east. The gradient, however, is much steeper; from an average of 4.2 weight per cent (ranging up to 9.3 per cent, which appears to match the ^highest MnS content yet

*Palache, Berman & Frondel (1944) cite one sphalerite from Sardinia with 5.81 per cent Mn (= 9.2 percent MnS). Gabrielson (1945) quotes a maximum of 5.4 per cent Mn in 78 Swedish sphalerites, and Oftedal (1941) reports two values of 5 per cent Mn among 70 Norwegian sphalerites, both in contact metamorphic deposits.
reported for a natural terrestrial sphalerite) in the ores of the Silver Stream Mine, MnS contents fall to around 1.0 per cent in the Comstock area, and almost all of the intermediate and sideritic zone sphalerites contain less than 0.1 per cent.

The averaged FeS and MnS contents for each locality are plotted against each other in Fig. 51, in which pyritic, intermediate (pyrito-sideritic) and sideritic ore types are distinguished. Apart from emphasising the parallel declines in both iron and manganese contents across the zoning, these diagrams show that the strong positive Fe/Mn correlation in the pyritic ores \( (r = 0.92) \) is markedly reduced in the intermediate \( (r = 0.34) \) and sideritic \( (r = 0.27) \) groups. It is obvious that the appearance of significant proportions of siderite in the Zeehan ores coincides with pronounced changes in the distribution of manganese. It is noteworthy that the high-iron sphalerites of the Queen Hill area, where pyritic and sideritic ores occur intermingled, do not show high manganese contents comparable with those of similar high-iron varieties in the Silver Stream - Comstock region.

In qualitative terms, these relationships may be attributed to the "lithophile" character of manganese in other than very strongly reducing environments (Goldschmidt, 1954) - the manganese sulphides alabandite and hauerite are very rare in crustal rocks, compared to the silicates, oxides and carbonates. Thus it appears that at Zeehan manganese precipitating in the
pyritic ores, in the absence of oxide, silicate or carbonate phases, entered the structure of sphalerite due to ready Mn\(^{++}\) - Zn\(^{++}\) diadochic substitution. However, in the presence of abundant carbonates, the lithophile character predominated over the effect of increasing solubility in sphalerite at higher temperatures, and most of the manganese entered the carbonate structure instead. Thus sideritic ores are characterised by low MnS in sphalerite, regardless of its FeS content or temperature of formation. Boyle & Jambor (1963), discussing the chemistry of sphalerites from the Keno Hill deposits in the Yukon (which show many mineralogical and chemical resemblances to the Zeehan ores), observed that "the manganese content of the sphalerites is relatively low despite the fact that associated siderites are rich in manganese (up to 17 per cent MnO). This probably means that the carbonate lattice has a greater affinity for Mn than the sphalerite lattice in a crystallizing milieu where manganese is abundant".

More precisely, the relative stabilities of MnS and MnCO\(_3\) at any temperature will, like the relative stabilities of pyrrhotite and siderite, depend on the fugacities of sulphur, oxygen and carbon dioxide, summarized in the reaction:

\[
\text{MnS} + \text{CO}_2 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{MnCO}_3 + \frac{1}{2}\text{S}_2
\]

According to the equilibrium diagrams of Holland (1965), MnCO\(_3\) is unstable at 600°C under CO\(_2\) fugacities of up to 100 atmospheres; the present author is not aware of any experimental
data on the thermal stability of rhodocrosite but, by analogy with siderite, instability at this temperature probably extends to much higher CO$_2$ fugacities. MnS, however, is stable over the whole of the pyrite and pyrrhotite fields at 600°C, regardless of CO$_2$ fugacities (up to 100 atmospheres) or the presence or absence of SiO$_2$ required to form rhodonite.

At 400°C, MnCO$_3$ is stable within Holland's "main-line" $f_{S_2O_2}/f_{O_2}$ field under CO$_2$ fugacities of the order of 100 atmospheres; under these conditions, the MnS/MnCO$_3$ equilibrium boundary crosses the "main-line" field, and the relative stabilities of MnS and MnCO$_3$ are dependent on the sulphur and oxygen fugacities. Under lower CO$_2$ fugacities (of the order of 1 atmosphere or less) only MnS or, in the presence of excess SiO$_2$, MnSiO$_3$ are stable.

At 250°C and CO$_2$ fugacities of the order of 100 atmospheres, only MnCO$_3$ is stable within the "main-line" field. Under CO$_2$ fugacities of the order of 1 atmosphere, either MnS or MnCO$_3$ may be stable within the pyrite stability field, depending again on sulphur and oxygen fugacities. The MnS stability field blankets the "main-line" area only under CO$_2$ fugacities of less than 10$^{-1}$ atmospheres.

The partition of manganese between co-existing sphalerite and siderite is therefore a function of temperature and of oxygen, sulphur and carbon dioxide fugacities, with the latter being particularly significant at any given temperature. Zonal
variations in any of these parameters, but particularly temperature and/or carbon dioxide fugacity, would account for the relationships observed in the Zeehan ores.

It should be noted that the FeS content of sphalerite is also a function of the same variables, with the role of sulphur fugacity becoming more significant because of its effect on the activity of FeS in pyrrhotite (Barton & Toulmin, 1966). Under certain circumstances, however, high CO₂ and/or oxygen fugacities could conceivably also exert profound influences on the FeS content of crystallizing sphalerite. This has important implications in geothermometric studies, since determination of the distribution of both iron and manganese between sphalerite and co-existing sulphide and carbonate phases may be of assistance in limiting the possible range of gas fugacities under which a natural assemblage may have crystallised. For example, Holland's data for 400°C show that an assemblage consisting of iron-bearing but low-manganese sphalerite in equilibrium with a manganiferous carbonate (a common association in the Zeehan ores) is stable over only a limited range of S₂, O₂ and CO₂ fugacities.

Attempts to pursue this reasoning sufficiently to define the environment of crystallization of the Zeehan ores have proved unsatisfactory, in view of the inadequacy of the high temperature thermochemical data currently available. It is however evident from Holland's (1965) data that MnS is stable,
under CO₂ fugacities greater than 10 atmospheres (such as are indicated for the Zeehan ores by the breakdown of pyrrhotite to marcasite + siderite), only at temperatures of approximately 300°C and higher. The abrupt zonal transition from manganiferous to non-manganiferous sphalerites can therefore be used to plot an approximate position for the 300°C isotherm (see below). It is apparent that studies of manganese distribution in sphalerite-carbonate assemblages are potentially highly informative and, subject to experimental definition of the phase equilibrium relationships, can be expected to form an essential part of future thermometric studies of such ore types.
Geothermometric implications

Despite some anomalies, the data of Fig. 48 are strongly suggestive of an overall chemical or physico-chemical control on the composition of sphalerite, particularly when it is recalled that they closely resemble similar trends observed in other zoned mineral deposits (e.g. Central City, Colorado; Sims & Barton, 1961). Since the compositional trends parallel probable temperature gradients around the Heemskirk Granite, it seems likely that temperature effects have been involved, probably in conjunction with progressive changes in chemical parameters such as sulphur fugacity (cf. Central City), which might themselves be to some extent temperature dependent (Holland, 1965).

Following the pioneering studies of Kullerud (1953), sphalerite compositions have been widely employed in geothermometric studies, in many instances giving results comparable with those obtained by other methods. In other cases, anomalies were found, and Barton & Kullerud (1958), on further investigation, found that the compositions of sphalerite in sphalerite-pyrite assemblages were controlled by both temperature and sulphur fugacity, (in addition to relatively minor pressure effects), so that determination of crystallization temperatures in such systems is severely limited unless independent methods of estimating sulphur fugacity at the time of crystallization are available.

More recently, Barton & Toulmin (1966) have shown that the
effects of sulphur fugacity are more widespread than had previously been thought, extending to control of the compositions of sphalerites in equilibrium with pyrrhotite. Barton & Toulmin also reported failure to attain useful approaches to equilibrium in experimental runs below 580°C, due to slow reaction kinetics; hence equilibrium relationships in the geologically interesting range below this temperature were perforce obtained by extrapolation of the high temperature data, with some ensuing uncertainty (see below).

For these reasons, it is currently considered unwise to assign crystallization temperatures based on the so-called "sphalerite geothermometer". The Zeehan ores, however, provide an example to suggest that it is possible in certain cases to derive at least approximate chemical and thermometric data from studies of sphalerite compositions.

Fig. 52, from Barton & Toulmin (1966), shows the experimentally determined and extrapolated compositions of sphalerite as functions of the two principal variables temperature and sulphur fugacity (broken lines are extrapolations); in addition, equilibrium boundary curves for the two reactions

(1) pyrrhotite + sulphur $\rightleftharpoons$ pyrite
(2) chalcopyrite + sulphur $\rightleftharpoons$ pyrite + bornite

are superimposed.

If the extrapolations are, for the moment, considered to be
Fig. 52: Composition of sphalerite as a function of temperature and sulphur fugacity (after Barton & Toulmin, 1966).
valid, then the following relationships can be deduced for the Zeehan ores:

Sphalerites from the Silver Stream, Doric, Comstock and several of the Queen Hill Mines all have relatively high iron contents, with compositions generally between 5 and 19 weight per cent FeS (approximately 5 to 20 mole per cent) - excluding the "alteration zones", which range a little higher. In the Comstock ore, the sphalerite occurs intergrown with pyrite and, in some sections, coarse-grained pyrrhotite or marcasite pseudomorphic after pyrrhotite; generally, however, pyrrhotite is absent although pyrite is invariably present.

The co-existence of pyrite and pyrrhotite provides a natural buffer which determines the sulphur fugacity at any given temperature; the composition of a sphalerite crystallizing in equilibrium with both pyrite and pyrrhotite is thus a function of temperature of crystallization and total pressure. On the assumption that pressure effects are relatively small, the temperature can then be estimated from Fig. 52 (although it will be noted that the sphalerite isopleths and the pyrite-pyrrhotite equilibrium curve are nearly parallel, which limits the accuracy with which the temperature can be determined).

If, as is the case in the majority of the Zeehan ores, the sphalerite co-exists with pyrite alone, then its composition is not solely a function of temperature; instead Fig. 52 shows that at any given temperature, increasing sulphur fugacity across
the pyrite field decreases the equilibrium iron content of the sphalerite, so that a temperature estimated from the intersection of the appropriate isopleth with the pyrite-pyrrhotite equilibrium curve is a minimum only - the same composition could be produced at higher temperatures under higher sulphur fugacities. For FeS contents higher than approximately 12 mole per cent, the isopleths intersect the pyrite-pyrrhotite curve twice, providing maximum as well as minimum temperature estimates.

In view of the very limited distribution of pyrrhotite in the Zeehan ores (apart from the "alteration zones"), assumption of pyrite-pyrrhotite-sphalerite equilibrium is generally unwarranted. Assumption of pyrite-sphalerite equilibrium, however, is probably justifiable, even though there is considerable textural evidence to suggest that the pyrite is paragenetically earlier. Barton, Bethke & Toulmin (1963) have suggested that under these circumstances (i.e. the crystallization of sphalerite in the presence of considerable earlier pyrite), the sphalerite can be considered to have been formed in equilibrium with pyrite, although the converse assumption that the pyrite (other than grain surfaces) was in equilibrium with sphalerite is not tenable.

In the case of the Silver Stream ores, which are the closest in outcrop to the Heemskirk Granite and which yielded the highest average FeS contents (apart from the Doric Mine, whose
determinations were made on a single, heavily altered specimen),
alyses of unaltered sphalerites ranged from 10.3 to 18.6
weight per cent (11.2 to 20.2 mole per cent). The lowest
values indicate only a minimum crystallization temperature of
approximately 250°C and a maximum of 700°C (Fig. 52), but
the highest values require, in the absence of pyrrhotite,
temperatures between 500°C (minimum) and 550°C (maximum).

In these ores, particular importance is attached to the
highest iron contents, because of the more stringent
restrictions which they impose on the possible ranges of
temperature and sulphur fugacity compatible with the observed
variation. Temperature ranges based on the low-iron varieties
are so wide as to be of very limited value. In this example, the
low-iron sphalerites could have formed in the same temperature
range as the high-iron varieties, as a consequence of changes
of less than an order of magnitude in sulphur fugacity (Fig. 52);
alternatively the sulphur fugacity could have remained more or
less constant and the observed compositional variations be
due to fluctuations of less than ± 20°C in temperature. It is
not necessary to invoke gross changes in temperature between
250 and 550°C or in sulphur fugacity between 10^{-13} and 10^{-3}
atmospheres; in view of the delicacy of growth zoning which is
often observed in similar assemblages, such large variations in
these parameters are thought to be unrealistic.

On the other hand, the deposits of the south-eastern part of
the Zeehan field contain very low-iron sphalerites, with maximum FeS contents ranging as low as 0.6 per cent, and minimum FeS contents down to less than the limit of detection (0.05 weight per cent Fe under the conditions of routine microprobe analysis). Again these deposits do not contain pyrrhotite which can be interpreted as having been in equilibrium with pyrite and sphalerite during crystallization of the latter. However, the common occurrence of chalcopyrite and pyrite (albeit in minor proportions) and the absence of bornite place upper limits on the possible range of temperature and sulphur fugacities (Fig. 52); under these circumstances, the minimum FeS contents have some thermometric significance, while the maximum contents tend to yield impracticably wide ranges of possible temperatures and sulphur fugacities. For example, FeS contents of unaltered sphalerites from the Austral Mines range from 0.1 to 1.4 weight per cent. Based on the data of Barton & Toulmin, the maximum of 1.4 per cent FeS indicates, for a sphalerite-chalcopyrite-pyrite equilibrium assemblage, a possible temperature range of $< 100 - 550^\circ C$, and a possible sulphur fugacity range of $10^{-18}$ to $10^{-1}$ atmospheres (subject to potentially large extrapolation errors in the low-temperature range). However, the minimum of 0.1 per cent limits the possible temperature range to less than $300^\circ C$ (and corresponding sulphur fugacities to less than $10^{-7.5}$). Within this range, the observed compositional variation can again be produced by relatively minor fluctuations.
in temperature, sulphur fugacity, or both.

Estimates of the possible temperature range for initial sphalerite crystallization in most of the deposits in the Zeehan field are tabulated in Table 6, and plotted geographically in Fig. 53. These estimates, based on the extrapolations of Barton & Toulmin, are derived from the range of iron contents observed in sphalerites from the locality concerned, according to the reasoning outlined above; they indicate in each case the maximum temperature range over which the observed compositional variation could have been produced by fluctuations in sulphur fugacity alone. It is apparent that, subject to the effects of post-mineralization faulting (indicated in Table 6 by grouping together all deposits occurring within individual fault-bound blocks, and arranging the blocks in an overall west-east sequence), the zonal relationships become much clearer when they are examined in terms of the full compositional range rather than the arithmetic means. The only major anomalies in a clear zonal sequence are those due to high-iron sphalerites in the Queen Hill area (Poverty Point, Stormsdown, Clarke's Lode, Fahey's and No. 4 Queen) and the Despatch Mine; these all coincide with mineralogical anomalies (cf. Fig. 45), and are further discussed in Chapter VII.

Although sphalerite temperatures cannot be assigned with great precision at any single locality, the clarity of the overall pattern and its remarkable correlation with the mineralogical
INITIAL SPHALERITE TEMPERATURE RANGES

LEGEND

Approximate Zone Boundaries

Fig. 53.
zoning (cf. Figs. 45, 46) and with the expected temperature gradient around the Heemskirk Granite appears too close to be fortuitous. It is therefore concluded that the zoning reflects, at least in part, some decline in both temperature and in sulphur fugacity, from 500-550°C and 10^{-3} to 10^{-5} atmospheres $f_{S_2}$ in the Silver Stream area to less than 200°C and less than 10^{-11} atmospheres $f_{S_2}$ in the Bell - Sunrise area.

The temperature gradient thus estimated is compared in Fig. 53 with independent estimates based on previously described mineralogical relationships, as follows:

(a) Siderite is absent from the Silver Stream ores, is present in small proportions in the Comstock and Doric lodes, and becomes abundant east of a line through the Sylvester, Britannia, Stonehenge and T.L.E. Mines. It has been suggested earlier that this distribution might reflect the thermal stability of siderite, which has been shown to be unstable above 530°C at 1 kb. $P_{CO_2}$ (O.F. Tuttle, pers. comm.). A 530°C isotherm drawn on the basis of siderite distribution agrees well with the sphalerite temperature estimates.

(b) Clark (1960) has shown that the assemblage arsenopyrite + pyrite is unstable above temperatures ranging from 491°C to 528°C, depending on confining pressure. The distribution of arsenopyrite in the Zeehan ores can therefore be used to plot a 500°C (approx.) isotherm, which again is in good
agreement with the sphalerite temperatures.

(c) It has been noted earlier that MnS is only stable, under CO₂ fugacities higher than 10 atmospheres, at temperatures higher than approximately 300°C. Sphalerites containing manganese in other than trace amounts are only observed within and west of the Sylvester - Britannia - T.L.E. group; a line passing somewhere to the east of these mines therefore marks the approximate position of the 300°C isotherm. Again agreement with the sphalerite geothermometry is good, apart from unexpectedly low MnS contents in the Doric and perhaps the Sylvester sphalerites.

(d) Coarse-grained paragenetically early marcasite is absent from the pyritic ores of the Silver Stream - Comstock district, but becomes abundant in the intermediate ores of the Grubb's - Spray - Argent Flat belt. Although pH may be a controlling factor, it is also possible that this distribution reflects the thermal stability of marcasite, and hence that a 430°C isotherm coincides approximately with the transition from the pyritic to the intermediate zone.

It is evident that the thermometric data from these various sources are generally consistent, to an extent which can hardly be attributed to coincidence. Hence it appears that the sphalerite geothermometer is capable of providing useful
information concerning the environment of ore deposition, providing adequate analytical data are available and proper caution is exercised in their interpretation.

The sphalerite temperatures of Table 6 and Fig. 53 have not been corrected for the effects of pressure, which are not well understood. The data of Kullerud (1953) indicate that the corrections, for a confining pressure of approximately 1 kb., would be of the order of +25°C - i.e. considerably less than the uncertainty in most of the estimated temperature ranges.

For sphalerite assemblages of intermediate overall composition, the estimated temperature ranges are relatively wide, so that it is not possible to trace in detail the rate of decline of temperature or sulphur fugacity through the intermediate ore zones in the absence of other assemblages (e.g. silver-argentite; tennantite-enargite) which could be used to limit sulphur fugacity ranges within the pyrite-chalcopyrite field. However, it can be observed from Fig. 52 that a hypothetical path directly between the high- and low-temperature $f_{S_2}$/$T$ fields defined above, resembling the path proposed by Sims & Barton (1961) for the Central City ores, would produce an initially rapid decline in sphalerite FeS contents, followed by progressively slower changes. This is in accord with the marked transition from pyritic to intermediate ores and the slower decline from intermediate to sideritic ores which has already been noted.

In view of the importance of examining the full range of FeS and MnS contents of sphalerites co-existing with pyrite, it is
apparent that studies of such assemblages must include an extensive analytical programme designed to determine the full extent of compositional heterogeneity at each locality. The electron microprobe is particularly suited to such investigations because of its facility for making large numbers of reasonably accurate analyses over the full compositional range of natural sphalerites (Barton & Toulmin, 1966; Williams, 1965, 1967).

It was noted earlier that much of this reasoning is dependent upon the accuracy of the extrapolation of Barton & Toulmin's experimental data into the low temperature region. One aspect of this extrapolation is of particular importance; Fig. 54 (after Barton & Toulmin) shows portion of the system Fe-Zn-S projected on to the FeS-ZnS binary. Attention is drawn to curve B which shows, as a function of temperature, the composition of sphalerite crystallizing in equilibrium with pyrite and pyrrhotite. Experimental data for this curve were obtained by Barton & Toulmin only at temperatures above 580°C, because of experimental difficulties in equilibration at lower temperatures. The reversal in slope of this curve below 580°C, indicating that the iron contents of sphalerites in sphalerite-pyrite-pyrrhotite assemblages decline with decreasing temperature, was based partly on observations of systematic changes in sphalerite compositions in zoned hydrothermal deposits (analogous to those described in the Zeehan ores), and partly on admittedly
Fig. 54 (from Barton & Toullmin, 1966).
tenuous extrapolations of the high temperature experimental data. It is clear from Fig. 52 that the extent of the required extrapolations and the magnitude of possible errors are such as to permit doubts concerning the accuracy of the postulated phase relationships at relatively low temperatures.

The problem of low-temperature equilibration in the system Fe-Zn-S has recently been studied by Boorman (1967), who used salt fluxing techniques to increase the reaction rates of synthetic sulphide mixtures, and by Scott & Barnes (1967), who crystallized synthetic sphalerite + pyrrhotite and sphalerite + pyrrhotite + pyrite assemblages across small temperature gradients in aqueous ammonium iodide solutions. The results reported for both studies indicate that the sphalerite solvus, in equilibrium sphalerite-pyrite-pyrrhotite assemblages, is sensibly vertical or, in other words, that the compositions of sphalerites in such assemblages are independent of temperature below about 580°C.

These findings conflict with the proposals of Barton & Toulmin and with interpretations based on the study of natural sphalerite occurrences. If the newer data are correct, then all sphalerites crystallizing in equilibrium with pyrite and pyrrhotite should have a constant iron content equivalent to approximately 21 mole per cent FeS (with the possible exception only of deposits forming between 580°C and 742°C - the upper stability limit of pyrite - whose original crystallization
composition is preserved metastably during subsequent cooling). Although the proof of equilibrium in natural assemblages is difficult, evidence available to date (including that derived during the present study and discussed below) does not altogether support this conclusion. Thus, for example, Campbell (1963 and pers. comm.), in a study of sphalerite compositions in the massive pyrite-pyrrhotite-sphalerite ores of the Quemont Mine in Quebec, found FeS contents varying from 10 to 20 mole per cent. Campbell was unable to reconcile pyrrhotite geothermometer temperatures averaging 325°C with sphalerite temperatures, averaging 540°C, estimated from the solvus of Sims & Barton (1961); it is noteworthy, however, that the same sphalerite compositions yield an average estimate of 350°C, in much closer agreement with the pyrrhotite data, when the revised solvus of Barton & Toulmin (1966) is employed.

Reported iron contents of sphalerites in the massive sulphide lodes of the Broken Hill lead-zinc deposit in New South Wales range from 13 to 21 mole per cent (Edwards, 1956); several Broken Hill sphalerites analyzed by the present author have all fallen in the lower part of this range (14 to 16 mole per cent), and the highest values quoted by Edwards appear to be atypical. Pyrite is rare in the Broken Hill ores, but pyrrhotite is relatively common. The coexistence of pyrrhotite (in an orebody widely thought to be of metamorphic origin) with sphalerites showing this compositional variation can only be explained in
terms of the phase diagram of Boorman (1967) by assuming metastable preservation of sphalerite-pyrrhotite assemblages originally formed at temperatures of 600-742°C (plus a pressure correction). Since Barton & Toulmin obtained equilibration of dry Fe-Zn-S runs at 580°C in twelve months, it is difficult to explain the metastable preservation of assemblages formed at significantly higher temperatures.

The Nairne Pyritic Formation of South Australia contains pyrite, pyrrhotite and sphalerite in a metamorphosed sequence of greywackes and siltstones (Skinner, 1958). Skinner (p. 558) noted that "a large number of pyrite, pyrrhotite and sphalerite samples from Shephard Hill...all have constant compositions", and suggested that they constituted an equilibrium assemblage. Like Campbell (1963 - see above) he found difficulty in reconciling temperature estimates of approximately 300°C and 600°C based on the pyrrhotite and sphalerite geothermometers respectively; again, however, when the data of Barton & Toulmin (1966) are substituted for those of Kullerud (1953) on which the original sphalerite estimation was based, the difference is reduced to one of experimental and analytical uncertainty. The average sphalerite FeS content of 15.2 mole per cent indicates a crystallization temperature of approximately 350°C. By contrast, the equilibrium diagram of Boorman (1967) requires metastable preservation of an assemblage originally produced at 700°C or higher, a temperature which is completely incompatible with the
regional metamorphic grade.

The banded lead-zinc ores of Mt. Isa, Queensland, contain pyrite, pyrrhotite and sphalerite intergrown in textures which are not unequivocally indicative of equilibrium; field relationships are strongly indicative of a syngenetic origin for the lead-zinc ores, and it is possible that complete equilibrium was not attained during recrystallization of the sulphides. Nevertheless, a small group of sphalerites from an unknown locality on the No. 11-level of the Mt. Isa Mine, analyzed by the author for Dr. P.J. Solomon, showed remarkably little variation around a mean of 11.8 wt. per cent FeS. If equilibrium between the iron and zinc sulphides is assumed, this composition indicates, from the data of Barton & Toulmin, a temperature of approximately 250°C, again comparable with the low regional metamorphic grade. If the interpretations of Boorman and Scott & Barnes are correct, these compositions can have been produced only under disequilibrium conditions, in which case their uniformity is surprising.

In a recent study of the Salton Sea brines of California and some of their effects on their reservoir rocks, Skinner, White, Rose & Mays (1967) have shown that changes in the composition of sphalerite grains exposed to the brine in the presence of both pyrite and (minor) pyrrhotite can best be explained in terms of a solvus similar in form to that proposed by Barton & Toulmin. Sphalerite grains with cores containing only 3.0 per cent FeS
have been altered around their margins to darker varieties containing 16.6 mole per cent FeS. Using Barton & Toulmin's curve, they calculated a temperature of about 325°C for the alteration, in excellent agreement with 300-350°C measured directly in the brines.

Rose (1967) observed FeS contents in sphalerite varying from 9.1 to 19.8 per cent in sphalerite-pyrite-pyrrhotite assemblages from the Central district of New Mexico.

In view of these examples, it seems that there is an inexplicable discrepancy between the field relationships of many sphalerite-bearing ores and the most recent experimental data. It has been noted that in some circumstances high CO₂ and/or oxygen fugacities might conceivably affect the composition of sphalerites, but carbonates or oxides are insignificant constituents of the ore mineral assemblages cited above, with the exception of those of Broken Hill and Mt. Isa. Even in the case of Broken Hill, Edwards (1956) has noted the absence of any correlation between the iron and manganese contents of sphalerite and the presence or absence of carbonate or silicate gangue. It is always possible that the observed compositions have arisen under conditions of disequilibrium, but if this is the case in the Quemont, Broken Hill and Nairne deposits then the probability of the attainment of equilibrium in any ore deposit appears to be remote.

The experimental data of Boornan are open to some criticism,
notably because of the failure to approach the equilibrium state from both compositional directions. At the time of writing, Scott & Barnes' results were available only in abstract form, giving few details of the methods employed. It must be conceded, however, that the close agreement between the results of the two studies is unlikely to be fortuitous.

Although the reason for the discrepancy is not apparent, mineralogical and chemical relationships in the Zeehan ores shed some further light on the problem, and suggest a further experimental approach which may provide useful information. Reference has already been made to the occurrence in the Zeehan sphalerites of "exsolution" particles of chalcopyrite, pyrrhotite and secondary pyrite in altered zones adjacent to galena-sphalerite and quartz-sphalerite replacement boundaries; similar phenomena have already been described in other sulphide deposits (e.g. in the ores of the Thackaringa mines near Broken Hill; Lawrence, 1967).

Barton & Toulmin (1966) state that "for pyrrhotite to 'exsolve' from sphalerite, extra sulfur must be introduced". While this statement appears from their experimental observations to be correct insofar as it refers to the simple unmixing of FeS-ZnS solid solutions, there are, however, several other possible mechanisms by which pyrrhotite can be formed during post-depositional re-equilibration of sphalerite-bearing assemblages. While none of these is "exsolution" in the strict sense, in several
instances the textures to be expected would be difficult or impossible to distinguish from those produced by unmixing in other mineral systems.

In fact, pyrrhotite could conceivably be produced by re-equilibration (complete or partial) consequent upon isochronal cooling of certain sphalerite-bearing assemblages, by isothermal changes in bulk chemical composition of some assemblages, or by combinations of the two.

Isochronal cooling:

Fig. 55 (after Barton & Toulmin, 1966) shows two isothermal sections in the system FeS-ZnS-S, one determined experimentally at 580°C and the second a hypothetical diagram for 200°C in which the exact positions of points B and C are uncertain. It will be noted that at the lower temperature, points A, B and C are all closer to the ZnS end of the FeS-ZnS binary; the position of each point depends on the form of curves A, B and C respectively in Fig. 54.

An assemblage having a bulk chemical composition lying between A and pure ZnS would consist of a sphalerite solid solution, and would undergo no change on cooling from 580°C, unless it lay close to the high temperature position of point A - in which case it could exsolve FeS (i.e. troilite) as A moved towards ZnS. Since no terrestrial sphalerites having adequately high iron contents or containing exsolved troilite are known, this mechanism is not relevant to the present discussion.
However, if the original assemblage consisted of sphalerite + pyrite (i.e. with bulk composition in the FeS-ZnS-S ternary rather than on the FeS-ZnS binary) and if, on cooling, the tie-lines between pyrite and point B and between pyrite and point C moved to the right as postulated by Barton & Toulmin, then the bulk composition could conceivably leave the pyrite-sphalerite field and pass into the three phase pyrite-pyrrhotite-sphalerite field.

As the tie lines move with falling temperature, the composition of the sphalerite would undergo no change until the pyrite - point B join intersected the bulk composition. Thereafter (providing equilibrium is maintained), as point B moves further towards ZnS, the FeS content of the sphalerite would decrease; the released FeS would precipitate as pyrrhotite, which very probably would nucleate and grow within the sphalerite from which it was derived, giving rise to "exsolution" textures.

In several crustified ore samples from the Comstock Mine early layers of pyrite on the vein walls are succeeded by layers of dark sphalerite. Under the microscope, narrow bands in the sphalerite immediately adjacent to the sphalerite-pyrite contacts are seen to contain abundant bleb-like inclusions of pyrrhotite (Fig. 28); microprobe analysis of the sphalerite in these bands shows it to be depleted in iron relative to nearby inclusion-free areas (8 to 11 weight per cent FeS compared to 13 to 14 wt.
These relationships are consistent with the mechanism of isochemical cooling proposed above, providing Barton & Toulmin's form of curve B is substantially correct. If the sphalerite-pyrrhotite-pyrite solvus is vertical below 580°C, as proposed by Boorman and Scott & Barnes, it is impossible to account satisfactorily for the coincidence of the pyrrhotite inclusions and the areas of FeS depletion in the sphalerite, together with the obvious spatial relationship to the earlier pyrite. Even the addition of sulphur to sphalerite of this composition should have produced pyrite rather than pyrrhotite, unless point B coincided with a lower-iron composition at the temperature of re-equilibration.

These relationships are actually not common in the Zeehan ores, and the mechanism of isochemical cooling cannot explain the much more common abundance of pyrrhotite, chalcopyrite and second-generation pyrite in "alteration" zones adjacent to younger veins or replacement boundaries of galena or quartz. In these cases microprobe analyses of the zones in which the inclusions occur almost invariably show them to contain more iron than the inclusion-free areas more remote from the sphalerite boundaries. In many similar cases, vein or replacement boundaries in the sphalerite are bordered by high-iron zones which contain no inclusions, or perhaps inclusions of chalcopyrite alone. Fig. 35 shows an FeS profile measured by microprobe analysis across such a zone, adjacent to a late quartz vein. (In general,
inclusions of pyrrhotite and pyrite are most common adjacent to galena replacement boundaries).

It is therefore necessary to seek a feasible mechanism which is capable of increasing the FeS content of sphalerite under these circumstances, and of producing inclusions of pyrite and pyrrhotite. The spatial relationship to paragenetically younger mineralization strongly suggests that chemical changes may be involved.

**Isothermal changes in bulk chemical composition:**

Examination of the ternary phase diagrams of Barton & Toulmin suggests that pyrrhotite may be produced from sphalerite or equilibrium sphalerite-pyrite assemblages if the bulk composition is changed by the addition or removal of components of the ternary system. The final products will depend on the initial composition, the extent of the changes, and whether or not equilibrium is maintained throughout the whole system during the alteration. They may also be further complicated by changes in temperature; for simplicity, isothermal changes will be considered first.

An exhaustive analysis of all the possible changes in unnecessarily tedious; however, it is instructive to consider several examples which are pertinent to the Zeehan mineralogy. In most of the Zeehan lodes, sphalerite co-exists with pyrite, so that it is first necessary to consider possible changes in which equilibrium with pyrite is maintained throughout the
alteration. However, since the phenomena under discussion are confined to narrow zones adjacent to vein or replacement boundaries and frequently relatively remote from pyrite grains (i.e. beyond the limits of solid, though not necessarily solution, diffusion), the possibility of changes affecting only the sphalerite must also be considered.

The two points marked I and II on Fig. 55 respectively represent coexisting sphalerite + pyrite, typical of the Zeehan association, and sphalerite alone. Possible chemical changes (of reasonably modest magnitude) and their effects on these assemblages, are summarised in Table 7.

It is apparent from Table 7 that pyrrhotite can be produced from sphalerite-pyrite assemblages by the isothermal addition of Fe, Zn, FeS or (FeS + S)*, and from sphalerite alone by the addition of (FeS + S). The production of pyrrhotite by the addition of sulphur alone, as postulated by Barton & Toulnin, can be achieved if the composition of the original sphalerite lies between points A and B, but would be accompanied by a decrease in the FeS content of the sphalerite.

Similarly, in the case of sphalerite-pyrite assemblages, the addition of Fe or Zn ultimately produces pyrrhotite at the expense of pyrite, by reactions which may be approximated by

\[
\begin{align*}
\text{Fe} + \text{FeS}_2 & \rightleftharpoons 2\text{FeS}, \\
\text{Zn} + \text{FeS}_2 & \rightleftharpoons \text{FeS} + \text{ZnS}
\end{align*}
\]

* See footnote to Table 7.
**TABLE 7.**  
Response of sphalerite to isothermal changes in bulk composition

<table>
<thead>
<tr>
<th>Point</th>
<th>Initial assemblage</th>
<th>Chemical change</th>
<th>Final assemblage</th>
<th>Change in sphalerite FeS content</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Sp + Py</td>
<td>+Fe</td>
<td>Sp + Py + Po</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + α-Fe</td>
<td>None</td>
</tr>
<tr>
<td>II</td>
<td>Sp</td>
<td>+Fe</td>
<td>Sp + Py + Po</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + α-Fe</td>
<td>Decrease</td>
</tr>
<tr>
<td>I</td>
<td>Sp + Py</td>
<td>+Zn</td>
<td>Sp + Py + Po</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + α-Fe</td>
<td>Decrease</td>
</tr>
<tr>
<td>II</td>
<td>Sp</td>
<td>+Zn</td>
<td>Sp + Py + Po</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + Py + S</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td>I</td>
<td>Sp + Py</td>
<td>+S</td>
<td>Sp + Py + S</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td></td>
<td>Sp</td>
<td>+S</td>
<td>Sp + Py + S</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td>I</td>
<td>Sp + Py</td>
<td>+FeS</td>
<td>Sp + Py + Po</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td></td>
<td>Sp</td>
<td>+FeS</td>
<td>Sp</td>
<td>Increase towards A</td>
</tr>
<tr>
<td>II</td>
<td>Sp</td>
<td>+FeS</td>
<td>Sp + Py (+S)</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + α-Fe</td>
<td>Decrease towards ZnS</td>
</tr>
<tr>
<td>I</td>
<td>Sp + Py</td>
<td>+(FeS + S)*</td>
<td>Sp + Py + Po</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td></td>
<td>Sp</td>
<td>+(FeS + S)*</td>
<td>Sp + Po (+Py)</td>
<td>Increase to B, then constant</td>
</tr>
<tr>
<td>II</td>
<td>Sp</td>
<td>+(FeS + S)*</td>
<td>Sp + Py + S</td>
<td>Decrease to C, then constant</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sp + Py + S</td>
<td>Decrease to C, then constant</td>
</tr>
</tbody>
</table>

* (FeS + S) has no stoichiometric or molecular implications - it is used to signify the addition of FeS under sulphur fugacities which, at the temperature under consideration, are higher than those of the FeS-ZnS join but lower than those of the FeS2-ZnS or FeS2-point C joins.
Although experimental confirmation is required, it seems probable that the pyrrhotite would thus be related to the pyrite rather than the sphalerite in its distribution, and "exsolution" textures are unlikely. In either case, the production of pyrrhotite would accompany or succeed increasing iron content of the sphalerite only if the whole system (pyrite + sphalerite + Fe or Zn) remained in equilibrium.

If FeS is added to sphalerite alone, pyrrhotite cannot be produced; it can, however, be formed if FeS is added to an equilibrium sphalerite-pyrite assemblage. In the latter event, a small proportion of the pyrite will be consumed to provide the extra sulphur required by non-stoichiometry of the pyrrhotite.

Only if FeS is added under sulphur fugacities higher than those of the FeS-ZnS join can pyrrhotite be produced from sphalerite or from sphalerite + pyrite, without affecting, or even necessarily involving, the original pyrite. In fact, if the sulphur fugacity is sufficiently high, additional or "secondary" pyrite can be formed.

These deductions are believed to explain the observed mineralogical relationships between sphalerite, pyrite and "exsolved" pyrrhotite in the Zeehan ores. The abundance of pyrrhotite blebs, the fine seams and occasionally coarser "reaction rims" of secondary pyrite, and the increase in iron content adjacent to galena replacement boundaries and quartz veins suggest strongly that the sphalerite was chemically and
minerallogically modified during the crystallization of the younger galena and/or quartz. The addition of Fe and/or Zn would probably not have produced the observed textures and would have consumed pyrite rather than producing more of it. Only the addition of \((\text{FeS} + S)\) can account for all the observed relationships.

The source of the additional FeS is speculative, since so little is known of the chemistry of hydrothermal fluids. However, it is possible that at least some of the FeS released during replacement of the sphalerite may have diffused as a "front" into the unreplaced sphalerite, particularly if the hydrothermal solutions were close to saturation in iron at the time of replacement. As for the sulphur, evidence suggesting fluctuation of sulphur fugacity during hydrothermal mineralization has already been discussed, and it is in fact necessary only that the sulphur fugacity during the replacement should exceed that of the FeS-ZnS join. In the continuing presence of pyrite, this will certainly be the case, so long as a reasonably close approach to equilibrium is maintained.

These observations are relevant to the shape of Barton & Toulmin's curve B, since pyrrhotite will only begin to form under these circumstances when the sphalerite is saturated with FeS at the temperature of replacement - i.e. when it has reached the composition indicated by point B at that temperature. If the curve is vertical, as proposed by Boorman and Scott & Barnes,
then this composition will be independent of temperature, and all such sphalerites altered at temperatures below $550^\circ C$ should have the same composition (20-21 mole per cent FeS). Lower iron contents would theoretically be possible if the temperature of alteration lies between $550^\circ C$ and $742^\circ C$, but the intersection of curves B and C at the invariant point where sphalerite, pyrite, pyrrhotite and liquid sulphur coexist imposes a minimum FeS content in the sphalerite of approximately 13 mole per cent.

The Zeehan sphalerites do not substantiate these predictions. It is argued here that the formation of pyrrhotite and secondary pyrite under these circumstances is the best possible evidence for sphalerite-pyrite-pyrrhotite equilibria; nevertheless, the observed FeS contents of sphalerites in such assemblages vary from 20.5 weight per cent at the Doric Mine and 20.0 weight per cent at the Silver Stream Mine down to 1.4 per cent at the King Mine, with a substantially complete, zonally distributed range in between (Table 6). This suggests that not only must curve B have the general form proposed by Barton & Toulmin, but further that at low temperatures the composition of sphalerite in equilibrium with pyrite and pyrrhotite must closely approach ZnS.

It appears therefore that this curve has geothermometric significance in the case of equilibrium pyrite-pyrrhotite-sphalerite assemblages, and the mineralogical relationships suggest
that additional information on the position of the curve
might be obtained from attempts to duplicate experimentally
the postulated natural processes. If FeS is added to sphalerites
under controlled conditions of sulphur fugacity, as described by
Barton & Toulmin (1966), it is not necessary to attain
complete equilibrium in the charge. If pyrrhotite and pyrite can
be produced in marginal zones around the charge sphalerite grains
(see, for example, Barton & Toulmin, Fig. 6), then microprobe
analyses of the co-existing sphalerites could be used to
locate the solvus. Since only short range diffusion is required,
it seems possible that useful data could be obtained at
temperatures significantly lower than those required to attain
equilibrium in the complete system.

The iron content of such alteration zones in natural
sphalerites could then be used to estimate the temperature
of the replacement, which may differ appreciably from that of
the original sphalerite crystallization. In this connection,
it was noted in the Zeehan ores that the following relations
obtained:

(a) Iron contents of the pyrrhotite + pyrite bearing
alteration zones were generally remarkably uniform within a
particular vein, often despite wide variations in the
compositions of the unaltered sphalerites. For example,
analyses of the altered sphalerites in six sections of
Silver Stream ore showed iron contents ranging from 12.8
to 20.0 weight per cent FeS. The low value was measured on a zone which contained only a few scattered blebs of chalcopyrite; the remaining five analyses were of zones containing pyrrhotite and pyrite, and showed a much more limited range, from 18.6 to 20.0 weight per cent.

Unaltered sphalerites in the Silver Stream ore vary from 10.3 to 18.6 per cent FeS.

(b) For the Zeehan field as a whole, compositions of the altered sphalerites show a zonal distribution which is even more clearly defined than that of the original unaltered sphalerites (Table 6, Fig. 56a). Temperatures calculated from the Barton & Toulmin solvus are plotted in Fig. 56b; where pyrrhotite was not observed in the zones analyzed, the corresponding temperatures are expressed only as minimum values.

(c) Although the paragenetic sequence at any point in a hydrothermal deposit is generally thought to be a sequence of decreasing temperature of crystallization, comparison of Figs. 53 and 56 suggests that this is not necessarily the case. In almost all deposits for which adequate data are available, the galena replacement temperatures are comparable with those of original sphalerite crystallization. This suggests that temperature does not necessarily play a dominant role in the establishment of zonal and paragenetic successions.
FeS CONTENTS OF ALTERED SPHALERITES

( ) = Pyrrhotite absent

Fig. 56a.
Fig. 56b.
(d) As a corollary of (c) and of the general preceding discussion, it should be stressed that if replacement and alteration take place at temperatures significantly lower than those of original sphalerite crystallization, then it is possible for the sphalerite in the alteration zone to be depleted in iron as a consequence of the slope of the solvus, particularly if the temperature difference is pronounced or if the original sphalerite is rich in iron. This effect has been observed in several instances (e.g. in Barnett's Lode). It should be noted that it is difficult to explain in terms of a vertical solvus; addition of sulphur to a sphalerite-pyrite assemblage, such as that of Barnett's Lode, would deplete the sphalerite in iron, but would produce secondary pyrite instead of the observed pyrrhotite.

When all the possible variables are taken into account, the situation becomes rather complicated, and it is not possible to make a succinct generalization relating variations in temperature, sulphur fugacity, chemical composition and mineralogy. The present study, however, has demonstrated that individual problems can be resolved by reference to the experimentally determined phase relationships, providing adequate textural and chemical data are available.

Although reference has been made to the frequent occurrence
of chalcopyrite in the alteration zones, interpretation of its origin has been hampered by the limited experimental data for the system Cu-Fe-Zn-S currently available. Qualitative speculation suggests that it might well be produced by chemical changes similar to those which have been proposed for the origin of the pyrrhotite and pyrite, instead of by isochemical unmixing of sphalerite solid solutions. Further experimental studies of the feasibility of this mechanism are required.
Trace Element Studies

For several decades, studies of the distribution of trace elements within rock-forming minerals have represented one of the major fields of geochemical research, and the resulting literature is of massive proportions. Fleischer (1955) has reviewed the trace element data pertaining to the more important sulphide minerals, and has presented a comprehensive bibliography. Since 1955, much additional analytical data has been obtained from a wide variety of geochemical studies, such as are represented by the contributions of Fryklund & Fletcher (1956), El Shazley, Webb & Williams (1957), Burnham (1959), Hawley & Nichol (1961), and Rose (1967). The general trends of research in this field have largely continued to follow those summarized by Fleischer.

Early studies of the trace element contents of sulphide minerals were essentially of a practical nature, aimed at the detection of new elements or new sources of rare elements. With the development of rapid spectrographic analytical techniques, considerable interest has developed in the possibility of using trace element abundances as indicators of various features of the ore-forming environment. Thus the literature abounds with qualitative proposals relating the abundances of various trace elements and the crystallization temperatures of their host minerals, and also with as many reports of conflicting or uncertain relationships. Thus Fleischer (1955, p. 992) was
unable to detect any "clear indication of systematic differences (in the cadmium contents) in sphalerites from low-temperature and high-temperature deposits", despite previous suggestions to the contrary. Fleischer did note, however, that "in banded zinc sulfides, the tendency is towards higher cadmium content in the light-coloured bands, and less cadmium in the dark, iron-rich bands", as observed by Kutina (1953). Hawley (1952) found that Co and Ni contents and Co:Ni ratios in pyrite apparently increased with increasing temperature of crystallization; on the other hand, Gavelin & Gabrielson (1947) found no comparable systematic variations in Ni contents and, although they observed higher Co contents and Co:Ni ratios in high temperature deposits, they also noted several marked exceptions. Björlykke & Jarp (1950) considered the Co contents of Norwegian pyrites to be temperature dependent. Auger (1941) thought the Co and Ni contents of pyrrhotite in the Noranda orebody to vary systematically with depth, but Fryklund & Harner (1955) found no similar variation in other ore deposits.

Gavelin & Gabrielson (1947), Kullerud (1953), Fryklund & Harner (1955), Fryklund & Fletcher (1956) and others have all stressed that concentrations of trace elements will only be quantitatively temperature-dependent under saturation conditions which, with several exceptions, are probably not met in hydrothermal ores. Nevertheless, characteristic trace element associations have been observed in certain types of ore, and some writers have
vigorously defended empirical inferences relating the two. Thus high Ge and low In in sphalerite, and low Ag, Sb, and Bi in galena are often thought to be indicative of low temperatures of formation (El Shazly, Webb & Williams, 1957; Haberlandt, 1948; Haberlandt & Schroll, 1954; Baumann, 1965). Fleischer (1955) expresses the belief "that the available data support many of the generalization that have been made linking the concentrations of minor elements with temperature of formation or other factors... We have no explanation of why this is so;... It seems justifiable... to infer that a sphalerite of high gallium and germanium content was probably formed at a low temperature, provided that it is understood that exceptions are to be expected, as, for example, if a regional trend has a greater effect than the generally observed trend due to temperature of formation".

Partition of a trace element between two or more co-existing phases is theoretically temperature dependent, and, providing saturation is not attained in any of the hosts, offers considerable geothermometric promise (Bethke & Barton, 1959). McIntire (1963) has discussed partitioning of Cd and Se between sphalerite and galena, and of Se between chalcopyrite and galena, in a review in which he concludes that trace element partition coefficients may be useful in geothermometry (and geobarometry) providing the mineral pairs were in equilibrium during crystallization. The erratic nature of results obtained by Fryklund & Harner (1955),
Fryklund & Fletcher (1956), Wilson & Anderson (1959) and others may therefore be due to disequilibrium. Alternatively, it is necessary to point out that in many cases the analytical techniques employed for trace element determinations are not satisfactory in the concentration ranges involved. The results reported for an interlaboratory comparison of trace element analyses on a standard sulphide sample (Webber, 1965) are illustrative of the problems encountered. When the partitioning of cadmium between galena and sphalerite is studied, the cadmium content of the galena is often well within the range of unavoidable contamination from the co-existing sphalerite (see below). In general, precisions much better than those normally obtainable from optical emission spectrography (the standard technique for most studies described to date) are required for useful data to be obtained.

Many metallogenic provinces are characterised by more or less specific types of magmatism, sedimentation and tectonic activity (Turneaure, 1955; Bilbin, 1955; Abdullaev, 1964; McCartney & Potter, 1962; Radkeyvich, 1961; Tvalchrelidze, 1964), and several geochemical investigations have suggested that these are paralleled by systematic variations in the trace element contents of sulphides produced during orogenic mineralization (Burnham, 1959; Itsikson, 1960; Ivanov & Lisunov, 1960; Harris, 1965; and others). Furthermore, Burnham (1959) and Harris (1965) were able to define sub-provinces within larger metallogenic units by studying trace
element distributions in minerals such as chalcopyrite, sphalerite and galena. Harris (1965) showed, in his study of base-metal mineralization in south-eastern New South Wales, that different tectonic environments and metallogenic epochs were reflected, within a single metallogenic province, by characteristic differences in trace element geochemistry.

The trace element contents of sulphide minerals presumably reflect both the compositions of the fluids from which the minerals crystallized and the physico-chemical conditions of precipitation. Since both composition and environment can be expected to vary considerably for different ore-forming processes, several aspects of trace element geochemistry have been proposed as indicators of ore genesis. Thus Goldschmidt and co-workers (Goldschmidt & Hefter, 1933; Goldschmidt & Strock, 1935) and Carstens (1941) have suggested that S:Se ratios might be used to distinguish between hypogene and sedimentary sulphide deposits, and a similar significance has been attached to Co:Ni ratios in magmatic, hydrothermal and sedimentary pyrites (Carstens, 1943; Hegemann, 1943; Keith & Degens, 1959; Hawley & Nichol, 1961; Davidson, 1962; Roscoe, 1965). In both these cases, conclusive cases for or against the discriminants have not yet been made out, partly because of inadequate sampling, and partly because of the analytical difficulties mentioned above. In particular, relatively few studies have been devoted to determining the extent of trace element variations within a single ore deposit or genetically related groups of deposits.
Since the zoning at Zeehan is thought to have been produced by progressive changes in the physico-chemical environment of ore deposition, a pilot study of trace element distribution in the major ore and gangue minerals was undertaken to determine the extent of variation and relate it to the overall zonal pattern. Although this study was considerably hampered by the relatively poor sample coverage and some analytical difficulties, several clear trends emerged and there is little doubt that similar investigations of other deposits will provide much valuable information.

The minerals chosen for study were pyrite, sphalerite, siderite and galena. Samples from 20 selected localities in the Zeehan field were crushed and sized, and concentrates of each (where possible) of these minerals were prepared for analysis. (Obviously it was difficult to obtain adequate samples of pyrite from ores from the siderite zone, and vice versa.) Each of the concentrates was analysed by atomic absorption spectrophotometry for Sn, Co, Ni, Mn, Sb, Bi, Ag and Cd. The reasons for using atomic absorption as the analytical method, and details of the analytical procedures, are summarised in Appendix II. The choice of elements determined was governed partly by the small amounts of sample available, and partly by the limitations of the analytical method (see Appendix II); this explains the absence of such potentially informative elements as Ga, Ge, In, Tl, Hg, Cr, Se, Te etc.
All mineral concentrates were examined microscopically prior to analysis, and some degree of contamination was almost invariably found. In many cases aberrant results due to contamination could be corrected by a procedure described in Appendix II; in other cases it was necessary either to discard the concentrates or to weigh carefully the possible effects of the contamination when assessing the results.

The presentation and discussion of the trace element data obtained during this study require several comments. The data are presented in most instances in two forms. For each mineral the analytical data are tabulated to show the variation from one deposit to another (Tables 8 - 11). However, systematic zonal variations in trace element abundances are most clearly displayed in scatter diagrams (Figs. 57 - 78); in these diagrams, all analyses of samples from the pyritic zone are plotted as solid circles, those from the intermediate zone as solid triangles, and those from the sideritic zone as open circles. The same diagrams conveniently illustrate both zonal variations in individual elements and the extent of correlation between various pairs of elements.

In selecting a system of co-ordinates for plotting the scatter diagrams, a choice of linear or logarithmic (or other) systems is available. Data from the present study contribute little to the relative merits of various distribution "laws" which have been proposed to describe trace element abundances (Ahrens, 1954; Chayes, 1954; Shaw, 1961; Butler, 1964; Ahrens, 1966; and other
discussions), except that it will be shown that in almost every instance the dispersion of the analytical data for a particular element (expressed as one standard deviation as a percentage of the mean) is considerably reduced if the distribution is assumed to be lognormal. This is not necessarily support for the universal assumption of lognormal distributions; as Chayes (1954) has pointed out, almost any transformation of positively skewed data which reduces large values more than small ones will achieve an apparent reduction in the dispersion.

Shaw (1961) has shown that if the coefficient of variation (standard deviation divided by the mean) of a small body of geochemical data is less than 20 per cent, either normal or lognormal laws may be used with similar results for subsequent statistical tests. When the coefficient of variation exceeds 20 per cent, the lognormal law is "more realistic". Although the latter situation almost invariably applies to the data reported in this study, Shaw has also noted that the coefficient of variation which is employed for this test should take into account manipulative as well as analytical errors (e.g. sampling, crushing, quartering etc.) or it will be biased towards a lognormal distribution.

In the present work, the sampling error is impossible to estimate, and the small amounts of sample prevented the repetitive manipulation required to establish the manipulative variance. Insufficient data are available to employ the method of Laffitte (1957) to estimate these parameters, and the extent of possible bias towards
the lognormal model is thus unknown.

Both linear and logarithmic co-ordinates are commonly used for the presentation of trace element data in scatter diagrams, but the logarithmic method appears to be favoured (e.g. Turekian, 1963), since it has the advantage of conveniently displaying relatively wide ranges of concentrations. Most of the diagrams illustrating this discussion have therefore been drawn on this basis. It is necessary to point out, however, one limitation of logarithmic plots, namely that it is impossible to plot zero concentrations accurately. In Figs. 57 - 78, points plotted on either the ordinate or the abscissa therefore usually represent failure to detect the element concerned, but cannot be distinguished from occasional points representing the numerical value of the origin. This seldom causes confusion, but does explain occasional discrepancies between visually apparent correlations and the calculated correlation coefficients. In cases of doubt, reference can be made to the appropriate table of analytical data, where the symbol "n.d." is used to denote "not detected" (a dash is used to indicate that an element was not sought).

The possibility of related systematic variations in two or more trace elements was investigated for each mineral by calculating correlation coefficients for all corresponding pairs of analytical data. In each case, two sets of coefficients were calculated, one based on normal and the other on logarithmic co-ordinates. While the latter may possibly reflect to some extent tendencies to
lognormal distributions, they also have the practical advantage of being less subject to spuriously high correlation coefficients resulting from one or two points plotting remote from the others on the scatter diagram. For example, Fig. 61 shows the Ni-Mn data of Fig. 58 plotted with normal co-ordinates; it is apparent that the high "normal" correlation coefficient of 0.962 results from the inclusion of one sample which is high in both elements. If logarithmic co-ordinates are used, the relative contribution to the regression of this single point is considerably reduced, and a much smaller and more realistic correlation coefficient (0.578) results. In general, it appears that genuine correlations are either improved or relatively unaffected by logarithmic transformation, while spurious correlations are in almost all instances reduced.

For each element in each mineral, it is desirable to know the significance or otherwise of any apparent difference between the mean concentrations in samples from each of the pyritic, intermediate and sideritic zones. For example, it is apparent from Fig. 57 that the range of cobalt contents in intermediate zone pyrite samples overlaps the range of those in the pyritic zone, and also that more samples were analysed from the intermediate zone (this latter difference becomes even more significant in the other mineral groups). It is necessary to question whether the analysis of more samples of each type would reduce the apparent differences between the two distributions.
In other words, although the mean cobalt contents of the two groups are different, the difference is not statistically significant if the variance of either or both groups is sufficiently large.

The grouped analytical data were therefore subjected to variance analysis to determine the significance of the apparent differences. In such analysis, allowance must be made for the different number of samples in each group, and for the possibility that the variances within the different groups may themselves be different. Analysis allowing for these factors is a little more complex than the comparison of equal samples from populations of homogeneous variance.

The procedure adopted in the present instance was to assume heterogeneous variance, and to calculate for each group of data a pair of weighted mean squares, whose ratios were then tested against the $F$-distribution (Snedecor, 1956). $F$ is the variance ratio, defined as the mean square of sample means, divided by the mean square of the individuals. $F'$ is distributed approximately as $F$ with $f_1$ and $f_2$ degrees of freedom; these parameters were calculated according to procedures set out by Snedecor (1956), and from tables a probability $P$ can be calculated for the null hypothesis

$$H_0: m_1 = m_2 = m_3 \ldots \ldots$$

where $m_1$, $m_2$, $m_3$ \ldots are the means of the data groups. A low value of $P$ indicates that the variance between the means is
significantly greater than the variances within the individual groups - i.e. that apparent differences between the means are statistically significant at a confidence level indicated by the calculated probability.

In examining the correlation coefficients calculated for the various element pairs, it is also necessary to know to what extent the observed correlation may have arisen by chance. The significance of a correlation coefficient will obviously depend on whether it has been calculated from a small or large number of analysis pairs.

The simplest test procedure is to use tables of the distribution of Student's "t", where

\[ t = \frac{r(N - 2)^{\frac{1}{2}}}{(1 - r^2)^{\frac{1}{2}}} \]

\( N = \) number of analysis pairs, and \( r = \) calculated correlation coefficient.

The tables, which are found in most standard statistical texts, are entered with \((N - 2)\) degrees of freedom, and limiting values of "t" appropriate to various confidence levels can be determined.

In the correlation data presented in this study, limiting values of the correlation coefficients have been calculated for each mineral for the 0.1, 1.0 and 5.0 per cent significance levels, and these are appended to the coefficient tables (Tables 8b - 11b). For example, the limiting values for the pyrite analyses
were found to be 0.87, 0.75 and 0.63 respectively (Table 8b). For these analytical data, there is thus less than one chance in one thousand of a correlation coefficient higher than 0.87 arising fortuitously, less than one in a hundred for coefficients higher than 0.75, and less than one in twenty for coefficients higher than 0.63. The three classes may be distinguished in general terms as "highly significant", "significant" and "probably significant" respectively.
Trace element analyses of ten pyrite samples from the Zeehan field are summarised in Table 8. Four of these samples are of ore from the Pyritic Zone, five from the Intermediate Zone, and one from the Sideritic Zone.

Tin: Hawley (1952) observed an irregular variation of the tin content of pyrite with depth in some Canadian deposits. His determinations were made by emission spectrography, and his results were quoted as intensity ratios instead of absolute concentrations. Fleischer (1955) tabulated the results of 18 analyses reported in the literature, in which tin was not detected in 11 samples (sensitivities approximately 10 ppm) and ranged from 10 to 400 ppm in the remainder.

No tin was detected in any of the Zeehan pyrite samples. Tin, however, is a relatively insensitive element for atomic absorption determination, and detection limits ranged from 25 to 50 ppm, depending on the amount of sample available and hence on the dilutions employed. For example, only 90 mgm of pyrite could be concentrated from the sideritic Mt. Zeehan ore, which necessitated over twice the normal dilution to obtain sufficient solution for the analysis of eight elements; this is reflected in the high limit of detection. Nevertheless, it appears that tin is an insignificant trace constituent of Zeehan pyrite, in agreement with
Table 8
Trace Elements in Pyrite

<table>
<thead>
<tr>
<th>Pyritic:</th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comstock</td>
<td>n.d.</td>
<td>34</td>
<td>17</td>
<td>n.d.</td>
<td>120</td>
<td>n.d.</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td>Boss</td>
<td>n.d.</td>
<td>54</td>
<td>10</td>
<td>38</td>
<td>370</td>
<td>n.d.</td>
<td>10</td>
<td>n.d.</td>
</tr>
<tr>
<td>Sylvester</td>
<td>n.d.</td>
<td>55</td>
<td>30</td>
<td>77</td>
<td>1800</td>
<td>n.d.</td>
<td>37</td>
<td>110</td>
</tr>
<tr>
<td>Despatch</td>
<td>n.d.</td>
<td>46</td>
<td>23</td>
<td>44</td>
<td>560</td>
<td>n.d.</td>
<td>35</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Intermediate:</th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tasmanian</td>
<td>n.d.</td>
<td>20</td>
<td>23</td>
<td>155</td>
<td>520</td>
<td>n.d.</td>
<td>86</td>
<td>6</td>
</tr>
<tr>
<td>Fahey's</td>
<td>n.d.</td>
<td>18</td>
<td>73</td>
<td>150</td>
<td>320</td>
<td>n.d.</td>
<td>64</td>
<td>20</td>
</tr>
<tr>
<td>Oonah</td>
<td>n.d.</td>
<td>13</td>
<td>240</td>
<td>130</td>
<td>870</td>
<td>n.d.</td>
<td>1070</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Siderite:</th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Zeehan</td>
<td>n.d.</td>
<td>24</td>
<td>15</td>
<td>120</td>
<td>280</td>
<td>n.d.</td>
<td>60</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Approximate detection limit</th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-50</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>30</td>
<td>30-50</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 57.

PYRITE
Co - Mn

Fig. 58.

PYRITE
Ni - Mn
PYRITE
Co - Ni

Fig. 59.

PYRITE
Sb - Mn

Fig. 60.
Fig. 61.
the data summarised by Fleischer.

Cobalt: The cobalt content of pyrite has been the subject of considerable investigation, as has been noted in the discussion above and is apparent from the tabulated data of Fleischer (1955). Fleischer summarised a total of 1,097 analyses, ranging from less than detection limits of 10 - 30 ppm up to more than 2.5 per cent. Although cattierite is isostructural with pyrite, Fleischer observed that intermediate members of a possibly complete solid solution series appear to be rare (except for one isolated early analysis with 13.90 per cent cobalt; Johannson, 1924). Hegemann (1943) noted that nearly all pyrite samples containing more than 1 per cent cobalt are zoned, and that many clearly contain admixed cobaltite.

Fleischer concluded that although generalisations must be made with caution, pyrite from sulphide ore deposits generally contains "appreciable amounts of cobalt" and has Co > Ni, whereas pyrite of sedimentary origin has less than 100 ppm cobalt and Co < Ni (Carstens, 1941, 1943; Hegemann, 1943).

Hawley (1952) analysed four pairs of pyrite samples for which temperatures of formation had been estimated, and found that the cobalt content was higher in the higher-temperature sample in all four pairs, and that the Co:Ni ratio was higher in the high-temperature sample in three of the four. However, as noted earlier, others have not always found the same relationships (Fryklund &

The cobalt contents of Zeehan pyrites, listed in Table 8, range from 6 to 60 ppm (cf. Fleischer's observations), with a mean of 33 ppm and a standard deviation of 20 ppm. Analytical errors, expressed as coefficients of variation, ranged from 4 per cent in the high cobalt samples to more than 25 per cent near the limit of detection (cf. Appendix Fig. A14). The standard deviation of the range of cobalt contents is 60 per cent of the mean if a normal distribution is assumed, or 23 per cent of the mean after logarithmic transformation.

Fig. 57, in which the concentrations of cobalt and manganese in pyrite are plotted, shows that the pyritic zone pyrite samples have higher cobalt contents (with one exception) than those of the intermediate and sideritic zones. The mean contents of the pyritic and intermediate samples are 47 and 24 ppm respectively, and the probability that the null hypothesis of equivalence of the means is correct is only 2.5 per cent. (Alternatively, there is 97.5 per cent probability that the cobalt contents of pyritic and intermediate pyrites are different). Since only one analysis of a sideritic sample was available, the variance within this group cannot be calculated, and it is not known whether the trend of declining cobalt contents continues into the sideritic zone. However, the rarity of primary pyrite in the latter zone makes this question of little consequence.

If it is conceded that ores of the intermediate zone were
deposited at lower temperatures than those of the pyritic zone, as would be predicted from the probable form of the thermal aureole around the Heemskirk granite, then the limited data of the present study supports the conclusions of Hawley (1952), Gavelin & Gabrielson (1947), Bjørlýkke & Jarp (1950) and Auger (1941), to the effect that the cobalt content of pyrite in a particular deposit decreases with decreasing temperature. As will be discussed below, however, it should be stressed that the variation in cobalt contents is not necessarily directly controlled by temperature.

Nickel: Fleischer's (1955) compilation of 1,055 determinations of nickel in pyrite show a range from approximately 2.5 per cent down to less than detection limits of 2 - 20 ppm; approximately 15 per cent of the analyses failed to detect any nickel. Again Hegeman (1943) observed zoning or admixtures of other nickel minerals in almost all samples containing more than 1 per cent Ni.

Fleischer's data show that nickel contents are generally lower than those of cobalt, but that "generalizations as to the nickel content of pyrite from various types of deposits are even less certain than those for cobalt. Pyrite of high-temperature and hydrothermal sulfide deposits has only a slightly higher average nickel content than pyrite of sedimentary origin and the ranges of concentration overlap". Hawley (1952) found that the nickel content was a little higher in pyrite samples thought to be of high-temperature origin, but Gavelin & Gabrielson
(1947) found no such relationship.

The nickel contents of Zeehan pyrites, summarised in Table 8, range from 10 to 980 ppm, with a mean of 144 ppm and a large standard deviation of 302 ppm which reflects the presence of two unusually high values (240 and 980 ppm). Analytical errors (coefficients of variation) ranged from 6% in the high-nickel samples to 30% near the limit of detection; the slightly poorer precision relative to cobalt results from interference by iron. The standard deviation of the nickel contents is 210 per cent of the normal mean and 38 per cent of the lognormal mean.

Fig. 58 suggests that the nickel contents of pyrite samples from the pyritic zone are lower than those of the intermediate zone, but considerable overlap and pronounced variation in the intermediate samples are apparent. Variance analysis shows a probability of approximately 25 per cent for equivalence of the means. Careful examination of the samples yielding anomalously high nickel contents, which strongly affected the variance of the intermediate samples, showed no evidence of contamination by nickel minerals. One of these samples (Payne's) was run in duplicate, but insufficient sample was available to check the Oonah result. The high values thus cannot be disregarded, particularly since they accord with a pronounced negative Co-Ni correlation (see below). The nickel data alone give no firm indication of a temperature relationship, but the cobalt correlation (Fig. 59) suggests that, if the cobalt content decreases
with decreasing temperature of formation, the nickel content shows an opposite, but less clearly defined, tendency.

The data of Berg & Friedensburg (1944) indicate that in hydrothermal sulphides the Co:Ni ratio is higher than 0.1 and often higher than 1.0; in hydrothermal pyrite it may be as high as 830 (Loftus Hills, 1967). With the exception of the high-nickel pyrites from Payne's and the Oonah Mine (0.006 and 0.05 respectively), the Zeehan pyrites have Co:Ni ratios ranging from 0.2 to 5.4, at the low end of the range proposed by Berg & Friedensburg.

Manganese: Among the 927 analyses of manganese in pyrite reported by Fleischer (1955), 427 were below detection limits of 5 to 100 ppm, and the remainder ranged from less than 10 ppm up to 1 per cent. The relative intensity data of Auger (1941) and Hawley (1952) failed to establish any clear relationship between manganese content of pyrite and its depth or temperature of formation, although Auger reported a decrease in manganese content with depth at one mine. Gavelin & Gabrielson (1947) found no appreciable differences in the manganese contents of pyrite samples from low- and high-temperature deposits, although they observed a weak tendency for pyrite from zinc ores to contain more manganese than pyrite from copper ores.

The manganese contents of Zeehan pyrites were found to range from less than a limit of detection of approximately 5 ppm up to a maximum of 650 ppm; coefficients of variation were mostly
less than 10 per cent. The mean manganese content is 143 ppm, and the standard deviation 185 ppm, corresponding to 130 per cent of the normal mean or 40 per cent of the lognormal mean.

Fig. 58 suggests a distinctly lower manganese content for sphalerite from the pyritic zone relative to that of the intermediate zone. The mean manganese content of pyritic zone samples is 40 ppm, and that of intermediate zone samples is approximately 300 ppm; variance analysis indicates 93 per cent probability that the difference is significant. Hence it appears that increasing manganese content in the Zeehan pyrites may parallel decreasing temperature of crystallization, although again the two may not necessarily be directly related.

Antimony: Fleischer (1955) tabulated 35 analyses of antimony in pyrite, of which 27 showed concentrations below detection limits of about 50 ppm, and the remaining 8 were more or less uniformly dispersed over the range from less than 10 ppm up to 700 ppm. Fleischer concluded that "the data...are too few to permit any conclusions to be drawn; the antimony reported may well be due to impurities".

Analyses of ten Zeehan pyrite samples (Table 8) revealed antimony present above a detection limit of 30 ppm in all except one, and ranging up to 1800 ppm. Coefficients of variation for the analytical error varied from approximately 5 per cent in the high-antimony samples to 40 per cent at low concentrations. The mean antimony content is 520 ppm, and the standard deviation
of 510 ppm is 98 per cent of the mean (normal distribution) or 37 per cent of the mean (lognormal distribution).

Fig. 60 shows a very large overlap of the antimony concentration ranges for pyritic and intermediate zone samples. The means for the two zones are 712 and 414 ppm respectively, but the variance in both groups is large, and the calculated probability of equivalence of the means is much greater than 25 per cent (the maximum value for which tabulated values were available). It is therefore concluded that the antimony content of pyrite shows no significant zonal trends.

The possible extent of contamination could be assessed only by microscopic examination of the concentrates analyzed; such contamination would not be corrected by the normal cross-correction procedure, since no separate concentrates of high-antimony minerals such as tetrahedrite or boulangerite were prepared. Traces of tetrahedrite were observed in the Sylvester, Oonah and Tasmanian pyrite concentrates, and a few boulangerite inclusions in galena grains were noted in the Mt. Zeehan sample. It is doubtful whether these are sufficient to explain the observed antimony contents. The moderate correlation between antimony and silver (see below) suggests that the presence of tetrahedrite alone cannot explain all of the measured antimony, although it is undoubtedly significant that tetrahedrite was observed in three of the four highest-antimony samples. The general lack of antimonial mineral contaminants in the remaining samples
(antimony in galena would be compensated by the cross-correction) suggests that antimony may in fact be present in pyrite in concentrations up to at least several hundred ppm.

**Bismuth:** Fleischer (1955) reports 17 determinations of bismuth in pyrite; measurable concentrations were found in 6 of these samples, ranging up to 100 ppm. In addition, Hawley (1952) recorded intensity ratios for 28 samples, 19 of which were from the Powell-Rouyen Mine, Quebec. The latter group showed a slight apparent increase in bismuth content with depth.

The sensitivity of atomic absorption techniques for the detection of bismuth is relatively poor, and detection limits in the present work ranged from 30 to 50 ppm. At these levels, no bismuth was detected in any of the Zeehan samples. Traces of bismuth were observed in some of the pyrite samples examined by emission spectrography but, in the absence of suitable calibration standards, they could not be assigned quantitative values.

**Silver:** Of 73 pyrite analyses summarised by Fleischer (1955), silver was detected in 34, in concentrations ranging up to 200 ppm. Auger (1941) and Hawley (1952) found both increases and decreases with depth in the silver contents of pyrite samples from several Canadian mines; Hawley also observed that in one instance the silver content of pyrite appeared to decrease with increasing distance from a porphyry contact.

Silver was detected in 8 of the 10 Zeehan pyrite samples, in
concentrations of up to 1070 ppm. The sensitivity of silver
determination by atomic absorption is high and is reflected
in relatively high precision; at concentrations only twice the
limit of detection (c. 5 ppm), measured coefficients of variation
(Appendix Figure 14) were less than 20 per cent in both
sphalerite and pyrite samples. The dispersion of the concentrat-
ions is high; the mean is 141 ppm and the standard deviation
328 ppm - 233 per cent of the normal distribution mean or
64 per cent of the lognormal mean.

The analyses (Table 8) are erratically distributed and
show no clear zonal tendencies. It should be noted that the
single high value of 1070 ppm was measured on a sample from the
Oonah Mine which, as observed above, contained visible
tetrahedrite contamination, and contamination of this type was
probably responsible for some of the silver detected in other
samples. However, even in the Oonah sample, the corresponding
antimony contents are not sufficiently high to permit the silver
to be wholly assigned to tetrahedrite contamination. It is
concluded that some silver, possibly as much as several hundred
ppm, may be included in the pyrite structure (possibly as
sub-microscopic inclusions), but the limited data of the present
study are clearly inadequate to suggest quantitative limits to
the extent of the solubility.

Cadmium: The only quantit{}ative data on the possible presence of
cadmium in pyrite appear to be those of Noddack and Noddack
(1931), who reported 10 ppm in one of three samples. In most other instances, any observed cadmium has been assigned to sphalerite contamination.

In the present study, cadmium was observed in only four of ten samples, at concentrations up to 110 ppm. These are clearly well within the limits of error of the cross-correction technique, particularly in view of the relatively high cadmium content of sphalerite (see below), which is almost invariably present as composite contamination particles. Significantly, cadmium was detected in all ten samples analysed; the small residues left after cross-correction are probably an indication of the success of this technique.

The small concentrations of cadmium are therefore assigned to incompletely compensated sphalerite contamination.

The data of Table 8b show correlation coefficients larger than ± 0.5 for Co-Ni, Co-Mn, Ni-Mn and Sb-Cd when normal co-ordinates are employed. If lognormal distributions are assumed, correlation coefficients larger than ± 0.5 (an arbitrary "figure of merit") are observed for Co-Ni, Co-Mn, Co-Sb, Ni-Mn, Ni-Sb and Sb-Ag, and for Cd and the average iron content of sphalerite at each locality. Of the latter, only Co-Ni (r = -.842) is sufficiently strong to be regarded with confidence. An apparently strong normal correlation between Sb and Cd (r = +.822) is considerably reduced (to r = +.296) when the data are transformed to a lognormal distribution, and the Ni-Mn correlation coefficient
is likewise reduced from +.962 to +.578; most of the remaining coefficients are either increased or not significantly affected by the transformation.

It is concluded that cobalt and nickel show a pronounced negative correlation in the Zeehan pyrites, but that the data available do not indicate consistent relationships between any other element pairs at significance levels better than 1 per cent.

On the assumptions that mean FeS contents of sphalerites from the various localities are broadly indicative of temperature of deposition (see earlier discussion) and that sphalerite temperatures show a consistent relationship to the crystallisation temperatures of the paragenetically earlier pyrite, the correlation of each element with the mean FeS content of sphalerite from the same locality was also tested, and the calculated correlation coefficients are listed in the first column of Table 8. The highest correlation coefficients were found for Co, Ni and Mn, which are the three elements for which possible zonal variations have already been noted. However, the coefficients are all low (less than 0.5), which suggests either that the assumptions are invalid, or that the systematic zonal variations are at least partly controlled by factors other than temperature of crystallization. In this respect, the possible importance of progressive changes in the pH of the hydrothermal fluids will be further discussed below.
Table 8b.

Correlation coefficients for trace elements in pyrite

I. Normal co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>FeS in sphalt.</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphalt.</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Co</td>
<td>.018</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-.427</td>
<td>-.582</td>
<td>1.000</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Mn</td>
<td>-.367</td>
<td>-.632</td>
<td>.962</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-.051</td>
<td>.369</td>
<td>-.300</td>
<td>-.313</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-.334</td>
<td>-.390</td>
<td>.073</td>
<td>-.049</td>
<td>.250</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>.221</td>
<td>.344</td>
<td>-.184</td>
<td>-.173</td>
<td>.822</td>
<td>-.150</td>
<td>1.000</td>
</tr>
</tbody>
</table>

II. Logarithmic co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>FeS in sphalt.</th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphalt.</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>.303</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-.482</td>
<td>-.842</td>
<td>1.000</td>
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<tr>
<td>Mn</td>
<td>-.475</td>
<td>-.532</td>
<td>.578</td>
<td>1.000</td>
<td></td>
<td></td>
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<tr>
<td>Sb</td>
<td>.301</td>
<td>.672</td>
<td>-.639</td>
<td>-.257</td>
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<tr>
<td>Ag</td>
<td>.261</td>
<td>-.096</td>
<td>-.101</td>
<td>-.143</td>
<td>.589</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>.643</td>
<td>.203</td>
<td>-.167</td>
<td>-.306</td>
<td>.296</td>
<td>.232</td>
<td>1.000</td>
</tr>
</tbody>
</table>

Significance levels: 0.1% - 0.87

1.0% - 0.75

5.0% - 0.63
Sphalerite

Trace element analyses for a total of 25 sphalerite samples from 14 localities in the Zeehan field are summarised in Table 9. The multiplicity of analyses for several localities arises from the variable iron content of most of the Zeehan sphalerites, leading to several fractions in the magnetic concentrates. In some cases the fractions were analysed separately to yield information concerning possible correlations between the contents of iron and the various trace elements at a single locality. Four of the 25 samples analysed were from two localities in the pyritic zone, 18 from 10 localities in the intermediate zone, and the remaining three from two localities in the sideritic zone.

Tin: Tin has been reported in about half of the sphalerite analyses tabulated by Fleischer (1955), in concentrations of up to 1 per cent. Although most of the high-tin samples appear to have been contaminated, Fleischer concluded that "there is little doubt that some tin is present in sphalerite". He believed, however, that the maximum tin content of pure sphalerite is probably about 1000 ppm; samples containing higher concentrations are usually found to contain stannite, cassiterite or both.

There is some evidence to suggest that tin contents are more likely to be relatively high in deposits formed at high to intermediate temperatures. Thus Kullerud (1953) found appreciable
Table 9
Trace Elements in Sphalerite

<table>
<thead>
<tr>
<th></th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>*Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
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<td></td>
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<tr>
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<td>n.d.</td>
<td>n.d.</td>
<td>50</td>
<td>17000</td>
<td>n.d.</td>
<td>270</td>
<td>83</td>
<td>2890</td>
</tr>
<tr>
<td>Med. iron</td>
<td>n.d.</td>
<td>n.d.</td>
<td>32</td>
<td>9500</td>
<td>n.d.</td>
<td>300</td>
<td>n.d.</td>
<td>3070</td>
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<td>Boss</td>
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<tr>
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<td>n.d.</td>
<td>n.d.</td>
<td>12</td>
<td>14700</td>
<td>n.d.</td>
<td>240</td>
<td>12</td>
<td>2640</td>
</tr>
<tr>
<td>Med. iron</td>
<td>n.d.</td>
<td>n.d.</td>
<td>15</td>
<td>3300</td>
<td>n.d.</td>
<td>250</td>
<td>22</td>
<td>2690</td>
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<td><strong>Intermediate:</strong></td>
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<td>Tasmanian</td>
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<td>23</td>
<td>6000</td>
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<td>220</td>
<td>550</td>
<td>2850</td>
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<tr>
<td>Med. iron</td>
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<td></td>
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<td></td>
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<tr>
<td>T.L.E.</td>
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<tr>
<td>High iron</td>
<td>n.d.</td>
<td>120</td>
<td>560</td>
<td>-</td>
<td>n.d.</td>
<td>200</td>
<td>320</td>
<td>2920</td>
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<tr>
<td>Med. iron</td>
<td>n.d.</td>
<td>65</td>
<td>373</td>
<td>4800</td>
<td>65</td>
<td>170</td>
<td>220</td>
<td>2900</td>
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<tr>
<td>Low iron</td>
<td>n.d.</td>
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<td>91</td>
<td>2900</td>
<td>n.d.</td>
<td>100</td>
<td>330</td>
<td>3360</td>
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<tr>
<td>V. low iron</td>
<td>n.d.</td>
<td>25</td>
<td>45</td>
<td>n.d.</td>
<td>360</td>
<td>275</td>
<td>110</td>
<td>3410</td>
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</tr>
<tr>
<td>High iron</td>
<td>n.d.</td>
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<td>103</td>
<td>-</td>
<td>n.d.</td>
<td>220</td>
<td>170</td>
<td>3310</td>
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<tr>
<td>Med. iron</td>
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<td>2470</td>
<td>182</td>
<td>165</td>
<td>280</td>
<td>3290</td>
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<tr>
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<td>18</td>
<td>19</td>
<td>200</td>
<td>317</td>
<td>100</td>
<td>210</td>
<td>3580</td>
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<tr>
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<td>n.d.</td>
<td>25</td>
<td>45</td>
<td>n.d.</td>
<td>360</td>
<td>275</td>
<td>110</td>
<td>3410</td>
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</tr>
<tr>
<td>Low iron</td>
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<td>52</td>
<td>175</td>
<td>n.d.</td>
<td>4540</td>
<td>125</td>
<td>270</td>
<td>3540</td>
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<tr>
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<td>750</td>
<td>58</td>
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<td>n.d.</td>
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<td>21</td>
<td>3600</td>
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<td>n.d.</td>
<td>460</td>
<td>-</td>
<td>n.d.</td>
<td>2900</td>
<td>1450</td>
<td>3050</td>
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<tr>
<td>Med. iron</td>
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<td></td>
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<td></td>
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<td>Fahey's</td>
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<tr>
<td>High iron</td>
<td>1280</td>
<td>n.d.</td>
<td>85</td>
<td>-</td>
<td>n.d.</td>
<td>524</td>
<td>1200</td>
<td>3150</td>
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<td>Med. iron</td>
<td>980</td>
<td>26</td>
<td>65</td>
<td>-</td>
<td>300</td>
<td>210</td>
<td>320</td>
<td>3400</td>
</tr>
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<td>4 Queen</td>
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<tr>
<td>High iron</td>
<td>1390</td>
<td>n.d.</td>
<td>47</td>
<td>-</td>
<td>n.d.</td>
<td>320</td>
<td>180</td>
<td>3170</td>
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<td>-</td>
<td>100</td>
<td>150</td>
<td>230</td>
<td>3280</td>
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<tr>
<td>Low iron</td>
<td>720</td>
<td>41</td>
<td>120</td>
<td>-</td>
<td>340</td>
<td>180</td>
<td>340</td>
<td>3840</td>
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<td>Payne's</td>
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<tr>
<td>Low iron</td>
<td>1200</td>
<td>n.d.</td>
<td>16</td>
<td>-</td>
<td>260</td>
<td>220</td>
<td>760</td>
<td>3050</td>
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<tr>
<td><strong>Sideritic:</strong></td>
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<td></td>
<td></td>
<td></td>
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<td>6 Argent</td>
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</tr>
<tr>
<td>Low iron</td>
<td>400</td>
<td>67</td>
<td>130</td>
<td>-</td>
<td>4100</td>
<td>240</td>
<td>2650</td>
<td>3110</td>
</tr>
<tr>
<td>Mt. Zeehan</td>
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<td></td>
<td></td>
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<tr>
<td>Med. iron</td>
<td>490</td>
<td>40</td>
<td>120</td>
<td>-</td>
<td>n.d.</td>
<td>400</td>
<td>350</td>
<td>2560</td>
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<tr>
<td>Low iron</td>
<td>1390</td>
<td>53</td>
<td>73</td>
<td>-</td>
<td>5500</td>
<td>400</td>
<td>410</td>
<td>3230</td>
</tr>
</tbody>
</table>

*Mn figures subject to severe contamination by siderite; values are quoted only for siderite-free concentrates.

**"High iron" ≈ > 10% FeS; "Med. iron" ≈ 5-10% FeS; "Low iron" ≈ 1-5% FeS; "V. low iron" ≈ < 1% FeS."
Fig. 62.

SPHALERITE
Co-Ni

Fig. 63.

SPHALERITE
Ag-Ni
SPHALERITE
Sb - Ag

Fig. 64.

SPHALERITE
Av. Cd vs. Av. FeS

Fig. 65.
SPHALERITE
Av. Sn vs. Av. FeS

Fig. 66.

SPHALERITE
Av. Co vs. Av. FeS

Fig. 67.
SPHALERITE
Av. Ni vs. Av. FeS

Fig. 68.

SPHALERITE
Av. Sb vs. Av. FeS

Fig. 69.
SPHALERITE
Av. Bi vs. Av. FeS

Fig. 70.

SPHALERITE
Av. Ag vs. Av. FeS

Fig. 71.
contents of tin in 21 of 54 sphalerite samples; 20 of these 21 were from deposits thought to have crystallized at high to intermediate temperatures, and most of the tin-free samples were from low-temperature types. Harris (1965) recorded tin contents of up to 8500 ppm in sphalerites from a wide range of ore deposits in south-eastern New South Wales; he observed "a clear tendency for high contents of Co, In, Sn and Mn to occur more frequently, though not exclusively, in Fe-rich sphalerite". If the iron content of sphalerite is conceded to be in at least a broad sense an indication of its temperature of formation, then Harris' data support Kullerud's proposals, which were based on a similar premise. Similarly, Rose (1961, 1967) reported a pronounced statistical tendency for the FeS contents of sphalerites to increase with depth in the B limestone section of the Bingham district, and for trace tin to show a pronounced positive correlation (r = .70) with the FeS contents. Harris, however, noted many exceptions to the overall correlation, and suggested that temperature might not be the only operative control. Rose (1967) also observed, but did not comment on, a negative correlation between tin and FeS in sphalerites from the Central district of New Mexico.

Tin was detected in 11 of the 25 samples analysed during the present study. Concentrations range from 400 to 1390 ppm, with a mean of 685 ppm and a standard deviation of 634 ppm; the latter is 93 per cent of the normal mean, and is equivalent to 80 per
cent of the lognormal mean. It is evident that the tin
contents show a moderately wide dispersion which is not signif-
icantly reduced by logarithmic transformation (Fig. 66).

Table 9 shows that detectable tin in sphalerite is confined
to deposits of the central eastern part of the intermediate
zone and of the sideritic zone. Mean tin contents in sphalerites
of the pyritic, intermediate and sideritic zones are 0, 920 and
760 ppm respectively. The pyritic samples have zero variance,
and the probability of equivalence of their mean with those of
the other two zones is vanishingly small. On the other hand there
is a very high probability that the means of the intermediate and
sideritic groups are equivalent.

These data are thus apparently directly opposed to those of
Kullerud, Rose (Bingham) and Harris, since it has already
been proposed that sphalerite compositions indicate the zonal
sequence to be one of overall decreasing temperatures of
sphalerite crystallization. However, it will be observed from
Table 9 that the high-tin sphalerites show a pronounced
concentration around the mineralogically anomalous Queen Hill
area (although the dispersion of the tin extends somewhat
further south and east than the evident mineralogical anomalies).
This suggests that the tin distribution may be a function of the
processes responsible for the unusual tin-bearing mineral
assemblages in this area (which are further discussed below), and
not of the overall district zoning. It will be shown below that
the tin contents of Zeehan sphalerites correlate very poorly with their iron contents: they do not even show the negative correlation reported by Rose (1967) for the Central district samples.

Cobalt: Fleischer (1955) reported cobalt present in nearly half of his tabulated quantitative analyses of sphalerites, in concentrations of up to 3000 ppm. Ofstedal (1941) suggested that sphalerites from high temperature deposits (e.g., contact metamorphic and skarn-type deposits) contain more cobalt than low temperature varieties, but there is little correlation between cobalt and iron contents. Kullerud (1953) also found little correlation between cobalt and iron contents in 54 sphalerite samples. Harris (1965) observed a narrow dispersion of cobalt contents (0-450 ppm) in samples from a wide variety of geological occurrences, and his data indicate a poor correlation between iron and cobalt.

On the other hand, Rose (1967) found a negative correlation between sphalerite cobalt contents and zonal distance from parent stocks in the ores of the Central district of New Mexico; the lateral zoning of the cobalt contents parallels a zonal variation in zinc-lead ratios. The zoning is obscured by a wide scatter when individual analyses are plotted (see Rose's Fig. 6), but becomes clear when the analyses are grouped in intervals of 2000 feet distance from the nearest stock. The cobalt contents measured by Rose ranged from 10-1000 ppm in samples from the Central
district; by contrast, sphalerite samples from Bingham, Utah, contain at most only a few ppm of cobalt, which may thus be a sensitive indicator of geochemical provenance (Burnham, 1959), despite its relatively narrow dispersion.

Cobalt was detected in 17 of the 25 Zeehan sphalerite samples, in concentrations of up to 120 ppm. The mean cobalt content was found to be 24 ppm with a standard deviation of 25 ppm, equivalent to 103 per cent of the normal or 91 per cent of the lognormal mean.

Scatter diagrams (Figs. 62, 67) show clear zonal tendencies in cobalt distribution. No cobalt was detected in sphalerites from the pyritic zone, but the mean cobalt contents of those from the intermediate and sideritic zones are 30 and 55 ppm respectively. The probability of mean equivalence of the pyritic samples on one hand and the intermediate and sideritic samples on the other is again vanishingly small; further, the probability of mean equivalence of the latter two groups is only 10 per cent. It seems clear, therefore, that cobalt in the Zeehan ores increases with increasing distance from the parent intrusion, a trend which is directly opposite to that observed by Rose (1967) in the Central district of New Mexico and by Baumann (1965) at Freiberg. Rose also noted a tendency for cobalt contents to decrease in the presence of carbonate gangue, which again conflicts with the present observations. The reasons for these discrepancies are not known.
Nickel: Fleischer (1955) observed that there is relatively little published data concerning the distribution of nickel in sphalerites. Of 211 analyses in which nickel was sought, it was detected in only 69, in concentrations of up to 300 ppm. Rose (1967) reported nickel in most of his analyses of both Central district and Bingham sphalerite samples, but only in proportions of less than 60 ppm and seldom exceeding 10 ppm.

In the present study, however, nickel was detected in each of the 25 samples, in concentrations ranging up to 560 ppm; a careful study of the high-nickel samples failed to show the presence of any potential contaminant apart from chalcopyrite, whose nickel contents would have to be abnormally high to explain the observed concentrations.

The mean nickel content was found to be 113 ppm and the standard deviation 123 ppm, equivalent to 108 per cent of the normal mean, or 24 per cent of the mean after logarithmic transformation. Scatter diagrams (Fig. 62) show that there again appears to be a marked distinction between samples from the pyritic zone on one hand and the intermediate and sideritic zones on the other. The respective means are 27, 130 and 110 ppm; statistical calculations show less than 1 per cent probability of equivalence of the means of these three groups, but a very high probability that the means of the intermediate and sideritic groups are indistinguishable.

Nickel, therefore, apparently shows zonal trends which
resemble those of cobalt but are somewhat less clearly defined.
The reason for the relatively high nickel contents of Zeehan sphalerites, relative to those of other similar deposits, is unknown but is possibly related to the Cambrian nickel mineralization which, although low grade, is widespread in the West Coast region. Contamination of the Heemskirk granite by the basic host rocks of the nickel mineralization might well have given rise to nickel concentrations higher than those normally produced in hydrothermal fluids.

**Manganese:** As noted above and in the footnote to Table 9, atomic absorption analyses of manganese in Zeehan sphalerites were of limited value, due to the severe effects of contaminating siderite. Limited data are presented in Table 9 only for those samples which were uncontaminated. In general, these atomic absorption determinations were found to agree well with the ranges determined on samples from the same localities by electron microprobe analysis. Some significant aspects of the distribution of manganese in Zeehan sphalerites have been discussed earlier.

**Antimony:** Although antimony has been reported in about 75 per cent of published sphalerite analyses, Fleischer (1955) has questioned whether it is indeed a true trace constituent. Oftedal (1941) found antimony in only 14 of 111 sphalerite samples studied; nine of these contained appreciable amounts of lead, suggesting the possibility of contamination by galena. Fleischer concluded that "it seems probable that admixed galena accounts for much of
the antimony reported in zinc sulfides". Harris (1965) found antimony in most of his sphalerite samples, but reported that high-antimony samples invariably contain contaminating tetrahedrite. Rose (1967) detected antimony in 11 of 25 sphalerite samples from Bingham, in concentrations as high as 1500 ppm; he did not discuss the possibility of contamination.

In the present study, antimony was detected in 13 of the 25 samples, in concentrations as high as 5500 ppm. The mean antimony content was found to be 938 ppm, with pronounced dispersion being reflected in a high standard deviation of 1780 ppm, or 190 per cent of the mean. Even after logarithmic transformation, the standard deviation remains 96 per cent of the mean. Such high dispersions are often produced by a relatively high incidence of aberrant values due to contamination, and examination of the Swansea, Mt. Zeehan and No. 6 Argent samples, all of which showed apparent antimony contents in excess of 4000 ppm, revealed antimony sulfo-salt contamination in each case. No such contaminants were visible in any of the other concentrates, but it is clearly impossible to state categorically that their apparent antimony contents are due to genuine trace substitution. A surprisingly good negative Sb-Fe correlation is found (see below). As a consequence of the high variances in the intermediate and sideritic groups, statistical analysis reveals a probability higher than 25 per cent for equivalence of the three means (0, 370 and 3200 ppm
respectively for the pyritic, intermediate and sideritic zones). However, the relatively high antimony contents of the sideritic samples do not correlate with the observed distribution of sulpho-salts, either on a district scale or in the concentrates analysed. It is concluded, therefore, that there is a distinct possibility that the antimony content of sphalerite increases with increasing distance from the Heemskirk granite, although the data are not adequate to establish the extent to which the apparent trend results from sulpho-salt contamination.

Bismuth: Although bismuth was detected in 43 of 186 sphalerite analyses reported by Fleischer (1955), many of the samples were evidently contaminated, and Fleischer suggested that "much of the bismuth reported in sphalerite is from admixed galena or other impurities". Harris (1965) found the distribution of bismuth in sphalerite to be erratic, but suggested that the dominance of antimony over bismuth in sphalerite might be a consistent geochemical feature, in agreement with the results of Burnham (1959). Rose (1967) found bismuth to be greatly subordinate to antimony in sphalerites from the Bingham district, but also found bismuth to be a persistent constituent of Central district sphalerites (in concentrations up to 900 ppm), for which he did not report any antimony contents. Surprisingly, Rose offered no discussion of the distributions of either of these elements, apart from observing that some of the bismuth in the Central sphalerites and antimony in the Bingham samples might be due to
contamination.

Fleischer (1955) commented on the tendency of bismuth to concentrate almost exclusively in galena rather than sphalerite, a relationship which would not be predicted from considerations of the ionic radii of the metals involved.

Since no bismuth was detected in any galena samples from the Zeehan field (see below), its detection in each of the 25 sphalerite samples was therefore unexpected. It appears that the bismuth content of sphalerite might be another sensitive indicator of geochemical provenance; its presence in sphalerite rather than galena might also be interpreted, in view of the conflicting relationships elsewhere, as evidence for a paragenetic discontinuity and consequent disequilibrium between these two minerals.

The bismuth contents of Zeehan sphalerites were found to vary from 52 to 2900 ppm. The latter value, for a concentrate from the Nubeena Mine, is anomalous (the next highest value being 520 ppm), but no bismuth-bearing contaminants were visible in the sample analysed. The mean bismuth content is 446 ppm, with a standard deviation of 713 ppm, or 160 per cent of the mean. Logarithmic transformation reduces the dispersion considerably, to a standard deviation of 13 per cent of the mean.

No zonal variations in bismuth content are apparent (Fig. 70). The mean bismuth contents for sphalerites from the pyritic, intermediate and sideritic zones are 265, 400 and 345 ppm.
respectively, and statistical analysis indicates a very high probability for equivalence of the three means.

**Silver**: Silver has been reported in about 80 per cent of published sphalerite analysis, but Fleischer (1955) has commented that it might well be a measure of the amount of impurities in the samples. Ofstedal (1941) observed potential contaminants in nearly all of the samples in which he found more than 50 ppm silver. Rose (1967) detected silver in almost all of his sphalerite samples; he noted a correlation between silver content and the abundance of chalcopyrite inclusions in some sections from the Central district, and commented in discussion of the analyses of Bingham samples that "contamination... is doubtless the most important factor in determining the concentrations of lead, antimony, arsenic and possibly silver". In a review of partition data, he noted that "the data do show that Ag... tend(s) to be concentrated in chalcopyrite relative to sphalerite".

Silver was detected in 24 of the 25 samples analysed during the present study, with concentrations ranging from 12 to 2650 ppm. The mean silver content was found to be 600 ppm, with a standard deviation of 727 ppm. The latter is equivalent to 121 per cent of the normal mean, or 24 per cent of the lognormal mean.

The mean silver contents of sphalerites from the pyritic, intermediate and sideritic zones are 30, 445 and 1140 ppm.
respectively; statistical analysis indicates less than 2 per cent probability of equivalence of the three means, although the intermediate and sideritic means are probably indistinguishable (the probability being greater than 25 per cent). These relationships are apparent from scatter diagrams, such as Figs. 63 and 64.

Although the zonal distribution of silver contents thus follows the general distribution of sulpho-salts such as tetrahedrite and boulangerite, the data of Table 9 show clearly that these minerals cannot be responsible for more than a fraction of the silver detected in the analyses. In ten cases, silver contents of up to 1450 ppm were measured on samples which were free of detectable antimony, but antimony exceeds silver in the composition of all of the sulpho-salts observed in the Zeehan ores. Most of any silver due to galena contamination would have been detected and eliminated by the cross-correction procedure, and serious errors in this respect are unlikely. Minute, "exsolved" inclusions of chalcopyrite are present in many of the analysed samples and, in view of Rose's observations on the sphalerite-chalcopyrite partitioning of silver, it is possible that these inclusions may partly explain the high silver contents observed. However, they are not sufficiently abundant to account for more than 200 ppm at the most; it is therefore concluded that silver may be present as a trace constituent in sphalerite, in concentrations
up to at least several hundred ppm. In the Zeehan ores, the sphalerite silver contents are evidently lower in the pyritic zone than in the intermediate or sideritic zones.

**Cadmium:** Reference has already been made to the suggested inverse correlation between iron and cadmium contents of sphalerites, and to Fleischer's (1955) conclusion that the cadmium content of sphalerite is independent of the conditions of formation. Rose (1967) has commented that the ratios of cadmium to zinc are evidently much less sensitive to variations in the processes of transportation and deposition than are those of other trace elements.

Cadmium was detected in all of the 921 analyses tabulated by Fleischer (1955), in concentrations varying from 10 ppm to 4.4 per cent; a pronounced concentration is observed in the range 1000-5000 ppm.

Cadmium contents of the Zeehan sphalerites were found to vary from 2640 to 4090 ppm, with a mean of 3180 ppm. Very narrow dispersion is reflected in the standard deviation of 290 ppm, equal to 9 per cent of the mean. Logarithmic transformation reduces the standard deviation to less than 2 per cent of the mean (despite Shaw's (1961) suggestion that the transformation would have little effect for coefficients of variation of less than 20 per cent).

Mean cadmium contents for sphalerites from the pyritic, intermediate and sideritic zones are 2820, 3340 and 2970 ppm.
The probability of equivalence of the three means is 5 per cent, but again the pyritic and sideritic groups are indistinguishable; scatter diagrams (Fig. 65) suggest that the cadmium content increases slightly from the pyritic through the intermediate to the sideritic zone but, as Rose noted, the changes are of small magnitude.

Reid (1924) reported assays of up to 2 per cent cadmium for ore from the Swansea Mine. The data of the present study are inconsistent with the assumption that this cadmium was present in sphalerite, and the suggestion that it may have occurred in bournonite and/or other sulpho-salts is discussed below.

Correlations:

Correlation coefficients for the trace elements determined in the Zeehan sphalerite samples are summarised in Table 9b.

In the case of sphalerite, it is of particular interest to examine the relationship between trace element and iron contents, both on a district scale and within single ore deposits. Relationships observed for the various elements are as follows:

Tin: In two of the three cases where tin was detected in sphalerite fractions of different iron content but from the same locality, the low iron sphalerite contains the higher tin content; the third case shows the reverse relationship. On a district scale, tin contents correlate poorly with average iron content (Fig. 66). If the latter is presumed to be an approximate
indicator of temperature, as has previously been indicated, then it is apparent that temperature is not the only variable parameter responsible for the zonal variations in tin distribution described above. The Fe-Sn correlation coefficients are -.172 or -.438, assuming normal or lognormal distributions respectively.

**Cobalt:** At single localities, cobalt contents do not show a consistent relationship to iron contents. The four fractions from the T.L.E. Mine show a uniform decline with decreasing iron content, but this tendency is less apparent in the concentrates from the Stonehenge Mine (Table 9) and is reversed (but much less pronounced) in the concentrate pairs from the Swansea, No. 2 Queen and Mt. Zeehan Mines. However, on a district scale, cobalt shows moderately good negative correlations with iron (Fig. 67), regardless of the assumption of normal or lognormal distributions ($r = -.587$ and $-.543$ respectively).

Thus decreasing crystallization temperatures appear to be accompanied by increasing cobalt contents, although it cannot be assumed that the cobalt content is controlled by temperature.

**Nickel:** At individual localities, nickel contents show almost exactly the same relationships to iron contents as do those of cobalt. On a district scale, the correlations with iron content are also negative, but less significant than those of cobalt (Fig. 68).
Antimony: At individual localities, antimony contents appear to be more or less independent of the iron content of the sphalerite in which they occur. On a district scale, a modest negative correlation with iron content \( r = -0.433 \) is apparent if normal distributions are assumed; on logarithmic transformation, the coefficient is significantly increased to \(-0.763\) (Fig. 69). As noted above, however, this relationship may be deceptive, since it may simply reflect increasing abundance of sulpho-salt contaminants in the intermediate and sideritic zones.

Bismuth: The bismuth content of sphalerite shows no relationship to the iron content, either within individual deposits or between different deposits. Fe-Bi correlation coefficients are low, regardless of the assumed distribution (Fig. 70).

Silver: Silver contents also show no relationship to iron contents, on either single-deposit or district scales (Fig. 71).

Cadmium: With only one minor exception, the cadmium content of sphalerites within individual deposits increases with decreasing iron content; on a district scale, cadmium and iron show moderately good negative correlation coefficients (Fig. 65). It appears that the cadmium contents of Zeehan sphalerites increase with decreasing temperatures of crystallisation, but the differences are not pronounced, and again it is uncertain whether temperature is actually the controlling parameter.

Other possibly significant correlations which are apparent
from Table 9b include Bi-Sn (r = .511 (normal) or .393 (lognormal)), Co-Sb (r = .646 (normal) or .757 (lognormal)), and Co-Cd (r = .624 or .592). The Co-Sb and Co-Cd correlations suggest that the correlations noted between each of these three elements and iron are not fortuitous.

In summary, trace element concentrations in sphalerite are, with the exception of manganese, low in the pyritic zone and generally higher in the intermediate and sideritic zones. Co, Sb and Cd contents show some correlation with iron contents, and may be at least in part temperature sensitive; on the other hand, the coincidence of their trends with the general temperature gradient may be fortuitous. The pattern of trace element distributions in sphalerite shows some resemblances to that of galena; it is suggested below that pH of the hydrothermal fluids may be an important control of galena geochemistry, and similar considerations may also apply to sphalerite.
Table 9b

Correlation coefficients for trace elements in sphalerite

I. Normal co-ordinates:

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<tr>
<th></th>
<th>FeS</th>
<th>Sn</th>
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</tr>
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<td>Sb</td>
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<td></td>
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II. Logarithmic co-ordinates:

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<tr>
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<tr>
<td>Co</td>
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<tr>
<td>Sb</td>
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<td>Ag</td>
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<td>Cd</td>
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<td>0.366</td>
<td>0.592</td>
<td>0.534</td>
<td>0.584</td>
<td>-0.293</td>
<td>0.359</td>
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</tbody>
</table>

Significance levels: 0.1% - 0.76
1.0% - 0.66
5.0% - 0.52
SIDERITE.

Trace element analyses of 17 siderite samples from the Zeehan field are summarised in Table 10. Four samples are from the Pyritic Zone, nine from the Intermediate Zone, and four from the sideritic zone.

Previous trace element studies of ore deposits have mostly concentrated on the sulphide minerals, and data concerning the gangue minerals are fragmentary and insufficient to provide a basis for comparison. This discrimination is unwarranted, and any attempt at a comprehensive geochemical study should encompass both ore and gangue minerals, particularly when fresh samples of the latter are available from underground exposures.

Tin: Tin was detected in only three of the 17 samples, at apparent concentrations close to the limit of detection. The precision of these determinations is poor, and the data do not establish that tin is a genuine trace constituent of any of the Zeehan carbonates; apparent concentrations of this order of magnitude are very likely to arise from small errors in cross-correction. In the present instance, sphalerites co-existing with two of the three siderites in which tin was apparently detected are characterised by relatively high tin contents and also constitute the principal contaminants in the siderite concentrates analysed.
<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
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<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
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<th>Ag</th>
<th>Cd</th>
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<td></td>
<td></td>
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<tr>
<td>Boss</td>
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<td>17</td>
<td>8.68</td>
<td>280</td>
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<td>120</td>
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<tr>
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<tr>
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<td>46</td>
<td>105</td>
<td>2.68</td>
<td>1960</td>
<td>n.d.</td>
<td>n.d.</td>
<td>66</td>
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<tr>
<td>Nubeena</td>
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<td>n.d.</td>
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<td>610</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>Oonah</td>
<td>n.d.</td>
<td>72</td>
<td>n.d.</td>
<td>3.79</td>
<td>3640</td>
<td>n.d.</td>
<td>540</td>
<td>940</td>
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<tr>
<td>4 Queen</td>
<td>n.d.</td>
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<td>10</td>
<td>4.18</td>
<td>430</td>
<td>n.d.</td>
<td>20</td>
<td>n.d.</td>
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<tr>
<td>2 Queen</td>
<td>n.d.</td>
<td>18</td>
<td>18</td>
<td>8.52</td>
<td>200</td>
<td>n.d.</td>
<td>22</td>
<td>n.d.</td>
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<td>Payne's</td>
<td>n.d.</td>
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<td>18</td>
<td>4.58</td>
<td>2620</td>
<td>n.d.</td>
<td>340</td>
<td>1880</td>
</tr>
<tr>
<td><strong>Sideritic</strong></td>
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<tr>
<td>6 Argent</td>
<td>n.d.</td>
<td>40</td>
<td>52</td>
<td>8.07</td>
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<td>n.d.</td>
<td>n.d.</td>
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<tr>
<td>King</td>
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<tr>
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<td>260</td>
<td>33.27</td>
<td>1380</td>
<td>76</td>
<td>92</td>
<td>82</td>
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</tbody>
</table>
SIDERITE
Ni - Co

Fig. 72.

SIDERITE
Ni - Mn

Fig. 73.
Cobalt: 13 of the 17 siderite samples contained detectable cobalt, with measured concentrations ranging from 15 to 910 ppm (Table 10). The mean cobalt content was found to be 92 ppm, with a standard deviation of 215 ppm, equivalent to 235 per cent of the mean, or 65 per cent of the mean after logarithmic transformation.

The data of Table 10 and Fig. 72 suggest that siderite samples from the pyritic zone contain low cobalt by comparison with those from the intermediate and sideritic zones, the respective means being 4, 143 and 63 ppm. However, the variance in both intermediate and sideritic samples is large, and the probability of equivalence of the three means is 20 per cent; the probability of equivalence of the means of the pyritic and intermediate groups is only slightly lower, at 15 per cent.

Hence, although it appears that the cobalt content of siderite declines from the pyritic into the intermediate zone, it is also clear that more data are required to establish confidence in the trend.

Nickel: 14 of the 17 samples contained detectable nickel, with measured concentrations ranging from 10 to 374 ppm (Table 10). The mean nickel content was found to be 65 ppm, with a standard deviation of 101 ppm, equivalent to 155 per cent of the mean, or 57 per cent of the mean after logarithmic transformation.
Fig. 72 shows clearly that there is pronounced overlap of the dispersions of nickel analyses for the three zonal types, and although there appears to be a systematic increase in the means, from 40 ppm for the pyritic zone samples through 57 ppm to 100 ppm for those from the intermediate and sideritic zones respectively, statistical calculations show a very high probability (i.e. much higher than 25 per cent) that this apparent trend is fortuitous and the means are indistinguishable.

**Manganese:** All siderite samples analysed contained substantial proportions of manganese, and their solutions required considerable dilution to bring them into the concentration range of the sensitive atomic absorption technique. An attempt was made to reduce the ensuing dilution errors by replicate analysis of three dilution aliquots for each sample; the figures quoted in Table 10 in each instance represent the mean of these three determinations. Reproducibility was uniformly good, with coefficients of variation of less than 2 per cent in most cases, and always less than 5 per cent.

The manganese content of Zeehan siderites was found to range from 2.68 per cent to 33.3 per cent (so that the term "siderite" is in some instances a misnomer). The mean manganese content is 11.5 per cent, with a standard deviation of 7.9 per cent. The latter is equivalent to 65 per cent of the normal mean or 10 per cent of the lognormal mean.
Fig. 73 shows a pronounced overlap of the dispersions of manganese contents in samples from the three zones. The means vary from 11.7 per cent in the pyritic zone to 9.3 per cent in the intermediate zone and 17.4 per cent in the sideritic zone. Statistical calculations show that the probability of equivalence of the three means is again much higher than 25 per cent, and hence no clear zonal trends can be established.

**Antimony:** Although antimony was detected in every siderite sample analysed, microscopic examination of the concentrates showed that several samples were visibly contaminated by antimony-bearing sulphosalts (principally tetrahedrite, bournonite and boulangerite). The obviously contaminated samples include those from the Swansea, Oonah, Payne's and Austral Mines, and it is not surprising to see that these yielded the highest antimony contents, ranging from 1380 to 3640 ppm.

The other samples, which showed no apparent contamination, yielded apparent antimony contents ranging from 170 to 610 ppm. The arithmetic mean of this group is 338 ppm, with a standard deviation of 133 ppm, or 39 per cent of the mean. The standard deviations of the logarithms of the antimony concentrations is 10 per cent of the mean.

No systematic trends in antimony concentration in siderite are apparent, and statistical calculations reveal probabilities much higher than 25 per cent for equivalence of the means of the three
groups (regardless of whether the high values are included or not).

Correlation studies (see below) suggest that the observed antimony contents might all be due to contamination, despite the frequent lack of visible inclusions of antimony minerals.

**Bismuth:** Bismuth was detected in only one of the 17 samples; 76 ppm were measured in a siderite sample from the Austral Mine. Insufficient sample was available to run a duplicate, but this solitary result is probably due to contamination. Certainly no zonal regularities in bismuth distribution are apparent.

**Silver:** Silver was detected in 9 of the 17 siderite samples, with observed concentrations varying from 12 to 540 ppm. The mean silver content is 71 ppm, with a standard deviation of 146 ppm, or 205 per cent of the mean. Even after logarithmic transformation the standard deviation remains 105 per cent of the mean, which reflects the high dispersion of these results.

The high dispersion is also reflected in very high probabilities for equivalence of the means of the three groups, either as a group of three or as three pairs.

Again correlation studies (see below) suggest that much or all of the silver might be due to contamination. The highest silver contents (340 and 540 ppm) were both measured on samples containing visible tetrahedrite, which would account for the dispersion.
Cadmium: The distribution of cadmium was also found to be highly erratic. Cadmium contents ranging from 44 to 1880 ppm were detected in 8 of the 17 samples. The mean cadmium content was found to be 190 ppm, with a standard deviation of 490 ppm, or 258 per cent of the mean. After logarithmic transformation, the standard deviation remains 117 per cent of the mean.

Again no systematic trends were observed, except that the two extremely high cadmium contents (Table 10) were both measured on samples containing visible tetrahedrite contamination. Although it is natural to attribute cadmium contamination to the presence of sphalerite, both of these values (940 and 1880 ppm) are far too high, requiring 30 to 50 per cent of unobserved sphalerite for their explanation. This question is further discussed below.

Correlations:

Correlation coefficients for the various pairs of elements detected in the siderite samples are listed in Table 10b.

Ni-Co and Ni-Mn have relatively high correlation coefficients (+.839 and +.725 respectively) if a normal distribution is assumed, but both are substantially reduced (to +.215 and +.401) on logarithmic transformation. Examination of the data shows that the normal correlation arises from the coincidence of unusually high Ni, Co and Mn contents in samples from the Stonehenge and Austral Mines (see also Figs. 72 and 73); the remaining analyses
show wide scatters and poor correlations. The pronounced reduction in the correlation coefficients on logarithmic transformation suggests that they are fortuitous, or that the distribution of one or both elements in each pair is poorly described by the lognormal "law". A possible explanation for the latter is that the sporadic high values arise from contamination, but the cause of such contamination is not apparent.

Sb, Ag and Cd show similar relationships. Sb-Ag, Sb-Cd and Ag-Cd have normal correlation coefficients of +.881, +.765 and +.811 respectively, with corresponding lognormal coefficients of +.456, +.607 and +.623. Examination of Table 10 reveals that the apparently good normal correlations result from the coincidence of high Sb, Ag and Cd contents in samples from the Oonah Mine and the Payne's deposit; the contribution of these values to the regression is reduced when the logarithmic transformation is effected. In this case, however, it will be recalled that these two samples were visibly contaminated by tetrahedrite and boulangerite, as were those from the Austral and Swansea Mines. The Austral sample also contains relatively high Sb, Ag and Cd, while the Swansea sample, which is contaminated with bournonite rather than tetrahedrite-boulangerite, contains high Sb and moderately high Cd, but no detectable Ag.

These relationships suggest that most, if not all, of the observed Sb, Ag and Cd contents in the siderite samples result from sulphosalt contamination. Apparently where tetrahedrite is
### Table 10b.

**Correlation coefficients for trace elements in siderite.**

#### I. Normal co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphal</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>-0.100</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>-0.235</td>
<td>0.839</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-0.106</td>
<td>0.463</td>
<td>0.725</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-0.382</td>
<td>-0.011</td>
<td>-0.010</td>
<td>-0.266</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-0.239</td>
<td>-0.077</td>
<td>-0.152</td>
<td>-0.259</td>
<td>0.881</td>
<td>1.000</td>
</tr>
<tr>
<td>Cd</td>
<td>-0.234</td>
<td>-0.077</td>
<td>-0.173</td>
<td>-0.307</td>
<td>0.765</td>
<td>0.811</td>
</tr>
</tbody>
</table>

#### II. Logarithmic co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphal</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Co</td>
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<tr>
<td>Ni</td>
<td>-0.344</td>
<td>0.215</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-0.002</td>
<td>0.000</td>
<td>0.401</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-0.381</td>
<td>0.444</td>
<td>-0.120</td>
<td>-0.454</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-0.197</td>
<td>0.025</td>
<td>-0.002</td>
<td>-0.194</td>
<td>0.456</td>
<td>1.000</td>
</tr>
<tr>
<td>Cd</td>
<td>-0.478</td>
<td>0.201</td>
<td>0.066</td>
<td>-0.273</td>
<td>0.607</td>
<td>0.623</td>
</tr>
</tbody>
</table>

**Significance levels:**

- 0.1% - 0.72
- 1.0% - 0.60
- 5.0% - 0.48
the principal contaminant, all three are introduced. The absence of silver from the Swansea sample suggests that bournonite contamination introduces little or no silver and, although the evidence is limited, boulangerite apparently contains less silver than tetrahedrite and little cadmium; an impure boulangerite concentrate from the Spray Mine (see Appendix p. A105) contained only 30 ppm Cd and 1100 ppm Ag.

If this hypothesis is correct, the observed abundances of the sulphosalts in the samples analysed suggest that they must have cadmium contents up to several per cent or more (the Payne's sample, which contains 1880 ppm Cd, is estimated to have contained no more than 5 per cent tetrahedrite). This provides a possible explanation for the otherwise puzzling report of Reid (1924) of assays of up to 2 per cent Cd for ore from the Swansea Mine, and for the reported production of 40 tons of cadmium from that mine (see Appendix I, p. A117); several analyses of Swansea sphalerite undertaken during the present study showed Cd contents uniformly less than 4000 ppm, but bournonite and tetrahedrite are both abundant in the Swansea ore, and might well account for the production and assays reported by Reid. This aspect of the geochemistry of the sulphosalts evidently merits further study; the trace element data for galena (see below) give somewhat conflicting results.

Uniformly poor correlations between the abundances of the various trace elements on one hand and the average FeS contents
of co-existing sphalerites on the other (Table 10b) again suggests either that the trace element abundances are not strongly temperature controlled or that the FeS content of sphalerite is a poor indicator of the crystallization temperature of siderite in the same deposit (or both).

It is noteworthy that high trace contents of Sn, Co, Ni, Sb, Ag and Cd are all largely confined to the intermediate and sideritic zones - i.e. the zones in which siderite is an abundant gangue constituent. Similar relationships were observed in the trace element geochemistry of galena, and their possible significance is discussed below.
Trace element analyses of 18 galena samples are summarised in Table 11. Four of these samples were obtained from the pyritic zone, ten from the intermediate zone, and four from the sideritic zone.

The problem of sulphosalt contamination of galena presented some difficulties in the present study. Tetrahedrite and, to a lesser extent, boulangerite and bournonite are commonly intimately intergrown with galena, particularly in samples from the intermediate and sideritic zones. The sulphosalt inclusions are usually very small and mechanically inseparable, and in most cases there was no alternative to the analysis of composite concentrates. However, this problem is perhaps not as serious as it seems. There is no doubt concerning the generally close paragenetic relationships between galena and the sulphosalts, which in fact represent the precipitation of trace elements in concentrations exceeding those which can be accommodated in the galena structure. Since the objective of this portion of the present study was to seek any systematical trends in trace element distribution which might throw light on progressive changes in the physico-chemical environment of ore deposition, it is logical to include the "trace elements" of the sulphosalts in the analytical programme. Since their deposition was so closely related to that of the galena, there is little practical objection to considering them together. It should be stressed,
<table>
<thead>
<tr>
<th></th>
<th>Sn ppm</th>
<th>Co ppm</th>
<th>Ni ppm</th>
<th>Mn ppm</th>
<th>Sb ppm</th>
<th>Bi ppm</th>
<th>Ag ppm</th>
<th>Cd ppm</th>
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<tr>
<td><strong>Pyritic:</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Sylvester</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>61</td>
<td>1060</td>
<td>n.d.</td>
<td>880</td>
<td>11</td>
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<tr>
<td>Despatch</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>68</td>
<td>775</td>
<td>n.d.</td>
<td>1320</td>
<td>10</td>
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<tr>
<td><strong>Intermediate:</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Tasmanian</td>
<td>n.d.</td>
<td>n.d.</td>
<td>930</td>
<td>230</td>
<td>1420</td>
<td>n.d.</td>
<td>1200</td>
<td>27</td>
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<tr>
<td>T.L.E.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>22</td>
<td>66</td>
<td>1100</td>
<td>n.d.</td>
<td>1230</td>
<td>38</td>
</tr>
<tr>
<td>Stonehenge</td>
<td>250</td>
<td>n.d.</td>
<td>28</td>
<td>n.d.</td>
<td>1810</td>
<td>n.d.</td>
<td>2560</td>
<td>31</td>
</tr>
<tr>
<td>Swansea</td>
<td>250</td>
<td>n.d.</td>
<td>34</td>
<td>15</td>
<td>1830</td>
<td>n.d.</td>
<td>2600</td>
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<tr>
<td>Nubeena</td>
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<td>130</td>
<td>45</td>
<td>4320</td>
<td>n.d.</td>
<td>2280</td>
<td>30</td>
</tr>
<tr>
<td>Fahey's</td>
<td>120</td>
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<td>21</td>
<td>71</td>
<td>1540</td>
<td>n.d.</td>
<td>1310</td>
<td>20</td>
</tr>
<tr>
<td>Oonah</td>
<td>52</td>
<td>n.d.</td>
<td>13</td>
<td>12</td>
<td>2730</td>
<td>n.d.</td>
<td>2120</td>
<td>59</td>
</tr>
<tr>
<td>4 Queen</td>
<td>150</td>
<td>n.d.</td>
<td>131</td>
<td>38</td>
<td>4280</td>
<td>n.d.</td>
<td>2260</td>
<td>32</td>
</tr>
<tr>
<td>2 Queen</td>
<td>105</td>
<td>n.d.</td>
<td>160</td>
<td>58</td>
<td>2520</td>
<td>n.d.</td>
<td>2050</td>
<td>36</td>
</tr>
<tr>
<td>Payne's</td>
<td>49</td>
<td>n.d.</td>
<td>n.d.</td>
<td>10</td>
<td>3490</td>
<td>n.d.</td>
<td>2990</td>
<td>66</td>
</tr>
<tr>
<td><strong>Sideritic:</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 Argent</td>
<td>n.d.</td>
<td>n.d.</td>
<td>14</td>
<td>130</td>
<td>940</td>
<td>n.d.</td>
<td>1060</td>
<td>28</td>
</tr>
<tr>
<td>Mt. Zeehan</td>
<td>n.d.</td>
<td>n.d.</td>
<td>10</td>
<td>85</td>
<td>1075</td>
<td>n.d.</td>
<td>1042</td>
<td>10</td>
</tr>
<tr>
<td>King</td>
<td>n.d.</td>
<td>n.d.</td>
<td>12</td>
<td>130</td>
<td>870</td>
<td>n.d.</td>
<td>970</td>
<td>22</td>
</tr>
<tr>
<td>Austral</td>
<td>n.d.</td>
<td>n.d.</td>
<td>12</td>
<td>190</td>
<td>2500</td>
<td>n.d.</td>
<td>1460</td>
<td>16</td>
</tr>
</tbody>
</table>
Fig. 74.

Fig. 75.
Fig. 76.

GALENA
Sb–Ag

Fig. 77.

GALENA
Sb–Cd
Fig. 78.
however, that the element abundances reported in this discussion are not necessarily (except where otherwise noted) those of true trace constituents in the galena structure. Similar considerations have been noted for some instances of sulphosalt contamination in several of the siderite samples.

Tin: According to Fleischer (1955), tin has been reported in about 40 per cent of published qualitative analyses of galena samples, and in 83 of 338 quantitative determinations. Among the latter group, the reported concentrations range from less than 10 ppm up to 1300 ppm; some or possibly all of the high-tin galenas also contain tetrahedrite. Harris (1965) reported sporadic tin concentrations in galena as high as 5000 ppm. These were not accompanied by unusually high antimony contents - in fact in some cases the concentration of tin exceeded that of antimony.

In the present study, tin was detected in 8 of the 18 samples. Concentrations ranged from 50 to 250 ppm, with an overall mean (including those samples in which none was detected) of 63 ppm and a standard deviation of 87 ppm. The latter corresponds to 140 per cent of the mean; the apparent dispersion is not greatly reduced by logarithmic transformation, which improves the standard deviation only to 116 per cent of the mean. Due to the absence of iron interference, the detection limit for tin in galena is about 25 ppm under favourable conditions, and the precision near the
The data of Table 11 and the appropriate scatter diagrams (Figs. 74, 75) show a marked concentration of tin in galena samples from the intermediate zone. Statistical calculations show a probability of less than 1 per cent for equivalence of the means of the three zone groups (less than 25 ppm for the pyritic and sideritic zones and 100 ppm for the intermediate zone). With zero variance in each, the pyritic and sideritic groups are of course indistinguishable. The tin contents thus show strong zonal relationships which, as will be shown, are shared by other trace constituents in galena.

Cobalt: Fleischer (1955) observed that "cobalt has been reported in a few (galena) samples, but may be present in pyrite or other minerals". No cobalt was detected in any of the Zeehan samples (detection limit 5 ppm).

Nickel: Nickel was reported in 15 of 40 analyses summarised by Fleischer (1955), in concentrations ranging up to 100 ppm. In the present study, nickel was detected in 15 of the 18 galena samples; concentrations generally varied between 10 and 160 ppm, with one anomalous value of 930 ppm for a sample from the Tasmanian Mine. Minute inclusions of several nickel minerals (uilmannite, breithauptite, rammelsbergite or pararammelsbergite) were observed in
galena samples from several localities in the Zeehan field and, although none was observed in grain mounts of any of the analysed samples, it is possible that the observed nickel contents result at least in part from inclusions of these minerals. The mean nickel content of the analysed samples is 85 ppm, with a standard deviation of 216 ppm, or 253 per cent of the mean; the dispersion is markedly reduced by logarithmic transformation, which reduces the standard deviation to 62 per cent of the mean.

The means of the pyritic, intermediate and sideritic zone samples are 6, 160 and 12 ppm respectively. Statistical analysis reveals a probability of less than 5 per cent for equivalence of the three means, and a probability of 20 per cent that the pyritic and sideritic means are indistinguishable. The distribution of nickel in galena thus parallels that of tin, with a pronounced concentration in the ores of the intermediate zone.

Manganese In reporting 37 determinations (out of 90 samples) of manganese in galena, Fleischer (1955) suggested that "some, if not all of the manganese reported was due to admixed sphalerite"; manganese contents as high as 2000 ppm have been recorded.

Manganese was detected in all but one of the Zeehan galena samples; the observed concentrations varied from 10 to 230 ppm, with a mean of 74 per cent and a standard deviation of 62 ppm, or 83 per cent of the normal mean. The standard deviation about the lognormal mean is 34 per cent. Considering the high
manganese contents of siderite, and of sphalerite in the pyritic zone, these concentrations are well within the range of possible error in contamination correction.

Means for samples from the pyritic, intermediate and sideritic zones are 62, 55 and 134 ppm respectively; the statistical probability of equivalence of these means is higher than 25 per cent (cf. Fig. 78). Manganese in galena therefore shows no systematic zonal variations; this contrasts with the distribution of most other trace elements in galena, and supports the suggestion that the observed abundances result from contamination.

**Antimony:** Antimony has been detected in most analyses of galena; Fleischer (1955) summarised 224 analyses, of which 189 reported concentrations between 10 ppm and 3 per cent. As Fleischer observed, many of these samples were undoubtedly contaminated by sulphosalts such as tetrahedrite; nevertheless, high antimony contents have been reported for many samples in which no contamination was evident. Harris (1965) determined antimony contents of up to 4500 ppm for galena samples from south-eastern New South Wales. According to Fleischer, Tjenschendorf (1955) found that the antimony content of Freiberg galenas (including that resulting from galena contamination) decreased with decreasing temperature of formation.

Antimony was found in all samples of galena analysed during the present study, with concentrations ranging from 540 to 4320
ppm (Fig. 76); the mean content was found to be 1860 ppm, with a standard deviation of 1200 ppm, or 64 per cent of the mean. The dispersion is reduced markedly by logarithmic transformation, with the standard deviation being reduced to 9 per cent of the mean of the lognormal distribution. As noted above, most of the Zeehan galena samples are contaminated to some degree by tetrahedrite, boulangerite and/or bournonite, and there is little doubt that most of the antimony detected in the present analyses is due to inclusions of one or more of these minerals.

Mean antimony contents of galena samples from the pyritic, intermediate and sideritic zones are 760, 2500 and 1340 ppm respectively, and the calculated probability of mean equivalence is less than 2 per cent. The data of Table 11 and Figs. 64, 66, 67 and 68 show that samples from the intermediate zone have antimony contents clearly higher than those of the pyritic zone and (a little less clearly) the sideritic zone. The distribution of antimony in galena thus parallels the zonal distributions already noted for tin and nickel.

**Bismuth:** Bismuth was reported in 202 of the 327 analyses summarised by Fleischer, in concentrations of up to 5 per cent. It seems clear that some of the high-bismuth samples were contaminated by native bismuth, bismuthinite or bismuth-bearing sulpho-salts, but moderately high contents of bismuth have also
been reported in optically homogeneous galena samples. Ofstedal (1942) showed that high-bismuth galenas invariably contain exsolved matildite if sufficient silver is present, but samples containing high bismuth and low silver show only a pronounced octahedral parting.

Schroll (1951, 1955), Tischendorf (1955) and Baumann (1965) have all reported bismuth contents of galena to decrease with decreasing apparent temperature of formation, sometimes with sympathetic decreases in silver and antimony. Much of the information in this respect was derived from studies of the zoned lead-zinc ores of the Freiberg district, and therefore it was hoped that bismuth in Zeehan galenas would prove as informative.

Unfortunately, atomic absorption sensitivity for bismuth is seldom better than that for tin; detection limits for most samples varied from 30 to 50 ppm, depending on dilution, and the lower values at least fall within the ranges reported by Baumann (1965). No bismuth was detected in any of the Zeehan samples, which is a little surprising in view of its ubiquitous occurrence in sphalerite (q.v.). Traces of bismuth were detected in some of the spectrographic analyses but in the absence of calibration standards could not be given quantitative limits. The possibility of loss of bismuth in the solution procedure was investigated, but rejected since recovery tests were all satisfactory (all better than 90 per cent) and since no bismuth
is lost when the same solution procedure is used for sphalerites. It is concluded that the Zeehan galena samples all contain less than 30 ppm bismuth.

Silver: Silver was reported in 220 of the 233 galena analyses tabulated by Fleischer (1955); concentrations range from less than 10 ppm up to a maximum of 3 per cent, with almost half of the analyses lying in the 1000-5000 ppm category. Schroll (1951) observed that the silver content of East Alpine galena varied directly with those of antimony and bismuth, and inversely with that of arsenic; Tischendorf (1955) suggested that silver, bismuth and antimony contents all decreased with decreasing temperature of formation. A possible similar temperature correlation was therefore sought in the Zeehan ores.

Silver was detected in all samples analysed; all concentrations were well above the limit of detection and the precision was consequently high; replicate analyses of several samples yielded coefficients of variation of less than two per cent for successive analysis of different dilution aliquots from the same solution, and less than 5 per cent for complete replicate analyses on different quarters of the original mineral concentrate.

Measured silver concentrations vary from 700 to 2990 ppm, with a mean of 1600 ppm and a standard deviation 720 ppm, or 45 per cent of the mean. The lognormal standard deviation is
6 per cent of the lognormal mean.

Scatter diagrams (Figs. 75, 76) suggest distinct differences between the silver contents of galenas from the three mineralogical zones, and these are confirmed by statistical analysis. The probability of equivalence of the means (920, 2000 and 1130 ppm for the pyritic, intermediate and sideritic zones respectively) is less than 5 per cent, although that of equivalence of the pyritic and sideritic means is 25 per cent. Hence the silver contents show the same pattern as has been observed for tin, nickel and antimony in the Zeehan galenas - contents are low and generally comparable in the pyritic and sideritic zone samples, and markedly higher in the intermediate zone.

Cadmium: Cadmium has been reported in many galena analyses, but Fleischer (1955) has observed that many of these samples were reported to contain zinc and probably contained sphalerite; nevertheless, Fleischer quotes Oftedal as reporting 1000 ppm cadmium in a high-bismuth galena which contained no zinc, and concluded that "it is possible that cadmium may be present in solid solution in galena". It has already suggested that sphalerite is not the only contaminant capable of introducing spurious cadmium contents into galena concentrates; however, the preliminary studies reported by Bethke & Barton (1959) indicate that small amounts of cadmium can in fact enter the galena
structure and might, under certain circumstances, be useful for geothermometry. Cadmium contents as high as 1000 ppm in natural galenas are evidently rare and, since the value reported by Oftedal was from a high-bismuth sample, possibly result from sulpho-salt contamination.

Cadmium was detected in 16 of the 18 galena samples examined during the present study, at uniformly low concentrations ranging from 8 to 66 ppm (Table 11). The mean cadmium content is 25 ppm, with a standard deviation of 18 ppm, equivalent to 73 per cent of the normal mean and 42 per cent of the lognormal mean.

Scatter diagrams (Fig. 77) again suggest similar trends to those observed for other trace elements in galena. Means for the pyritic, intermediate and sideritic zone samples are 5, 35 and 19 ppm respectively, and the statistical probability of equivalence is less than 0.1 per cent.

Precision for these determinations is good (coefficients of variation less than 10 per cent), and they are unlikely to have resulted from uncorrected sphalerite contamination, since most of the galena concentrates contained only small proportions of sphalerite which are insufficient to account for the observed cadmium contents even prior to correction. Either the cadmium is a true trace constituent of the galena, or it has been introduced by sulpho-salt contamination, a possibility which is further discussed below.
Correlations:

Correlation coefficients for the various pairs of elements detected in the galena samples are listed in Table 11b.

If normal distributions are assumed for all the elements, moderate to good correlations \((r = \pm 0.5 \text{ or better})\) are observed between Sn and Mn \((-0.557)\), Ag \((0.750)\) and possibly Sb \((0.487)\); between Ni and Mn \((0.582)\); between Mn and Ag \((-0.549)\); between Sb and Ag \((0.772)\) and Cd \((0.598)\); and between Ag and Cd \((0.635)\). The correlations are thus all positive with the exception of those involving Mn, which are nearly all negative (and relatively low). Although Ni shows the same overall tendency to increase in samples from the intermediate zone as Sn, Sb, Ag and Cd, it correlates poorly with each of these elements.

On lognormal transformation, the weak Ni-Mn correlation disappears, but the Mn-Sn and Mn-Ag negative correlations are slightly improved. Ni correlations with Sn, Sb, Ag and Cd are improved slightly, but not to significant levels.

Correlations between Sn, Sb, Ag and Cd are all improved, with the Sn-Ag \((r = 0.847)\) and Ag-Sb \((r = 0.861)\) correlations appearing to be particularly strong.

The strong Ag-Sb correlation is obviously related to the presence of contaminating tetrahedrite; it will be recalled from the mineralogical descriptions that this mineral is particularly abundant in the intermediate zone, which would
explain the tendency for both elements to increase in apparent concentration in galena samples from that zone. In this respect, the silver data from the present study are supported by recorded assay data (Table 5), providing the latter are critically evaluated and anomalous assays (e.g. of oxidised ore) are recognised and excluded.

The presence of tetrahedrite cannot explain all of the silver observed in the analyses. In most cases the concentration of silver is comparable with that of antimony and frequently exceeds it, whereas even the most argentian tetrahedrites contain no more than 17.7 per cent silver, by comparison with 26.6 per cent antimony (Palache, Berman & Frondel, 1944). It appears therefore that the galena structure is capable of containing appreciable amounts of silver apart from those contained in admixed sulfo-salts, in agreement with general opinion (e.g. Fleischer, 1955). Edwards (1954) noted that argentiferous galena containing less than 1000 ppm silver tends to be homogeneous, but galena with silver in excess of this amount invariably contains included silver minerals. The present study confirms Edwards' observations; no sulfo-salts or other silver minerals were observed in concentrates from the pyritic zone, which contained up to 1320 ppm silver, and sulphosalts are not common in samples from the sideritic zone, which contain less than 1460 ppm silver. Within the intermediate zone, there is a direct correlation between the abundance of
sulpho-salts and the silver concentrations. The present data suggest a similar limit of approximately 1000 ppm for the solubility of antimony in galena; it appears that when antimony concentrations exceed this limit (which possibly varies somewhat with temperature) sulpho-salts are precipitated and silver is partitioned between the host galena and the sulpho-salt inclusions. In view of the particularly common association of tetrahedrite and galena, a study of the thermometric significance of silver partition coefficients could possibly yield useful results.

The strong correlations of Sn and Cd with both Sb and Ag were unexpected, but suggest that studies of the partitioning of these elements between galena and co-existing sulpho-salts could also prove informative. The low concentrations, however would present analytical difficulties more severe than those expected in the cases of Sb and Ag, both of which are potentially amenable to microprobe determination.

No element showed any significant correlation with the mean FeS content of co-existing sphalerites, and the general tendency to increasing concentrations in the intermediate zone followed by decreases in the sideritic zone suggests that temperature did not control the absolute concentrations of any of these elements. In this connection, attention is drawn to the observed close relationship between the distribution of sulpho-salt inclusions and the relative abundance of
paragenetically earlier siderite. Even on a microscopic scale, the sulpho-salt inclusions are commonly clustered around or adjacent to residuals of the earlier carbonates.

To explain these relationships it is proposed that reaction between the siderite and the paragenetically later galena-depositing solutions produced changes in the chemistry of the latter, causing precipitation of the silver and antimony contemporaneously with crystallization of the galena. Since the distributions of Sn and Cd, and to a lesser extent Ni, closely follow those of Sb and Ag, they may well have been deposited by the same mechanism.

The exact nature of this mechanism is speculative, since so little is known of the physical and chemical constitution of hydrothermal fluids. However, it is interesting to recall from the brief review given earlier that a substantial body of geochemical opinion currently favours (a) fluids which are initially slightly acid, becoming slightly alkaline by reaction with wallrocks during permeation of vein systems, and (b) transport of the ore metals as chloride complexes which become unstable with increasing alkalinity, causing precipitation of the ore minerals. By contrast, polysulphide complexes become increasingly stable with increasing pH. Helgeson (1964) has shown that the sequence of instability of metal chloride complexes matches the general paragenetic sequence, and therefore the zonal sequence of most sulphide ore deposits (although, as Helgeson points out, other potential ligands also satisfy this
requirement).

If the Zeehan galena is in fact distinctly later than the siderite, as textural evidence strongly suggests, then reaction between siderite and later solutions could conceivably cause a relatively abrupt increase in the pH of the latter; ensuing instability of metal chloride complexes could then account for the "dumping" of minor constituents along with the galena. The relatively abrupt precipitation of the trace elements would thus account for their sudden appearance in the zonal sequence, coinciding with the first zonal appearance of substantial proportions of siderite in the earlier assemblages. Upon attainment of equilibrium between solutions and carbonates, the "dumping" mechanism would cease, and further precipitation of the trace elements would be governed by the less severe effects of gradually declining temperature and the associated equilibrium adjustments.

While this proposal is undoubtedly oversimplified, it does explain the observed distribution and paragenetic relationships of the sulpho-salts (on both district zonal and microscopic scales) and of the galena trace elements. It suggests, for example, that the maximum silver contents should be found in the intermediate zone, with a relatively abrupt transition from the pyritic zone and a more gradual decline into the sideritic zone. These relationships coincide almost exactly with those observed in this study; interestingly, Twelvetrees & Ward's
postulate of maximum silver grades in galena from the sideritic zone is not in accord with the present data or even with the assays which they quoted in their own individual mine descriptions (Table 5).

These observations are significant, since they indicate clearly that systematic zonal variations in trace and minor element geochemistry are not necessarily controlled directly by progressively declining temperatures. Although temperature gradients may exist, they exert only partial control on the physico-chemical environment of ore deposition; as Helgeson (1964) and others have indicated, the actual direct controls of precipitation are equilibrium changes which may depend on such factors as adiabatic expansion of the hydrothermal fluids, reactions with the wallrocks, mixing with circulating groundwaters etc.; the present study suggests that reaction with the earlier hydrothermal minerals may also be of considerable significance. It is clear that geochemical studies are of limited value unless they are accompanied by detailed investigations of mineralogical relationships.
Table 11b

Correlation coefficients for trace elements in galena.

I. Normal co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphal.</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>-.096</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>.253</td>
<td>-.066</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>.026</td>
<td>-.557</td>
<td>.582</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-.251</td>
<td>.487</td>
<td>.060</td>
<td>-.296</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-.365</td>
<td>.750</td>
<td>-.042</td>
<td>-.549</td>
<td>.772</td>
<td>1.000</td>
</tr>
<tr>
<td>Cd</td>
<td>-.316</td>
<td>.140</td>
<td>.077</td>
<td>-.248</td>
<td>.598</td>
<td>.635</td>
</tr>
</tbody>
</table>

II. Logarithmic co-ordinates:

<table>
<thead>
<tr>
<th></th>
<th>Sn</th>
<th>Ni</th>
<th>Mn</th>
<th>Sb</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS in sphal.</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>-.039</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>.019</td>
<td>.321</td>
<td>1.000</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>-.049</td>
<td>-.667</td>
<td>.132</td>
<td>1.000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>-.225</td>
<td>.743</td>
<td>.348</td>
<td>-.337</td>
<td>1.000</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>-.226</td>
<td>.847</td>
<td>.215</td>
<td>-.638</td>
<td>.861</td>
<td>1.000</td>
</tr>
<tr>
<td>Cd</td>
<td>-.246</td>
<td>.422</td>
<td>.199</td>
<td>-.206</td>
<td>.681</td>
<td>.657</td>
</tr>
</tbody>
</table>

Significance levels: 0.1% - 0.72
1.0% - 0.60
5.0% - 0.48
PARTITION OF TRACE ELEMENTS

Some recent studies have examined the thermometric significance of partition coefficients for various trace elements distributed between co-existing mineral phases. Although few experimental data have yet been published, the trace element contents of the Zeehan minerals were examined to see if any empirical trends could be established. However, since thermodynamic equilibrium between the several phases involved is a pre-requisite for application of this technique, attempts to establish significant regularities were predictably unsuccessful. Of the four minerals studied, textural evidence clearly suggests that in most instances pyrite was not deposited in equilibrium with sphalerite (although sphalerite probably crystallized in equilibrium with pyrite; Barton, Bethke & Toulin, 1963) and sphalerite and siderite did not form in equilibrium with galena. While sphalerite and siderite may have been deposited in mutual equilibrium in some instances, most of the trace elements detected in the latter appear to be due to contamination; manganese is an exception, but it has already been shown that the distribution of manganese between co-existing sphalerite and siderite is dependent on \( \text{CO}_2 \), \( \text{O}_2 \) and \( \text{S}_2 \) fugacities as well as temperature.

Wide ranges of apparent partition coefficients were calculated for most elements and most mineral pairs; the only zonal patterns observed were those arising fortuitously from the
regularities described above. In the particular case of the partition of cadmium between sphalerite and galena, for which some experimental data are available (Bethke & Barton, 1959), the indicated depositional temperatures were frequently inconsistent with elementary geological reasoning.

Similar difficulties were encountered by Rose (1967), and it is apparent that the useful application of partition coefficients to the geothermometry of hydrothermal sulphide deposits must await experimental study of mineral pairs which commonly precipitate together in the paragenetic sequence and therefore offer some possibility of mutual equilibrium relationships. Such mineral pairs include pyrite-arsenopyrite, cassiterite-wolframite, sphalerite-chalcopyrite, chalcopyrite-pyrrhotite and galena-tetrahedrite. Elements which show a strong partitioning tendency towards one of the minerals in any pair under consideration are of limited value unless the analytical difficulties can be overcome by preparation of high purity concentrates or by the successful application of microprobe techniques.
CHAPTER VII : THE QUEEN HILL ORES

Several references have already been made to the unusual ores of the Queen Hill area, immediately to the north of the Zeehan township. These ores do not fit into a simple zonal pattern because of several anomalous features which may be summarised as follows:

1. Deposits in this area vary abruptly from sideritic to pyritic; in at least several instances (e.g. the Oonah and No. 2 Montana Mines) several veins occurring in close proximity differ markedly in their mineralogy, with strongly pyritic types intermingled with others which are relatively strongly sideritic.

2. FeS contents of many sphalerite samples from the Queen Hill area are relatively high, showing a reversal of the regional trend. Again, however, these high-iron sphalerites are intermingled with low-iron varieties more in keeping with the regional zoning. There is a clear tendency for sphalerites from pyritic samples to have higher iron contents than those from more strongly sideritic ore. Sphalerite iron contents range as high as those observed in the pyritic ores of the Comstock district, but even the pyritic samples from Queen Hill contain considerably more siderite than is apparent in samples from the pyritic zone.

3. High FeS contents in sphalerites are not matched, as they are in the Silver Stream - Comstock - Doric area, by
high MnS contents.

4. Tin is relatively abundant in these ores, but is rare or absent from the pyritic zone and from other ores of the intermediate and sideritic zones. Some of this tin occurs as trace constituents of sphalerite and other minerals, and appreciable contents of trace tin are confined largely to ores from this area.

5. Of the minerals in which tin occurs as a major constituent, stannite predominates in the Queen Hill area, but is rare or absent elsewhere in the Heemskirk and Zeehan fields. A small proportion of the tin occurs as cassiterite, much of which, however, is "needle tin" produced by breakdown of stannite.

6. Where primary cassiterite occurs in the Queen Hill ores, it is accompanied by small amounts of wolframite and bismuthinite. This assemblage only occurs elsewhere in the district in the tin ores of the Heemskirk Granite "zone".

Some account has been taken of these features in previous descriptions of the zonal relationships. Twelvetrees & Ward (1910) mapped an incursion of their Pyritic Zone into the Queen Hill area, but did not explain the anomalous tin mineralization, which is not a feature of other pyritic ores. Both (1966) drew attention to a high FeS content measured on a sphalerite sample from the Stormsdown Mine and, in view of the
unusual mineralogy, suggested that these ores may reflect a vertical rather than a horizontal zoning (as implied by Ward, 1911), possibly due to "a cupola-type of development of the granite in...this part of the field".

This explanation may be close to the truth, but in this simple form it does not adequately explain the low MnS contents, the occurrence of some sideritic veins, and the low FeS contents of sphalerites within them, or the abundance of stannite. The mere presence of a cupola of the Heemskirk granite beneath the Queen Hill area would be expected to produce veins whose mineralogies resembled those of the Granite Zone or of the Pyritic Zone, as typified by the Comstock ores, if spatial relationships alone are considered.

If, however, the "cupola" is interpreted as a second intrusive or mineralization phase, emplaced in this area some time after a broad regional zoning had been established around the main body of the Heemskirk Granite, then simple explanations can be found for all the anomalous features. These are thought to have arisen from superposition of a second mineralization on an initially zoned hydrothermal vein system, within a region of the latter characterised by abundant siderite and probably near the boundary between the intermediate and sideritic zonal types.

Sphalerite geochemistry (possibly having geothermometric significance) and vein mineralogy suggest that the second
mineralization may also have been zoned, about a centre in the Stormsdown – Poverty Point region; the dark arrows of Fig. 45 show proposed directions for the horizontal component of the zonal gradient of the second phase, contrasted with the corresponding gradient of the first phase which is represented by open arrows. In both cases the postulated directions are based on systematic mineralogical and geochemical changes; they may represent directions of flow of the mineralizing solutions, progressive changes in temperature and pressure, changes in ore solution chemistry or, most probably, combinations of all three.

These relationships are shown schematically in the block diagrams of Fig. 47; the corners of the blocks coincide approximately with the points marked 1 – 4 in Fig. 45. In Fig. 47, the superimposed zoning is attributed to a separate intrusion beneath the Queen Hill area, which is one possible explanation of the observed relationships. The actual presence of this intrusion is purely hypothetical, although, as noted previously, there is some geophysical evidence for a rise in the sub-surface granite profile in this area. It is also possible that no such intrusion exists, but that the second mineralization is zoned around a favoured channelway or system of channelways extending in depth to the granite surface. Rapid flow of hydrothermal fluids along such a system could bring them to this area at higher temperatures than earlier
fluids which migrated more slowly, thus accounting for the high sphalerite iron contents and the presence of tin minerals which normally would have precipitated closer to the parent intrusion.

Although obviously speculative, such hypotheses provide satisfactory explanations for the presence of cassiterite, wolframite and bismuthinite in the Queen Hill area, for the intermingling of sideritic and pyritic veins, and for the high FeS contents of the sphalerites.

The key to the low MnS contents of sphalerites from this area probably lies in the abundance of siderite, which is thought to have been present prior to the second phase of mineralization. Reaction of the latter fluids with the earlier vein minerals would then have had two important effects. Rapid changes in pH of the fluids, due to reaction with siderite, are thought to have triggered a "dumping" of major and trace elements, similar to the telescoping whose effects are observed elsewhere in the trace element contents of galena samples; this would explain the high contents of trace tin, antimony etc. observed in pyrite and sphalerite samples from this area. In addition, leaching of the siderite by reaction with fluids of initially relatively low pH presumably resulted in an effective increase in CO₂ fugacity, possibly to the point where MnS becomes unstable (see earlier discussion) and the manganese is subsequently precipitated as a constituent of siderite rather than sphalerite.
In the absence of appropriate experimental data, the presence of abundant stannite is more difficult to explain with certainty. It is feasible that reaction between tin-bearing fluids and pre-existing sulphides, in the presence of adequate copper, could result in the crystallization of stannite rather than cassiterite, particularly in a relatively reducing environment favouring the stability of stannous rather than stannic tin; significantly, Twelvetrees & Ward record graphitization and pyritization of the wallrocks in the Oonah Mine (1910, pp. 130, 132).

In brief descriptions of relationships in tin ores of the Brass Bottle Mine in Queensland and the Mt. Bischoff Mine in Tasmania, Edwards (1954, p. 191) implied changes in the relative stabilities of the two tin minerals accompanying changes in the chemical environment of ore formation. He noted that "the early deposited non-sulphide gangue consists of quartz and tourmaline, which gave place at a later stage of the mineralization to carbonates. The carbonate solutions tended to dissolve the already formed cassiterite, the tin being re-precipitated as stannite, which formed narrow rims about some of the residual grains of cassiterite". If cassiterite is indeed unstable in the presence of "carbonate solutions", then reaction between the mineralizing fluids and earlier carbonates in the Queen Hill area provides a ready explanation for the relative abundance of stannite. Declining CO₂ fugacity
might then account for the subsequent partial breakdown of some of the stannite to form the "needle tin" variety of cassiterite. These possibilities obviously need further experimental and mineralogical study, particularly in deposits such as those of central Bolivia which commonly contain co-existing cassiterite, stannite and siderite (Turneaure, 1960).
CHAPTER VIII: SUMMARY AND CONCLUSIONS

The present study generally supports the zonal concepts previously outlined by Waller (1904), Twelvetrees & Ward (1910) and Both (1966); several apparent anomalies have been shown to be due to limited displacement of the zones during post-mineralization movement on major fault systems, and to the effects of multiple mineralization in the Queen Hill area. Although the lack of underground exposures has severely hampered complete description of the zonal relationships, the interpretation shown schematically in Fig. 47 is in agreement with the available mineralogical and geochemical data.

Mineralogical and chemical relationships in the Heemskirk-Zeehan area are most conveniently described in terms of four zones, which are crudely concentric within and around the Heemskirk granite intrusive. The innermost zone is characterised by cassiterite-tourmaline mineralization, and is separated by a pronounced spatial break from a pyrite-sphalerite zone with relatively minor galena. This in turn passes eastwards into a pyrito-sideritic zone with abundant galena and then into a sideritic zone in which the ores are frequently of lower grade but contain shoots of high grade lead ore.

With the exception of the cassiterite and pyrite-sphalerite zones, which are more than a mile apart in present outcrop, zone boundaries are transitional and are based arbitrarily on a progressive decline in pyrite abundance and a parallel increase
in siderite. Zonal features are reflected in the minor and trace element geochemistry of the principal ore and gangue minerals, as well as in the distributions of the minerals themselves.

The zonal distributions of the major minerals generally match closely the paragenetic sequences deduced from the microscopic study of textural relationships. Notable exceptions include siderite, which is paragenetically indistinguishable from sphalerite, and the sulpho-salts which are related zonally to siderite, but paragenetically to galena (see below).

Mineralogical aspects of the zoning are summarised in Chapter V; among the most important changes accompanying the progressive decrease in pyrite and increase in siderite are the following:

1. Sphalerite is most abundant in the pyritic and intermediate zones.

2. Siderite is absent or rare in the pyritic zone, but rapidly becomes and remains abundant in the intermediate and sideritic zones.

3. The sulpho-salts, tetrahedrite, bournonite and boulangerite show paragenetic affiliations with galena and are mostly younger than siderite. Their zonal distribution, however, is more closely related to the siderite; their maximum abundance coincides with the first zonal appearance of
siderite as a major gangue constituent. These large scale relationships are also reflected on a micro-scale; sulphosalts inclusions often show pronounced concentration in the vicinity of small patches of carbonates.

4. Arsenopyrite is rare in the western part of the pyritic zone, becomes abundant in the eastern part and in the intermediate zone, and then declines again to relative rarity in the sideritic zone.

5. Paragenetically early marcasite shows a similar distribution to arsenopyrite, except that it does not become abundant until the intermediate zone. However, younger marcasite, formed during the replacement of sphalerite and siderite by galena, extends further westwards, well into the pyritic zone. Marcasite of either type is rare in the sideritic zone; in the "reaction rims" between galena and sphalerite or galena and siderite, pyrite takes the place of marcasite. A third type of marcasite, formed by breakdown of early pyrrhotite, is confined to the pyritic zone.

Geochemical aspects of the zoning have been reviewed in Chapter VI; these include the following:

1. The iron content of sphalerites, although variable at any one locality, shows a clear overall decline from west to east parallel to the probable temperature gradient around the Heemskirk intrusion.

2. Manganese in sphalerite shows a strong positive
correlation with iron in samples from the pyritic zone. However, the manganese content of sphalerite decreases sharply as soon as siderite becomes a major gangue constituent.

3. Both iron and manganese contents of sphalerite show the effects of partial re-equilibration accompanying subsequent veining and partial replacement by paragenetically late galena and quartz. The resulting compositions again show a clear gradient from west to east, parallel to that observed in initial sphalerite compositions. The re-equilibration is often accompanied by the formation of a second generation of pyrite, pyrrhotite and/or chalcopyrite.

4. Of the trace elements detected in pyrite, Co, Ni and Mn appear to show compositional trends related to the zoning, with the contents of Co decreasing and those of Ni and Mn increasing from the pyritic through the intermediate to the sideritic zones. Sb and Ag show no systematic trends.

5. In sphalerite, Co increases markedly, Ag, Sb and Ni show a less clearly defined increase, Cd increases slightly, and Bi shows no change with increasing distance from the intrusive. Sn is concentrated in part of the intermediate zone, but this appears to be due to superposition of a second phase of mineralization within this area, and not to general zonal trends.
6. In siderite, Co contents evidently increase from the pyritic into the intermediate zone and thereafter remain approximately constant. Ni and Mn show no zonal variations, and any variations in Sb, Ag and Cd were obscured by possible contaminations.

7. In galena, Sn, Co, Ni, Sb, Ag and Cd all show a tendency to reach their maximum concentrations in the intermediate zone, coinciding with the first zonal appearance of major siderite gangue. Since siderite is paragenetically earlier than galena, it appears that its presence has exerted a strong control over trace element abundances, or, in some cases, the distribution of contaminating sulpho-salts.

8. Studies of contamination effects suggest that much of the Cd reported in galena and siderite analyses may be due to contamination by sulpho-salts - particularly bournonite - rather than by sphalerite, to which it is conventionally assigned.

The zoning is thought to have arisen as a consequence of temperature and pressure gradients outwards and upwards from one or more parent granitic intrusions; in addition progressive changes in the chemistry of the hydrothermal fluids, due to both sequential precipitation of dissolved components and reaction with wallrocks and/or earlier hydrothermal minerals,
produced systematic mineralogical and chemical changes which accentuated the zonation.

In current European terminology, the mineralization is thought to have been polyascendant, in the sense that there is textural and geochemical evidence for a paragenetic discontinuity between pyrite, sphalerite and siderite on one hand, and galena on the other. Textural evidence for a further possible discontinuity between pyrite and sphalerite-siderite is less convincing. Hydrothermal fluids of the early phase are therefore presumed to have been enriched in tin, copper, iron, zinc, sulphur and carbon dioxide (with the high contents of the latter possibly resulting, at least in part, from extensive assimilation of carbonate-rich sediments); fluids of the later phase were richer in lead, antimony and possibly silver, but were relatively depleted in CO₂.

Various aspects of the mineralogy and geochemistry allow limitations to be placed on some critical physical and chemical parameters. These may be summarised as follows:

1. Temperature: Ore mineral deposition is considered to have taken place over a temperature range between approximately 550°C to less than 100°C. Conclusions in this respect have been largely based on the sphalerite geothermometer; despite recent criticisms of this method, it has been shown that temperatures estimated in this way coincide remarkably closely with those
predicted from the distributions of minerals other than sphalerite. The absence of arsenopyrite from the western portion of the pyritic zone (and the presence there of some pyrrhotite) suggests that crystallization temperatures in that area may have been higher than the upper stability limit for the assemblage arsenopyrite-pyrite, which is approximately 500°C. A 500°C "isotherm", drawn between areas in which arsenopyrite is absent and those in which it is abundant, coincides perfectly with sphalerite temperature ranges estimated from the data of Barton & Toulmin (1966).

Available data on the upper thermal stability limit of siderite, although incomplete, also allow a similar "isotherm" to be drawn between siderite-free and abundant-siderite zones, if it is assumed that the paragenetically unexpected absence of siderite from the western part of the pyritic zone is due to thermal instability. Again this isotherm agrees remarkably well with the temperature ranges estimated from sphalerite compositions.

Primary marcasite intergrown with the coarse-grained, paragenetically early pyrite is largely confined to the intermediate zone and the eastern border of the pyritic zone. As well as limitations on the fluid pH (see below), marcasite requires temperatures below approximately 430°C for its formation. If a line drawn immediately to the west of the known occurrences of such marcasite is therefore assumed to be a 430°C isotherm
rather than a pH limit, close coincidence with sphalerite, arsenopyrite and siderite temperatures is again observed.

Finally, data on the distribution of manganese between co-existing sphalerite and siderite suggests, from the calculations of Holland (1965), that an "isotherm" drawn between areas in which sphalerite contains appreciable concentrations of manganese and those in which it does not corresponds to approximately 300°C. This involves further assumptions concerning the CO₂ fugacity, but it is again apparent (Fig. 53) that the agreement with temperatures estimated from the sphalerite geothermometer is good.

Each of these "thermometers", viz. sphalerite, arsenopyrite, siderite, marcasite and manganese distribution, involves certain assumptions, so that none of them is absolutely valid in its own right. For example, the limited distribution of marcasite might be a function of pH rather than temperature; indeed, it will be shown below that the presence or absence of marcasite can be used elsewhere to assist in tracing progressive changes in pH. However, the combined picture is so singularly free of anomalies that it is difficult to avoid the conclusion that temperature has played a significant part in determining the zonal sequence, and that temperatures estimated from the sphalerite geothermometer, providing they are employed with due caution, are capable of providing considerable information concerning the temperature gradient.
The latter conclusion is in conflict with the results reported from some recent experimental studies (Boorman, 1967; Scott & Barnes, 1967), as are the data from the number of other sphalerite-bearing assemblages. The reason for the discrepancy is not known, but microprobe studies of re-equilibrated pyrite-pyrrhotite-sphalerite assemblages in the Zeehan ores have lent further support to the concept of sphalerite geothermometry and, for the present, the author places greater reliance on the data from natural mineral assemblages. Detailed studies of the geochemistry of sphalerites from massive pyrite-pyrrhotite deposits (e.g. the Quemont deposit), in which chemical parameters such as sulphur fugacity can be more accurately estimated, should prove of considerable assistance in resolving the controversy.

2. **Pressure**: No "geobarometers" are available to enable precise estimation of the confining pressures during the mineralization, or of their possible zonal variations. General geological considerations suggest total pressures of the order of 1 kilobar; errors in this estimate are unlikely to affect estimated temperatures by more than $\pm 25^\circ C$.

3. **Chemical Environment**: Hydrothermal fluids are chemically complex, and a complete description of their composition is obviously impossible. However, the mineralogical and geochemical data allow some limitations to be placed on important variables such as sulphur, $CO_2$ and oxygen fugacities, pH etc., as follows:
**Sulphur fugacity:** Sphalerite occurs throughout the Zeehan field in apparent equilibrium with both pyrite and chalcopyrite; the sphalerite compositions range from approximately 20 mole per cent FeS in the western pyritic zone to the order of 0.1 mole per cent FeS in the south-eastern part of the sideritic belt. These indicate a maximum possible range of sulphur fugacities of from $10^{-2}$ bars in the pyritic zone to less than $10^{-15}$ bars in the sideritic zone. If it is conceded that small fluctuations in sulphur fugacity are more likely to have caused the compositional differences in sphalerite at any one locality than relatively large fluctuations in temperature, then the overall variation in sulphur fugacity during initial sphalerite crystallization could have been as low as $10^{-6}$ to $10^{-8}$ bars (based on the equilibrium relationships determined and extrapolated by Barton & Toulmin, 1966; see Fig. 52). It is not possible to explain the compositional differences between the pyritic and sideritic zones by changes in either temperature or sulphur fugacity alone - each must have declined to some extent.

The zonal change from pyrite to siderite, and the progressively increasing metal:sulphur ratios are both indicative of outwardly declining sulphur fugacities.

During partial re-equilibration accompanying veining and replacement of sphalerite by later galena, sulphur fugacities appear to have been generally higher than those of the FeS-ZnS join at the temperatures concerned, but often did not reach
those of the FeS$_2$-ZnS joins. This permitted the formation of pyrrhotite $\pm$ pyrite, along with an increase in the iron content of the sphalerite. Where both pyrite and pyrrhotite formed as a result of the re-equilibration, both sulphur fugacity and alteration temperature can be determined, at least to a first approximation, from the Barton & Toulmin extrapolations (providing the latter are assumed to be valid). Reasons for accepting the latter extrapolation are discussed in the text, and are presently thought to be convincing.

Compositions of re-equilibrated sphalerites are generally indicative of lower sulphur fugacities than those which obtained during the crystallization of the original sphalerites; the re-equilibration temperatures appear to have been comparable with, or slightly lower than, the original crystallization temperatures and the production of pyrrhotite in the new assemblages clearly necessitates lower sulphur fugacities. Hence it appears that sulphur fugacities declined during mineralization, along both space and time co-ordinates.

**Carbon dioxide fugacity:** The presence of unusually abundant gangue carbonates is *prima facie* evidence for relatively high carbon dioxide fugacities which were, however, not sufficiently high to cause instability of the FeS in the sphalerite structure. Relatively few data pertaining to the stabilities of sulphide minerals as functions of $f_{CO_2}$ have been published. However, the
Thermochemical calculations of Holland (1965) suggest that fugacities of the order of 100 atmospheres must have been required to produce siderite at the temperatures indicated by the compositions of more or less contemporaneous sphalerites, and by the thermal stability of siderite itself. The partial decomposition of the limited amounts of paragenetically early pyrrhotite to marcasite and siderite also indicates, from thermochemical calculations, carbon dioxide fugacities of this order.

On the other hand, the subsequent formation of pyrrhotite during re-equilibration of some of the sphalerites is evidence that the carbon dioxide fugacity was somewhat lower during crystallization of the galena. The partial replacement of siderite by galena, with the formation of "reaction rims" of pyrite and marcasite, is also evidence for a decline in carbon dioxide fugacity between the stages of galena and siderite deposition. The contribution of temperature to the shifts in equilibrium is difficult to evaluate, but, as noted above, it appears that temperature changes between these two stages of the paragenesis were not substantial.

**Oxygen fugacity:** Apart from limitations imposed by siderite-magnetite equilibria, which generally place upper limits on the oxygen fugacity, and the interrelationships of oxygen, sulphur and carbon dioxide fugacities in controlling the relative stabilities of pyrrhotite, siderite and marcasite and/or pyrite, it has
not proved possible to define limiting values for oxygen fugacities in the Zeehan hydrothermal fluids. Generally, however, the observed relationships are consistent with the limitations imposed by the "main line" fields of Holland (1965).

pH: Although considerable effort has already been devoted to the definition of mineral stability fields in terms of pH, most of the results are applicable only at low temperatures. Experimental data on the effects of pH changes on mineral stabilities at high temperatures and pressures are currently limited, as is the present state of knowledge of pH changes in hydrothermal fluids.

As has been noted in Chapter II, it is unlikely that hydrothermal fluids can be either extremely acid or extremely alkaline because of the buffering effects of the wallrocks. At pH's near neutrality at any given temperature, reactions with wallrocks are not likely to be pronounced unless the latter are chemically reactive; unless there is evidence for pronounced wallrock alteration, zonal changes in pH are likely to be very gradual and possibly largely dependent on temperature changes.

If the hydrothermal solutions encounter reactive wallrocks such as limestone (or, in the Zeehan case, early carbonate gangue), changes in the pH may be much more abrupt and may have pronounced mineralogical and geochemical effects. Concentrations of hydrothermal mineralization in the vicinity of "favourable" carbonate host rocks are well known, and the "dumping" of minor
elements such as Ag, Sb, Sn, Ni etc. in the presence of abundant carbonate gangue in the Zeehan veins has been described in Chapter VI. If these effects are at least partly the results of pH changes then, since carbonates are stable in moderately alkaline solutions, the changes were most probably in the direction of increasing pH. Hence it appears that the ore metals were carried in fluids which were initially neutral or slightly acid, and that their precipitation was at least partly controlled by increasing pH as a consequence of reaction with the carbonates.

This qualitative concept is supported by the distribution of marcasite in the Zeehan ores. The absence of marcasite, such as that in sulphide-carbonate "reaction rims", from the western part of the field has already been attributed to the high crystallization temperatures believed to have prevailed in that part of the field. However, the same explanation cannot be invoked to explain the absence of such marcasite from the sideritic zone, where crystallization temperatures are believed to have been well within the marcasite stability field. However, Kullerud (1967) and others have noted that marcasite is only stable in a moderately acid environment; the absence of marcasite from the sideritic zone is therefore indicative of neutralization of initially acid fluids upon substantial proportions of carbonate gangue.

Coarse-grained marcasite, intergrown with paragenetically early pyrite, is also absent from the western part of the pyritic zone and the eastern part of the sideritic zone, but shows a
wider "dispersion" - it extends further both eastwards and westwards than the "reaction rim" type. The easterly transition is more gradual, and cannot be related to any single mineralogical feature such as the presence of gangue carbonates; this is not surprising, since it is paragenetically earlier than the carbonates. It appears that the distribution of this early marcasite is controlled by a more gradual increase in pH, such as might be expected from decreasing temperature, wallrock reactions, or both.

The data of Holland & Borcsic (1965) indicate that the carbonates themselves may have precipitated as a consequence of increasing fluid pH.

Transport of the ore metals: Fluid inclusions appear to be surprisingly rare in the Zeehan ores, and there is no direct way available for determining the form in which the ore metals were transported in the hydrothermal fluids. It is worth noting, however, that the zonal increase in pH postulated above is inconsistent with transport of the metals as polysulphide complexes, since these become increasingly stable with increasing pH. Of the transport mechanisms proposed to date, that of chloride complexes probably comes closest to providing a satisfactory explanation of the observed mineralogical and geochemical relationships, although it poses problems in explaining the transport of
sulphur.

In summary, it appears that the zonal relationships in the Zeehan field reflect progressive decreases in temperature and sulphur fugacity, and increasing alkalinity, in hydrothermal fluids migrating outwards through a system of faults and tension veins developed around an intrusive granite body. As well as the spatial changes, the hydrothermal fluids are thought to have changed with time in source composition, with an initial enrichment in Fe, Sn, Cu, Zn, S and CO$_2$ giving way to relative enrichment in Pb, Sb, and Ag, and a marked depletion in CO$_2$. The effects of the time and space parameters are closely interrelated, and have produced complex mineralogical relationships which require detailed field and laboratory studies for their resolution. The present study has been hampered by inadequate exposures and consequent deficiencies in the sampling, but is believed to have demonstrated that intensive mineralogical and chemical studies of hydrothermal mineral deposits are capable of yielding much valuable information concerning the changing environments of ore deposition, particularly as related experimental studies are extended into the high temperature hydrothermal range.
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