Chapter 6

Time-dependent changes in fluid-rock interaction: an investigation of syntectonic vein microchemistry

6.1 Introduction

Veins in rocks have been studied for well over 150 years, initially driven by interest in how economically mineralised veins formed (e.g. Buckland, 1836; Hulin, 1929). Veins provide information on how fluids migrate through the crust, and how material is transferred by these fluids.

Many studies have suggested that veins (including ‘crack-seal’ textured veins; Ramsay, 1980) form as a result of brittle failure, fracture dilation, fluid infiltration and subsequent mineral precipitation (e.g. Ramsay, 1980; Cox and Etheridge, 1983; Sibson, 1985; Cox, 1987; Urai et al., 1991). However, some recent studies have also suggested that vein formation can occur without fracture, with vein growth driven by diffusional transport of material from the immediately surrounding rock mass (Means and Li, 2001; Wiltschko and Morse, 2001).

The mechanism by which veins form has been increasingly debated over recent years, with argument centered over the necessity for void formation prior to vein growth, and whether veins record advective or diffusive mass transfer in the crust. Different vein textures (e.g. fibrous, elongate blocky, crack-seal, stretched crystal, blocky) form as vein opening and crystal growth kinetics vary (Ramsay, 1980; Cox and Etheridge, 1983; Cox, 1987; Urai et al., 1991; Oliver and Bons, 2001; Hilgers et al., 2001). Some previous workers have suggested that certain vein textures (e.g. fibrous textures) are related to diffusional mass transfer, while other textures (e.g. blocky) are related to advective flow regimes (Bons, 2000; Oliver and Bons, 2001).

Fibrous veins are of particular interest, as they provide a record of progressive displacement paths during vein opening (Durney and Ramsay, 1973). Regularly oriented and spaced inclusion bands across mineral fibres are interpreted to indicate that fibrous and elongate blocky vein textures develop via a crack-seal mechanism (Ramsay, 1980).
Recently, it has been suggested that veins (perhaps even ‘crack-seal’ textured veins) may form without fracture, as a result of growing crystals forcing the wall rock apart in a diffusional mass transfer regime (Means and Li 2001; Wiltschko and Morse, 2001). In addition, different experimental vein growth studies concluded that lateral advection of fluid through fractures and accompanying precipitation of material can lead to inlet clogging and cessation of flow (Lee et al. 1996; Hilgers et al. 2004). These studies call into question the influence of veins (particularly extension veins) on crustal permeability.

In this chapter, I highlight the importance of integrated microstructural observations and microchemical analyses to examine the growth history and fluid chemistry changes accompanying the formation of different textured veins. Within the same vein, trace element concentrations and C, O and Sr isotope ratios have been determined at high-spatial resolution ($\leq 200\mu m$), and are used to determine variations in mineral chemistry. Variations in mineral chemistry are interpreted in terms of variable fluid reservoir chemistry, and the effects of changing fluid-rock reaction along flow pathways during the growth of individual veins.

Previous studies, and calcite precipitation experiments (see Chapter 3) provide a basis for interpreting variations in trace element concentrations and rare earth element patterns measured in natural syntectonic veins.

Section 6.2 reviews mechanisms of vein formation, and the transport and deposition of minerals in different fluid flow regimes is outlined. The following sections (§ 6.4, 6.5, 6.6) describes the internal structure and microchemistry of several different veins.

6.2 Vein formation

6.2.1 Mass transport and deposition

Vein growth requires the transport and precipitation of vein-filling minerals. Transport of material occurs in solution, with precipitation of material occurring when a mineral becomes supersaturated in that solution. Three different mechanisms are suggested for the transport of material (Bons, 2000; Oliver and Bons, 2001):

1. **Diffusional transport** is driven by chemical potential gradients, with material moving through a fluid, which may be stationary or migrating. Diffusion through a fluid is relatively slow, and is most effective over distances of centimetres to decimetres in non-advecting fluid regimes (Etheridge et al. 1984).

2. During **advective transport** material is carried in a migrating fluid. This can occur throughout a permeable rock mass, or within discrete fractures. Advective fluid flow may occur over large distances, and is a very effective material transport mechanism. It has been suggested that elongate-blocky, blocky and crack-seal textures develop in advective flow regimes (Bons, 2000; Oliver and Bons, 2001).

3. **Mobile hydrofractures.** Fluid is contained within the fracture, and both fracture and fluid move at the same time, at the same rate. Transport rates are
6.2. Vein formation

rapid (metres per second), but intermittent. Mobile hydrofractures provide a mechanism for rapid, long distance transport of fluids, during which little or no interaction with the wall rock occurs (Secor and Pollard 1975; Bons 2001b).

Fractures are the most common sites for veins to form. Fractures provide space for mineral precipitation, and high permeability pathways for fluid flow. Precipitation of minerals in fractures may be caused by the following mechanisms:

1. Putnis et al. (1995) argue that a sufficiently low porosity in the rock inhibits precipitation of material. Thus, a pore fluid may become significantly supersaturated until a potential precipitation site is formed (e.g. a fracture). Transport to such a site may occur via diffusion or advective flow.

2. Differences in the fluid chemistry environment between the fracture and wall rock cause a change in the solubility of a vein-forming material. For example, both quartz and calcite solubilities are pressure dependent. If a fracture forms, a low fluid pressure site may be created (e.g. a dilational jog), causing supersaturation and precipitation of minerals.

3. Vein-filling material is derived from an external fluid, which enters the fracture. This fluid becomes supersaturated with respect to the vein-forming minerals. If transport of fluid occurs over significant pressure and/or temperature gradients then the solubility of minerals will change, and precipitation may occur. Additional controls on solubility include oxygen fugacity, partial pressure of CO$_2$, and activities of other chemical components.

Any change in the chemistry of a migrating fluid may change the solubility of a mineral species. This may be achieved by fluid-rock reaction, and/or cooling or depressurisation of fluids. Additionally, the mixing of two fluids may cause precipitation. In more complex fluids, depressurisation may cause phase separation and boiling. This can cause precipitation by lowering the activity of species in solution which are required to complex insoluble species (e.g. Bowers 1991; Cox 1999; Cox et al. 2001; Oliver and Bons 2001).

6.2.2 Vein growth

The mechanisms and processes which control vein growth are a source of ongoing debate (see Durney and Ramsay 1973; Ramsay 1980; Cox and Etheridge 1983; Ramsay and Huber 1983; Cox 1987; Passchier and Trouw 1996; Bons 2000; Means and Li 2001; Oliver and Bons 2001; Wiltschko and Morse 2001; Hilgers et al. 2003; Bons and Montenari 2005 for discussion of proposed mechanisms and controls on vein formation). The shape of crystals within a vein has been used to make inferences about growth direction and relative precipitation rates of minerals. Vein growth may proceed by:

1. Continuous growth of material into a void (opened in a single event, or a vein with an opening speed greater than the crystal growth rate).
2. Repeated fracture opening and sealing by hydrothermal material (*i.e.* the crack-seal mechanism of [Ramsay, 1980]).

During the last decade, several experimental studies have been carried out into vein growth. Studies by [Lee *et al.*, 1996] and [Hilgers and Urai, 2002] have attempted to grow synthetic veins with calcite and alum (KAl(SO$_4$)$_2$.12H$_2$O), respectively. These studies pumped supersaturated solutions through a fracture lined with seed crystals. In general, these studies noted that the fluid inlet site was sealed prior to the vein exit, and cavity space was left in the vein as a result of the entrance sealing. However, in a more recent study, [Nollet *et al.*, 2006] found that more homogeneous fracture sealing could be achieved at higher supersaturations.

Temperature gradients were measured as accurately as possible in the study of [Nollet *et al.*, 2006], to a precision of 0.05 °C or better to monitor absolute temperature and temperature gradients across the reaction cell. Given a reaction cell of 10 mm length (as used in the study of [Nollet *et al.*, 2006]), a normal continental geothermal gradient (25-30 °C km$^{-1}$) equates to a temperature difference of $\sim$0.0003 °C across the reaction cell. Hence, anything less than a homogeneous temperature will cause non-uniform supersaturation, and affect the resulting location and rate of mineral precipitation. This calls into question the extrapolation of these experiments to interpreting how vein formation in the natural environment.

‘Crack-seal’

[Ramsay, 1980] presented evidence suggesting that many extension veins were formed by an accretionary process. Large extension veins were formed by intergrowths of quartz and calcite, with fibres oriented perpendicular to the vein walls. Narrowly spaced ($\bar{x}$ 12 µm) regularly oriented lines of solid inclusions (termed inclusion bands) were found, which were oriented subparallel to the vein walls. Ramsay attributed these features to progressive incremental cracking along the vein-wallrock contacts (forming inclusion bands), followed by precipitation of hydrothermal material (forming quartz and calcite fibres). Hundreds of individual crack-seal increments may be found in a vein of less than 1 cm thickness. The link between hydrothermal material (indicating the presence of a fluid phase), and tensile fracturing led Ramsay to suggest that each crack-seal episode was driven by a rise in fluid pressure.

‘Force of crystallisation’

Work in the early 20$^{th}$ century by [Taber, 1918] demonstrated that fibrous crystals of water soluble salts (*e.g.* gypsum) could be grown by evaporation of salt solution in porous substrates, such as porcelain. More recently, [Means and Li, 2001] carried out a series of simple experiments utilising brine-soaked porous ceramic substrates. They showed that vein-like arrays of parallel, fibrous crystals could be grown by evaporation. Crystal growth occurred via an antitaxial mechanism, with no cracking parallel to the substrate surface. This led [Means and Li, 2001] to question whether fibrous veins are syntectonic (as originally suggested by [Durney and Ramsay, 1973]) or require a ‘crack-seal’ mechanism to form [Ramsay, 1980].
At a similar time, Wiltschko and Morse (2001) presented a theoretical study on the force that a growing crystal exerts on its surroundings. In this model, a supersaturated pore fluid is present, and begins precipitating minerals at sites of opportunity (e.g. pre-existing cracks or detrital crystals). Precipitation begins at the crack wall, and material is added at the base of the growing crystals.

Critical to the model described by Wiltschko and Morse (2001) is that no fluid motion is required (i.e. no fluid transport occurs in the surrounding rocks), and veins are inferred to grow by diffusion of material from the immediately surrounding rocks to the site of precipitation. Wiltschko and Morse (2001) proposed that a supersaturated solution precipitating quartz could induce a stress of up to 300 MPa, which is sufficient to propagate a crack (Jaeger and Cook 1979). From their study, Wiltschko and Morse concluded that banded veins (analogous to the crack-seal veins of Ramsay, 1980) could be produced simply by ‘crystallisation pressure’, with no requirement for fracturing via pore fluid pressure increase, as suggested by Ramsay (1980).

Vein textures and vein growth mechanisms were introduced in §4.4.1, and textures of different veins found in the TVS were examined. In this chapter, vein textures are used to determine the growth history of veins with contrasting textures; a anti-taxial growth fibrous calcite vein (results of which were published as Barker et al., 2006), two laminated bedding-parallel crack-seal veins and a crustiform banded vein. Microchemical analyses have been conducted on these veins to provide a record of temporal changes in fluid-rock reaction and fluid chemistry during the growth of individual veins. In the following sections, the methods used to analyse veins for stable and radiogenic isotope ratios, and trace element concentrations are outlined. Following that, the textures and mineral chemistry of several veins are described. The results are then interpreted in terms of variable fluid flow and fluid-rock reaction during vein growth.

6.3 Methods

6.3.1 Trace element analyses

The spatial distribution of selected minor and trace elements (Si, Mg, Fe, Sr) was investigated by production of electron microprobe maps conducted on a Cameca SX100 at the Research School of Earth Sciences, The Australian National University. A defocused 10 µm beam, set at 15 kV and 100 nA was used. Counts were collected for 200 ms per point, with 20 µm between adjacent points.

Distributions of trace elements were measured in situ by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Samples were analysed using a pulsed ArF Excimer laser (λ=193 nm) and a quadrupole ICP-MS (Agilent 7500s). The sample was moved at a steady speed (∼30 µm s⁻¹) beneath the laser beam, facilitating in situ, high spatial resolution, continuous data collection via a line scan or ‘traverse’ (Eggins et al. 1998). Samples were precleaned with ethanol, and the area chosen for analysis was ‘laser cleaned’ by a laser ablation pre-scan.

Multiple major and trace elements (²³⁵Na, ²⁴Mg, ²⁹Si, ⁴³Ca, ⁴⁴Ca, ⁴⁵Sc, ⁴⁹Mn, ⁵⁷Fe, ⁸⁵Rb, ⁸⁸Sr, ⁸⁹Y, ¹³⁸Ba, ¹³⁹La, ¹⁴⁰Ce, ¹⁴¹Pr, ¹⁴⁶Nd, ¹⁴⁷Sm, ¹⁵³Eu, ¹⁵⁸Gd, ¹⁶³Dy, ¹⁶⁶Er,
174Yb, 208Pb, 232Th, 238U) were simultaneously profiled during laser sampling by repeated, rapid sequential peak hopping, with a mass spectrometer cycle time of 0.65 s. Data reduction followed established protocols for time-resolved analysis (Longerich et al., 1996). High spatial resolution was achieved by using 20 µm spots at 20 laser pulses per second, with a moderately low laser fluence (5 J cm\(^{-2}\)), and by minimising mean particulate residence times in the ablation cell volume following each laser pulse. Internal standardisation is carried out using \(^{43}\)Ca.

For the continuous data traverses, the spatial resolution of data is dependent on the laser spot size and bin interval chosen. A smaller spot and shorter bin interval gives higher resolution, less precise data, while larger spot sizes and larger bin intervals give lower spatial resolution, and more precise results. Commonly, a moving average is used to smooth data.

### 6.3.2 Strontium isotope analyses

Sr isotope compositions were analysed \textit{in situ} by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS). Analyses were carried out using a HelEx ArF excimer laser ablation system, interfaced to a Finnigan MAT Neptune MC-ICP-MS (see Eggins et al., 1998; 2005, for details). These analyses have been performed using both a spot approach (137–233 µm size) and a ‘line traverse’ approach, whereby the sample moved at a steady speed (\(\sim 10\) µm s\(^{-1}\)) beneath the laser beam, facilitating \textit{in situ}, high spatial resolution, continuous data collection (Eggins et al., 1998).

The Finnigan MAT Neptune MC-ICP-MS is equipped with a moveable array of 9 Faraday cups that were located to monitor all Sr isotopes and peak-strip key interfering species (Kr, Rb and REE\(^{++}\)). Faraday cups were positioned to the high mass-side of peak-centres to minimize potential REE\(^{++}\) overlaps following the approach of Ramos et al. (2004, see Table 6.1). The Finnigan Neptunes gas flow and electrostatic lens settings were optimised for maximum Sr sensitivity and peak-shape while ablating a modern \textit{Tridacna} clam shell which has a measured \(^{87}\)Sr/\(^{86}\)Sr value of 0.709143 ± 15 (Woodhead et al., 2005). \textit{Tridacna} was additionally used to monitor reproducibility and accuracy of analyses. For 22 analyses of \textit{Tridacna}, the average \(^{87}\)Sr/\(^{86}\)Sr ratio was 0.709149 ±38 (2\(\sigma\)). All data were obtained using 1.024 s integration periods, for total analysis times of 200 seconds. The ‘traverse’ method has considerably lower analytical precision than spot analyses, due to the shorter period of time spent analyzing each area. For Sr isotope ‘line traverses’, 300 µm moving averages were calculated, accompanied by moving 2 SE variations about the average value.

Data reduction involved subtraction of on-peak baselines, measured every 20-30
minutes (every 5-6 spot analyses), from raw peak intensities. This was followed by correction of instrumental mass fractionation using an exponential law based on the measured $^{86}\text{Sr}/^{88}\text{Sr}$ ratio and a canonical value of 0.1194. Removal of any $^{87}\text{Rb}$ contribution to measured $^{87}\text{Sr}$ was undertaken using the measured $^{85}\text{Rb}$ and mass fractionation factor measured for Sr. Krypton interference was accounted for via stripping of on-peak baselines. REE$^{++}$ interferences were found to be negligible in all measurements.

### 6.3.3 Stable isotope analyses

In this study, high-spatial resolution measurements of stable isotope ratios have been made by (1) conventional stable isotope mass spectrometry on micromilled samples and (2) in situ measurements by laser ablation continuous flow gas chromatograph isotope ratio mass spectrometry (LA-GC-IRMS), following the approach adopted by Sharp and Cerling (1996). In situ stable isotope analyses are spatially precise (i.e., the exact location of an analysis is known), and have a very small sampling volume. However, analytical precision is lower than for conventional analyses (for $\delta^{18}\text{O}$ typically $\pm 0.15\permil$, 1σ).

In comparison, ‘bulk’ micromilling samples a much greater volume of material, meaning that in situ measurements cannot be easily correlated to micromilled isotope measurements, particularly in samples which have complex 3-D geometries (Fig. 6.1). However, this technique has considerably better analytical precision (for $\delta^{18}\text{O}$, typically $\pm 0.04\permil$, 1σ) than in situ laser ablation analyses.

![Comparison of micromilling and laser ablation sampling methods. Shown are increments of approximately 200 µm for micromilling, and laser ablation holes of approximately 200 µm diameter.](image)

**Micromill ‘bulk’ sampling**

An automated milling machine was used to sequentially remove samples over set intervals of either 100 or 200 µm (with a total volume of 1.6 x 4 x 0.1–0.2 mm collected for each sample), yielding approximately 2–4 mg of calcite (Gagan et al.)
High-pressure air was used to remove calcite dust from the mill between each sample to prevent cross contamination.

Oxygen and carbon isotope ratios were measured on a Finnigan MAT 251 mass spectrometer. For each sample, 200 ± 20 µg of powder was dissolved in 103% H$_3$PO$_4$ at 90° in an automated carbonate (Kiel) device. Carbon isotope ratios are reported relative to Vienna Peedee Belemnite (VPDB). Oxygen isotope results are reported relative to VSMOW, and were converted from VPDB values, where $\delta^{18}O_{\text{VSMOW}} = 1.03091 \delta^{18}O_{\text{VPDB}} + 30.91$ (Coplen et al., 1983). The standard deviation (2σ) for the 50 replicate standards used during the analysis of these samples was 0.02 ‰ for $\delta^{13}C$ and 0.06 ‰ for $\delta^{18}O$.

Isotope results have been normalised on the VSMOW and VPDB scales so that analyses of:

NBS-19 $\delta^{18}O_{\text{VPDB}} = -2.20 \, \%_o$; $\delta^{18}O_{\text{SMOW}} = + 28.64 \, \%_o$ and $\delta^{13}C_{\text{VPDB}} = +1.95 \, \%_o$

NBS-18 $\delta^{18}O_{\text{VPDB}} = -23.0 \, \%_o$; $\delta^{18}O_{\text{SMOW}} = + 7.2 \, \%_o$ and $\delta^{13}C_{\text{VPDB}} = +5.0 \, \%_o$

**Laser ablation GC-IRMS sampling**

Protocols for LA-GC-IRMS follow the method outline in Sharp and Cerling (1996). In situ isotope analyses were carried out in the Department of Earth and Planetary Sciences, at the University of New Mexico, under the direction of Prof. Z. Sharp and Dr. V. Atudorei. Briefly, a CO$_2$ laser is fired for a period of 40 ms, at a sample contained in a small ablation chamber, removing a small volume of calcite from the sample surface. Analyses typically sample an area of 150–200 µm diameter. Carbon dioxide released during ablation is carried into a liquid nitrogen cold trap in a continuous He gas flow, where CO$_2$ is frozen. After 5 minutes, the trap is removed from the liquid nitrogen and allowed to thaw, releasing the trapped CO$_2$ into the GC-IRMS (Finnigan Delta XL type).

A reference gas was analysed every 20 minutes to determine mass spectrometer drift. Solenhofen Limestone ($\delta^{13}C = -1.06$, $\delta^{18}O = -4.18$, VPDB) was measured to monitor reproducibility within each analytical session. Standards were measured approximately every 30 minutes, with 4 unknown samples analysed between standards.

The correction procedure for analyses is as follows:

2. Standard and sample analyses adjusted for linear standard drift (if present).
3. Sample values corrected for laser ablation fractionation using constant offset (determined by comparison of conventional and laser ablation analyses).

Mean standard values varied between each analytical session. To enable comparison of different analytical session values, immediately adjacent spots on unknown samples were analysed during multiple sessions. Furthermore, two LA-GC-IRMS analyses were analysed immediately adjacent to ‘bulk’ micromilled analyses on each sample, enabling fractionation produced during laser ablation to be corrected. Isotope fractionation varies as a function of sample density (i.e. crystal structure),
6.4 Microchemistry of an antitaxial, fibrous vein

Results reported in this section was published in Earth and Planetary Science Letters, as “S.L.L. Barker, S.F. Cox, S.M. Eggins and M.K. Gagan, Microchemical evidence for episodic growth of antitaxial veins during fracture-controlled fluid flow, 2006, vol. 250, pp. 331-344”. Sections of this paper including methods and geological background have been edited to avoid repetition of earlier material. A copy of this paper is appended to the end of the thesis.

6.4.1 Geological setting and sample description

The antitaxial fibrous vein (sample TS-20) described here occurs within the Cavan Bluff Limestone. This section focuses exclusively on the internal structure and chemistry of a subvertical bedding-parallel extension vein, which is approximately 1–1.5 cm thick, and at least 5 m long. The vein occurs around 20 m east of a larger (ca. 150 m long), subvertical, calcite-mineralised fault zone, and associated fault-fracture network (Location 0662860E 6132405N; Fig. 4.1). The vein is composed of calcite, with rare barite fibres also present. It has an asymmetric fibrous texture, with fibres increasing in width from a median line which is present approximately two-thirds of the distance across the vein (Fig. 6.2). Some fibres extend from the median line to wall rock (8–10 mm), with widths increasing from approximately 5–10 µm at the median line to ~ 250 – 300 µm near the vein margin.

Five distinct textural zones (TZ) are evident in hand specimen and thin sections. These zones are parallel to the vein walls (Fig. 6.2), and are characterised by variations in calcite colour, cathodoluminescence and/or fibre orientation and thickness. Textural zone 1 comprises a very thin zone (~150–200 µm) immediately adjacent to the wall rock, and has the brightest colour in cathodoluminescence (CL). Textural zone 2 is 0.5–1 mm thick, and has the brightest CL intensity (distinctly different to TZ1, see Fig. 6.2). Textural zone 3 is two mm thick, has moderate CL intensity, and fibres have a slightly different orientation (~ 5°) to those in TZ 2. Textural zone 4 is 5 mm thick, and together with TZ 5 (5 mm thick) forms the oldest part of the vein. TZ 4 and 5 have asymmetric microstructures, with TZ 5 developing thicker fibres than TZ 4.

This vein matches the strict definition for fibrous veins outlined in Oliver and Bons (2001), and has an antitaxial growth morphology, with the oldest material at the median line, and the youngest material at the vein margin (Durney and Ramsay, 1973; Bons, 2000; Oliver and Bons, 2001). Polished thick and thin sections were made perpendicular to bedding, and parallel to the fibre long axes. Trace element and isotopic analyses were conducted on the immediately adjacent polished thick
6. Temporal changes in fluid-rock reaction using vein chemistry

Table 6.2: Average $^{87}$Sr/$^{86}$Sr and 2 $\sigma$ errors for each textural zone determined from spot analyses.

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Textural Zone</th>
<th>Average $^{87}$Sr/$^{86}$Sr</th>
<th>±2 SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spot (TS20-01)</td>
<td>2</td>
<td>0.70828</td>
<td>0.00002</td>
</tr>
<tr>
<td>Spot (TS20-02)</td>
<td>2</td>
<td>0.70831</td>
<td>0.00006</td>
</tr>
<tr>
<td>Spot (TS20-03)</td>
<td>3</td>
<td>0.70812</td>
<td>0.00003</td>
</tr>
<tr>
<td>Spot (TS20-04)</td>
<td>3</td>
<td>0.70815</td>
<td>0.00003</td>
</tr>
<tr>
<td>Spot (TS20-05)</td>
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<td>0.00003</td>
</tr>
<tr>
<td>Spot (TS20-06)</td>
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<td>0.00002</td>
</tr>
<tr>
<td>Spot (TS20-07)</td>
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<td>0.00003</td>
</tr>
<tr>
<td>Spot (TS20-08)</td>
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<td>0.00003</td>
</tr>
<tr>
<td>Spot (TS20-09)</td>
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<td>0.00004</td>
</tr>
<tr>
<td>Spot (TS20-10)</td>
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<tr>
<td>Spot (TS20-11)</td>
<td>4</td>
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<td>Spot (TS20-18)</td>
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<td>0.70822</td>
<td>0.00003</td>
</tr>
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</table>

section from which the thin section was cut (illustrated in Figure 6.2).

6.4.2 Results

In the following section, results from the various chemical analyses are described. Variations on all scales are considered; fine scale ($<0.1–0.5$ mm), textural zone scale (0.5–5 mm) and over the whole vein. Potential causes for chemical variation are discussed in section 6.7.

Isotopes

The measured $^{87}$Sr/$^{86}$Sr ratios (and associated analytical errors) across the vein are shown in Figure 6.3. Strontium isotope ratios change significantly across the vein, with $^{87}$Sr/$^{86}$Sr ratios highest in TZ 2, and lowest in TZ 3. The most significant change is observed between textural zones 2–4, with TZ 4 and 5 being indistinguishable (Table 6.2, Fig. 6.3). The $^{87}$Sr/$^{86}$Sr ratio varies between 0.70812 and 0.70831. Textural zones 2 (average $^{87}$Sr/$^{86}$Sr=0.70829), 3 (average $^{87}$Sr/$^{86}$Sr=0.70815) and 4 (average $^{87}$Sr/$^{86}$Sr=0.70823) have different Sr isotope ratios (Fig. 6.3).

Values in vein calcite of $\delta^{18}$O and $\delta^{13}$C vary systematically with distance through the vein (Figure 6.4). Values of $\delta^{18}$O range between 17.0 $\%$ and 18.8 $\%$. The $\delta^{18}$O values are lower than those in the proximal host limestones (which are typically 19–21 $\%$). In comparison, $\delta^{18}$O in the distal limestones (more than 50 m from a major fault zone) is $\sim$23–25 $\%$. In Tzs 4 and 5, oxygen isotope ratios are most depleted immediately adjacent to the median line, and generally increase with decreasing age toward the vein margins. Notably, the oxygen isotope profiles on either side of the median line are distinctly asymmetric. With decreasing age in TZ 5, $\delta^{18}$O values become less depleted than at an equivalent distance from the median line in TZ 4. At the transition between Tzs 3 and 4, $\delta^{18}$O decreases from $\sim$17.5 $\%$ to 17 $\%$. 
Figure 6.2: Summary of textural zones in antitaxial vein calcite from the Murrumbidgee Group, New South Wales, Australia. (a) Polished thick section. The median line (ML, dotted) and five textural zones (TZ, dashed) are described in the text. Arrow indicates barite fibre within calcite. Note that wall rock on the lower side of the vein was removed during sample preparation. The red box indicates the approximate area in which Sr isotopes and trace elements were analysed by laser ablation (LA-ICP-MS). Carbon and oxygen isotopes were analysed along a sampling transect located immediately to the right of this box. (b) Polished thin section from sample area shown in (a). The boundaries between textural zones TZ1, TZ2 and TZ3 have not been marked to enable them to be seen more easily. (c) Cathodoluminescence photomicrograph of area ‘c’ shown in (b). Different textural zones have different luminescence. Note micron-scale and spatial precision of laser ablation analyses (LA-ICP-MS), which enable different textural zones to be individually sampled.
Oxygen isotope values reach their lowest point at the boundary between TZ 2 and 3, and increase toward the vein wall-rock boundary from 17 ‰ to 18.2 ‰ within TZ 1. Within each textural zone (particularly zones 4 and 5), oxygen isotope ratio changes are not monotonic, and positive and negative excursions of ± 0.3–0.4 ‰ from the general trend occur over distances of < 0.5 mm. The sampling method leads to smoothing of isotopic ratios due to the coarse sampling size employed.

Values of δ¹³C vary between -4.46 ‰ and 1.63 ‰. Carbon isotope values are similar throughout textural zones 4 and 5, with a slight decrease (about 0.5 ‰) with decreasing age from the median line in textural zone 5. There is no comparable decrease with distance from the median line in TZ 4. In textural zone 3, δ¹³C values generally decrease with decreasing age toward the vein-wall rock interface, from values of ca. 1 ‰ to -4 ‰, although there are departures from this trend in TZ 2 and near the boundary of TZ 3 and TZ 2. In comparison, the host limestones δ¹³C are between -1 and +3 ‰.
6.4. Microchemistry of an antitaxial, fibrous vein

Figure 6.4: Calcite $\delta^{13}$C (relative to VPDB) and $\delta^{18}$O (relative to VSMOW) as a function of distance from the median line of the vein. Spatial resolution is 100 µm. Note asymmetry of $\delta^{18}$O about the median line, and significantly lower $\delta^{13}$C values in TZ 1-3.

Trace elements

Trace element uptake by calcite varies as a function of precipitation rate, temperature, solution chemistry, crystal morphology and crystal growth rate (see Dromgoole and Walter 1990; Watson, 2004). Here, variations in selected trace and REEs are outlined. These results are further discussed and interpreted in §6.7.2. Electron microprobe maps and LA-ICP-MS analyses showing the distribution of Sr, Fe and Mg across the vein at two different locations (separated by 5 mm) are shown in Figure 6.5a. In the grey scale EMP maps, lighter colours represent areas of higher concentration. The wallrock-vein boundary is marked by a transition from high Si to low Si concentrations. The major textural zones can be distinguished by the concentrations of Fe and Sr. Strontium concentrations are highest in TZ 1, lowest in TZ 2, and are then relatively homogeneous excepting high spatial-frequency oscillations throughout the rest of the vein. An apparently late, crosscutting band of high Sr calcite occurs within TZ 5 (point ‘α’ in Figure 6.5a). Fe concentrations decrease with decreasing age in TZ 4 and 5, and drop markedly in TZ 3. In TZ 3 and 4, some adjacent fibres, which are interpreted to have grown at the same time, have distinctly different concentrations of Mg, Fe and Sr (Fig. 6.5a). Iron, Sr and Sc concentration changes can be correlated well between traverses, while Mg shows significant differences.

Key features indicated by the line profiles are:

1. Significant fluctuations (up to several thousand ppm) are shown by all elements on scales of < 1 mm.

2. TZ 1 has higher concentrations of Sr, Mg, Y, Sc, and the HREE than the other textural zones.

3. TZ 3 has generally lower concentrations of Fe than other parts of the vein.
Figure 6.5: (a) Electron microprobe maps of iron, magnesium and strontium across the vein. Accompanying 150 µm moving average LA-ICP-MS profiles are shown for Fe, Mg and Sr (traverse 1 is solid black, traverse 2 is dashed). Note that LA-ICP-MS profiles are separated by approximately 5 mm along the vein, and cross several different fibres. Fine-scale (<1 mm) heterogeneity of trace element concentrations are apparent, while broader trends correlate with the different textural zones. Point ‘α’ refers to an crosscutting, apparently late, high Sr region. (b) Comparison of traverse shown in (a) with profile along a single fibre (150 µm moving average). Note broad-scale agreement between profiles, with significant fine-scale variation.
6.4. Microchemistry of an antitaxial, fibrous vein

4. Within TZ 4 and 5, the highest concentrations of Yb, Sc and HREEs occur immediately adjacent to the median line.

5. Trace element and REE concentration profiles are generally asymmetric about the median line in TZ 4 and 5.

An analysis of a single fibre extending across TZ 1 to 4 shows similar variations for Fe and Sr as observed for the traverse carried across the vein (which sampled several fibres; Fig. 6.5b). Trace and REE concentrations vary significantly along this single fibre.

Trace and rare earth element concentrations vary on all scales. On the finest scale (between adjacent data points; 30 µm) Fe concentrations typically change by between 5 and 50%. Over larger distances (0.2–0.5 mm), there are systematic changes in the concentrations of all minor and trace elements analysed. For example, Fe concentrations change by more than 1000 ppm with decreasing age in TZ 4. Rubidium has concentrations at or near detection limits (< 0.5 ppm) throughout the calcite vein. Yttrium, Sc and the heavy REEs (Yb and Lu), show similar behaviour across the vein, with highest concentrations immediately adjacent to the median line and in TZ 1. The REE concentrations reported here are similar to those reported for calcite in filled fractures by Lee et al. (2003).

The REEs can provide information on fluid chemistry (e.g. complexing species) and oxidation state (Bau and Moller, 1992). Graphs of Ce/Ce* and Eu/Eu* are presented in Figure 6.6. Values of Ce/Ce* have an average of 1.05–1.1 throughout much of the vein. Values of Eu/Eu* are more variable, with changes of up to 0.5 from an average value of ~ 1.1. However, in TZs 1–3, Eu/Eu* values change markedly, and reach their lowest values (ca. 0.6). Over the same region of the vein, Ce/Ce* values increase to 1.3. Generally, Ce/Ce* and Eu/Eu* ratios are covariant, with an opposite sense of variation (i.e. an increase in Eu/Eu* is accompanied by a decrease in Ce/Ce*).

In addition to information on oxidation state, normalised REE patterns in calcite may provide information on changes in REE complexation in the parent solution, particularly changes in [CO$_2$] (see § 3.2.1, Fig. 3.1). Rare earth element concentrations were normalised to chondrite. The slope (atomic number plotted against normalised REE value) and regression coefficient of normalised REE patterns was calculated at 30 µm intervals across the vein (in the same manner as other elemental concentrations are plotted as distance versus concentration). All REE slopes are negative (indicating relative LREE enrichment) and generally linear (average $r^2$=0.86). The spatial distribution of slopes across the vein is presented in Figure 6.7. Over small distances (< 0.5 mm) slopes are highly variable, in a similar manner to the trace element concentrations. The distribution of REE slopes about the median line is distinctly asymmetric. In TZ 3, slopes decrease, indicating relative enrichment in the HREE. Textural zones 1 and 2 are distinctly enriched in the HREE, Y and Sc.
**Figure 6.6:** Cerium (Ce/Ce*) and europium (Eu/Eu*) anomalies as a function of distance from the median line of the vein (determined from LA-ICP-MS analyses, 150 µm moving average). The δ¹³C profile (from Fig. 6.4) has been replotted for comparison with the LA-ICP-MS analyses. Note the relatively high Ce/Ce* ratios, low Eu/Eu* ratios, and low δ¹³C values in TZ 1-3.

**Figure 6.7:** Plot of slope of chondrite normalised REE pattern (see text for explanation) as a function of distance from the median line (150 µm moving average). Note high-frequency oscillations and enrichment in heavy rare earth elements (HREEs) in TZ 1-3.
6.5 Microchemistry of laminated crack-seal veins

6.5.1 Introduction

In this section, the setting, texture and chemistry of two bedding-parallel, laminated veins are described. These are ‘crack-seal veins’, whereby veins grow by episodic fracturing and sealing by hydrothermal mineral precipitation (Ramsay, 1980). As such, the chemistry of calcite formed during crack-seal episodes provides insights into how fluid source, fluid pathways and fluid chemistry vary during successive permeability enhancement and destruction events.

These inferences are made via the integrated use of in situ strontium isotope analyses, in situ and milled stable isotope analyses and in situ trace element analyses.

6.5.2 Sample descriptions

This section provides a brief description of the setting and internal fabrics of two bedding-parallel laminated veins (BPVs), using the terminology of Koehn and Passchier (2000, see Fig. 4.15).

Sample ‘SM1’ is a piece of a gently dipping (~ 20°) BPV, found within the Spirifer yassensis Limestone. The vein occurs on the western limb of the ‘Shark’s Mouth’ anticline, and outcrops for approximately 30 m down dip (Location 0665701E 6128869N; Fig. 4.1). Macroscopically, the BPV has multiple (tens to hundreds) of inclusion bands, which lie subparallel to bedding. In some places within the vein, crack-seal bands occur between inclusion bands. However, these bands occur sporadically along the vein, and are isolated in localised regions (e.g. < 10 cm).

Sample ‘BPS’ formed part of a block of partly recrystallised BPV found in the Cavan Bluff Limestone, near the large fault-fold complex illustrated in Figures 4.11 and 5.10 (0662830E 6132470N). White calcite cross-cuts laminations, and may have a secondary origin. Preserved within the vein are two bounding surfaces. One surface is marked by a sliver of wall rock, the other surface is defined by a lamination, and a layer of white calcite. Between these two surfaces lie multiple crack-seal bands. Crack-seal bands are separated by intervals of 100 µm to 1.5 mm, and typically show a sigmoidal shape.

In thin section, inclusion bands are typically spaced at intervals of 0.5 to 2 mm. Crack-seal bands are spaced at intervals of approximately 500 µm (normal to the crack-seal band). However this spacing ranges between about 200 µm and 2 mm (Fig. 6.8).

Calcite fills the majority of space between inclusion and crack-seal bands. Pieces of wallrock are also found, and are identified by their irregular shape, mineralogy, texture and dark appearance in thin section. Inclusion and crack-seal bands are composed dominantly of muscovite and/or illite, with minor calcite and accessory rutile, albite and quartz. Wallrock inclusions are mainly calcite, with lesser muscovite and quartz, and accessory rutile. Individual calcite crystals are large, up to 1 cm in size, and single crystals contain multiple crack-seal bands and inclusion bands.

Each crack-seal band is interpreted to develop as a result of a single fracturing and subsequent sealing event. Hence, the small section (4 cm) of the BPV shown
Figure 6.8: (a) ‘Shark’s Mouth Anticline’. The bedding-parallel slip vein occurs on the lower left of the anticline. Photo in (b) is of the area covered by the red rectangle. (b) Part of BPV with obvious inclusion bands. Notebook is 15 cm wide. (c) Thin section of sample ‘SM1’ with obvious inclusion and crack-seal bands.
in Figure 6.8 represents ~ 50 separate fracturing events. Laminations (inclusion bands of Koehn and Passchier, 2000) develop as continued shearing on outside of veins localises along existing laminations (Fig. 4.15). A 30 cm wide bedding-parallel vein may contain many thousands of laminations and crack-seal bands, and thus requires thousands of separate fracturing and sealing episodes to form. This suggests a prolonged history of formation for these veins, involving numerous, episodic, low displacement events. Bedding-parallel veins formed relatively early during folding of the Murrumbidgee Group as a result of flexural-slip along bedding planes (4.5). The chemistry of laminated bedding-parallel veins is of particular interest, because they are formed by multiple failure events during sequential vein growth, resulting in a long history of fluid chemistry being recorded in these veins. Unfortunately, it is not possible to determine the younging direction within laminated veins. Thus, it is not feasible to infer how calcite chemistry evolved progressively forwards or backwards in time, but simply that calcite chemistry changed during multiple crack-seal events. Lee et al. (1997) and Lee and Wiltschko (1999) described the internal structures of laminated calcite veins from a dilatant jog on a normal fault, which appear texturally similar to bedding-parallel veins described in this study. In the earlier study, Lee et al. (1997) measured stable carbon and oxygen isotope ratios, and trace element concentrations in host rock inclusions and calcite within laminated veins. They concluded that δ¹⁸O variation within veins was primarily due to variable fluid temperature.

6.5.3 Results

Isotopes

Strontium isotope ratios were measured in situ on sample SM1 by laser ablation MC-ICP-MS, and ⁸⁷Sr/⁸⁶Sr vary between 0.70827 and 0.70843. This is generally higher than ⁸⁷Sr/⁸⁶Sr ratios for host rock carbonate, which vary between 0.70815 and 0.70828 (Table 5.1). Measurements were made within two inclusion layers, and across multiple crack-seal layers. Average Sr isotope ratios are identical within the two separate inclusion layers. However, differences are observed between some crack-seal layers at the 2σ confidence level (Fig. 6.9). Strontium isotope values change in both a relatively smooth manner (e.g. first three ‘blue’ analyses in Fig. 6.9) and a stepwise manner (e.g. first five ‘red’ analyses in Fig. 6.9). In any one direction within either inclusion layer, there is no systematic increase or decrease in ⁸⁷Sr/⁸⁶Sr.

Stable isotope measurements were made on SM1 using two different techniques; micromilled sampling followed by conventional phosphoric acid analysis, and in situ, laser ablation GC-IRMS mass spectrometry. Figure 6.10a shows the results of samples collected over 100 µm intervals from within a single inclusion layer. These samples were collected from multiple crack-seal layers (Fig. 6.10b), and, due to the sampling technique, material from groups of 3–4 crack-seal layers were mixed in each analysis. δ¹³C decreases from 0.3 ‰ to 0.2 ‰, and δ¹⁸O decrease from 21.7 ‰ to 21.5 ‰. The mixing of several crack-seal layers in each micromilled analysis makes it impossible to determine if any significant differences occur between individual crack-seal layers. However, in situ analyses indicate that small, but analytically sig-
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Figure 6.9: Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) and associated 2 SE for in situ laser ablation MC-ICP-MS analyses across multiple crack-seal layers in bedding-parallel vein, SM1.

Significant differences occur between inclusion layers (Fig. 6.10c,e), with values varying between 20.3 ‰ and 23.7 ‰.

Variations across crack-seal layers are small, and similar to the degree of change within individual crack-seal layers (Fig. 6.10d,e). Vein carbon isotope ratios (0.2–0.3 ‰, VPDB) are indistinguishable from surrounding host rocks (−1 to +3 ‰, VPDB). Vein oxygen isotope ratios (20.3–23.7 ‰, VSMOW) are generally lower than values for unaltered host rocks (23–25 ‰, VSMOW). These in situ results confirm earlier ‘bulk’ sampling oxygen isotope ratios reported in Cox [2007], which reveal that nonmonotonic stable isotope variations occur within bedding-parallel veins, between a narrow range of isotope values.

Trace elements

Figure 6.11 shows the edge of two inclusion bands in sample SM1, between which lies an inclusion layer containing multiple crack-seal layers. Three separate calcite crystals lie within the area of the photomicrograph, and may be differentiated by changes in colour, as well as twin density and orientation. Electron microprobe maps and LA-ICP-MS analyses showing the distribution of Sr, Fe and Mg across twenty crack-seal bands are shown in Figures 6.11 and 6.12. Crack-seal and inclusion bands are marked by high Si, consistent with the silicate minerals identified during SEM examination.

Strontium (and to a lesser extent Mg and Fe) show distinct zoning both between different crack-seal layers, and within individual crack-seal layers. For example, layer
Figure 6.10: (a) Milled stable isotope results from SM1. Samples were collected over 100 µm intervals. Error bars are 1σ. (b) Schematic showing the scale over which milled samples were collected. Bands are individual crack-seal bands such as those labeled in Fig. 6.8c. Red line (3.2 mm long, 100 µm wide) represents the total size of a single milled isotope sample, with samples progressively collected horizontally over 100 µm intervals. (c-e) δ¹⁸O (‰, VSMOW) results from laser ablation analyses within and across several sets of inclusion and crack-seal bands. Red spots show the location of laser analyses. Analytical uncertainty is ±0.17 (1σ).
‘α’ in Figure 6.12 has distinctly higher Sr concentrations, and somewhat higher Mg and Fe concentrations than the adjacent crack-seal layers. However, several distinct, sharply differentiated high and low Sr zones occur within layer ‘α’, and within several other layers (particularly toward the right hand side of electron microprobe maps shown in Fig. 6.11). Some zones terminate against crack-seal bands (e.g. zones in layer ‘α’ in Fig. 6.11), while other zones cut across crack-seal bands. For example, trace element zones in band ‘β’ terminate against the crack-seal band to the left of ‘β’, but continue across the crack-seal band to the right of ‘β’.

Laser ablation ICP-MS traverses were carried out over a section of the EMP maps. Figure 6.12 shows profiles of Mg, Fe, Sr, Sc (all 20 µm resolution) and Eu/Eu* and Ce/Ce* (smoothed by 300 µm moving average) along the red line marked in Figure 6.12. Strontium concentrations are between 3000 and 6000 ppm, while Fe concentrations vary between 3000 and 5000 ppm, with peaks of up to 7000 ppm occurring. Ce/Ce* and Eu/Eu* ratios show significant variation, particularly within individual crack-seal layers. For example, in ‘α’ layer, Eu/Eu* ratios change from ca. ten to two across the layer. Ce/Ce* and Eu/Eu* anomalies generally vary inversely to one another. For example, in band ‘α’ and immediately adjacent bands, the highest Eu/Eu* occur with the lowest Ce/Ce* (correlation between Eu/Eu* and Ce/Ce*; r² = −0.64). However, within some crack-seal layers, Eu/Eu* and Ce/Ce* show a poor correlation.

Laser ablation traverses agree well with the zoning observed in EMP maps. For example, in band ‘α’, the LA traverse travels across 3 distinct Sr concentration bands visible in the Sr EMP map. These zones are clearly visible in the laser ablation data. Concentrations change by ∼ 2000 ppm across these zones. Notable in
Figure 6.12: Results of LA-ICP-MS analyses showing concentrations of Mg, Fe, Sr, Sc and Eu/Eu* and Ce/Ce*. Blue dashed lines mark the location of crack-seal bands. The region between each crack-seal band is a crack-seal layer. ‘α’ and ‘β’ refer to specific crack-seal layers described in the text and Fig. 6.11.
the laser ablation traverses are fine-scale (\(< 100 \mu m\)) variations in trace element concentrations. For example, Sr concentrations vary by 2000–3000 ppm over distances of \(< 100 \mu m\), similar to variations described by Wogelius et al. (1997), and the changes in trace element concentrations noted in synthetic calcite in §3.4.3.

On larger distance scales (0.2 to 1 mm), systematic changes in trace element concentrations occur, which can be related to zones noted in EMP maps. Some crack-seal bands (e.g. ‘α’ and ‘β’ in Fig. 6.12) have Mg, Fe and Sr concentrations which are distinctly different to the immediately surrounding bands. However, concentration changes within individual crack-seal layers are as significant as concentration changes between different crack-seal layers.

Figure 6.13a shows a scan of a thin section of sample BPS. Electron microprobe maps and LA-ICP-MS analyses showing the distribution of Sr, Fe, Mg, as well as Ce/Ce* and Eu* across multiple crack-seal layers are shown in Figures 6.13b and 6.14. Crack-seal bands are marked by high Si and Fe, consistent with the presence of silicate and iron oxide minerals observed in these bands.

Zoning of trace elements is apparent within these veins, although zoning appears random, and does not relate to changes in vein microstructure. Patches of high Sr are observed in the vein. Electron microprobe EDS analysis suggest that these patches are strontianite (SrCO$_3$).

Three parallel laser ablation ICP-MS traverses were carried out parallel to the vein walls. Results of these analyses are presented in Figure 6.14. Results have been normalised to the same distance scale, using the position of crack-seal bands as markers. Significant, fine-scale (\(< 100 \mu m\)) variations are apparent, consistent with those found in the EMP maps. Strontium concentrations (median \(\sim 7,600\) ppm) are high in this vein, consistent with high Sr concentrations noted for veins generally in the Cavan Bluff Formation (Fig. 5.6). Iron (median \(\sim 4,200\) ppm) and Mg (median \(\sim 2,400\) ppm) concentrations are similar to SM1, above.

In general, concentrations determined in the three line traverses are in good agreement with each other, particularly over distances of a millimetre (e.g. band ‘α’ in Fig. 6.14) while on fine scales (\(< 100 \mu m\)) significant differences occur. However, some discrepancies occur, particularly where the traverses pass through different calcite crystals (within crack-seal layer ‘β’ in Fig. 6.14).

6.6 Microchemistry of a crustiform-banded vein

6.6.1 Sample description

A fault zone within the Receptaculites Limestone (Location 0665425E 6132082N; Fig. 4.1) is comprised of two oblique, well-developed shear planes. The intersection of these two faults is marked by a region of dense extension veining. The lower fault plane (Fig. 6.15) is formed of grey and white calcite bands (usually 1 to 3 cm thick), which lie subparallel to the walls of the fault plane. Within some larger bands, sub-bands occur, which are thin (typically \(< 1mm\)) bands of alternating grey and white calcite. Most bands are continuous for distances of at least 50 cm, but are crosscut by white calcite bands (typically c. 0.5–1 cm thick), which lie subperpendicular to the vein walls. Crystal terminations indicate that vein growth occurred on both
Figure 6.13: (a) Thin section photomicrograph and sketch highlighting laminations in sample ‘BPS’ thin section. Red lines mark the location of laser ablation line scans, the result of which are presented in Fig. 6.14, and layers ‘α’ and ‘β’ are referred to in Fig. 6.14. (b) Electron microprobe maps showing distribution of Si, Sr, Fe and Mg in sample ‘BPS’ in red rectangular area marked in (a).
Figure 6.14: Laser ablation ICP-MS results from sample ‘BPS’. Dashed, vertical grey lines represent the location of crack-seal bands. Note that results have been scaled on the horizontal axis so that crack-seal bands are at the same location for all traverses. Distributions of Mg, Fe, Sr and Eu/Eu* are shown, and different traverses correspond to the location of line traverses shown in Fig. 6.13. ‘α’ and ‘β’ refer to specific bands described in the text, and are marked in Fig. 6.13.
Calcite has both massive and euhedral textures. Typically, individual bands are composed of either massive or euhedral crystals. Within euhedral crystals, sub-bands are particularly common. Sub-bands often terminate against the edge of the adjacent crystal, but can occasionally be tracked between crystals (Fig. 6.15c). Black bands are composed of fine-grained, opaque inclusions (probable iron oxides) contained in single calcite crystals.

These textures are interpreted as crustiform banding, formed by quasicontinuous deposition of calcite from solution into an open fissure. Sub-bands within euhedral crystals are a zonal texture, thought to develop in response to cyclical chemical changes in the parent solution (Adams, 1920). Repetitive banding is interpreted as developing due to a cyclic process (i.e. fluctuating fluid chemistry) that caused repeated precipitation of calcite. Chemical variations between calcite bands are used here to reveal information on how fluid source and fluid chemistry have varied with time during progressive vein growth.

6.6.2 Results

Strontium isotope ratios were measured in situ by laser ablation MC-ICP-MS. Strontium isotope ratios were measured by means of a continuous traverse parallel to the inferred opening direction of the vein, and cross multiple bands of variably coloured calcite. Strontium isotope measurements were made immediately adjacent to where milled stable isotope samples were collected. Ratios of $^{87}$Sr/$^{86}$Sr vary between 0.7081 and 0.7084, which exceeds the range of host rock carbonate $^{87}$Sr/$^{86}$Sr compositions (0.70815–0.70828, Table 5.1).

Figure 6.16b shows the Sr isotope results. Plotted is a 300 µm moving average, with associated 2σ errors across the vein. Several bands contain higher Rb concentrations, resulting in higher and extremely variable $^{87}$Sr/$^{86}$Sr and large errors. Between 0 mm (marking the start of analysis) and 15 mm, $^{87}$Sr/$^{86}$Sr show little variation, with an average value of 0.70825. This is essentially the same as the host Receptaculites limestone $^{87}$Sr/$^{86}$Sr composition (0.70821 ± 0.00003). However, between 15 and 20 mm an increase in $^{87}$Sr/$^{86}$Sr from ~ 0.70815 to 0.70835 occurs. This is followed by a sharp decrease between 24 and 28 mm, from 0.70835 to 0.70815. Variations in $^{87}$Sr/$^{86}$Sr are broadly coincidental with changes in calcite colour. Notably, variations in $^{87}$Sr/$^{86}$Sr on the order of ±0.0001–0.00015 occur on a scale of 0.5 mm. These changes are significant at the 2σ level (Fig. 6.16c).

Oxygen isotope ratios ($\delta^{18}$O) vary between −1 and +6‰ (VSMOW), and carbon isotope ratios ($\delta^{13}$C) vary between −1.5 and +0.5‰ (VPDB). Changes in $\delta^{18}$O are coincident with changes in vein texture, with large excursions in $\delta^{18}$O occurring between different calcite layers. No significant fine-scale isotopic variation occurs within the region of zonal texture (labeled in Fig. 6.16), and $\delta^{18}$O values are low (~ 0‰) in this area. Changes in C and O isotope ratios are generally not covariant. Carbon isotope values are similar to host rocks in the Murrumbidgee Group, which lie between −1 and 3 %o (VPDB).

A comparison between in situ analyses from a region immediately adjacent to
Figure 6.15: (a) Crustiform vein in outcrop. Note hammer (15 cm long) for scale. (b) Polished slab of crustiform textured vein. Multiple bands of variably coloured calcite are present, some of which have prominent euhedral crystals containing subbanding. (c) Polished thin-section of vein. Note zonal texture and regions of opaque calcite.
6.6. Microchemistry of a crustiform-banded vein

Figure 6.16: (a) Crustiform vein sample from which calcite was milled (bottom of photo). Sr isotope measurements were made parallel to the vein edge. Scale is the same as that given for C and O isotope measurements. (b) Strontium isotope results (300 µm moving average; black line) and associated 2σ error bars (grey) for laser ablation line scan, black bands are the region of elevated Rb. (c) Enlargements of two sections of profile shown in (b) for Sr isotope measurements (300 µm moving average and 2σ error bars). Note that adjacent peaks and troughs are significantly different at the 2σ level. (d) Milled stable isotope results (δ18O filled diamonds, δ13C open circles) from crustiform vein. Samples were collected over 200 µm intervals. Errors are contained within the symbols.
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Figure 6.17: (a) Crustiform vein photomicrograph with individual laser spots and results ($\delta^{18}$O, relative to VSMOW) (b) results from Fig. 6.16 (c) Results from in situ laser ablation stable isotope analyses (same scale as (a) and (b)). Note that milled and in situ results show good agreement.

the location of milled analyses is shown in Figure 6.17. In situ and milled isotope analyses show good agreement, with both $\delta^{13}$C and $\delta^{18}$O showing trends which are very similar between the different techniques.

Two trace element laser ablation traverses are presented in Figures 6.18 and 6.19 which are traverses along a thin section, and adjacent thick section. The traverses were separated laterally by a distance of $\sim$ 5 mm. Notable in the laser ablation traverses are fine-scale ( $< 100 \mu$m) variations in trace element concentrations, similar to those described above for SM1, and in Wogelius et al. (1997) and Barker et al. (2006). Black calcite bands have higher Fe and Mn concentrations, consistent with thin section observation of black opaque grains (inferred to be Mn-Fe oxides) in these bands. These bands are also marked by elevated REE concentrations.
Average Mg concentrations (ca. 2000 ppm) and Sr concentrations (ca. 1750 ppm) are similar in both the crustiform banded vein and in sample SM1. Rare earth element concentrations are considerably lower (< 0.1 ppm) compared to other veins in the Murrumbidgee Group for most of the growth bands in the crustiform vein, excepting the black bands, which have significantly higher REE concentrations.

Mg concentration changes are poorly correlated between the two different traverses. Band ‘α’ is marked by a narrow area with high Sr concentrations, and the region of zonal texture has lower Sr concentrations. Band ‘β’, marked in Figures 6.18 and 6.19 is coincidental with higher Sr concentrations in both traverses. Changes in trace element concentrations are not coincident with changes in stable isotope ratios. Variations in trace element concentrations occur between different growth bands, and within the same growth band.

6.7 Discussion

6.7.1 Variations in fluid pathways during the growth of a fibrous, antitaxial vein

Generally, Sr isotopes are believed not to undergo any significant mass fractionation during most geological processes (Faure and Powell [1972]). Hence, the Sr isotope signature of a fluid will reflect the Sr isotope values of the rocks with which that fluid has equilibrated, and the extent of isotopic exchange along the flow pathway. In this vein, which has very little Rb (< 0.5 ppm) compared to Sr, the $^{87}\text{Sr}/^{86}\text{Sr}$ variations will reflect changes in the Sr isotope signature of the fluid from which that vein formed, rather than any effects of $^{87}\text{Rb}$ radioactive decay. Strontium isotopes can be used to provide insights about the chemistry of the fluid source and/or isotopic exchange along fluid pathways during vein formation. If fluids come from the same fluid source, and have the same degree of fluid-rock reaction (i.e. same fluid flow pathway and flow rate), then they would be expected to precipitate calcite with identical Sr isotope ratios.

In vein TS-20, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios vary between 0.70812 and 0.70831 (Fig. 6.3b). Two analyses of the carbonate component of Cavan Bluff Limestone collected at a distance from major fault zones have $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70828 ± 0.00003 (Table 5.1). Critically, it is the small differences in $^{87}\text{Sr}/^{86}\text{Sr}$ within the vein that reveal how fluid source compositions and/or fluid-rock reaction (and hence fluid pathways) may have varied as the vein grew.

The Sr isotope analyses indicate that small but significant $^{87}\text{Sr}/^{86}\text{Sr}$ changes occur across TZ 1–4. As the vein grew, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios became lower in TZ 3 and higher in TZ 2. These changes indicate that either the fluid pathways or the fluid source changed as the vein grew (Fig. 6.20). The fluctuating $^{87}\text{Sr}/^{86}\text{Sr}$ values suggest that each stage of vein growth (marked by the different textural zones) occurred from a fluid that had reacted with rocks with different Sr isotope compositions. This implies that fracture-controlled flow paths (or the chemistry of fluid reservoirs) changed dynamically with time (Fig. 6.20). The study of Elburg et al. (2002) examined the Sr isotope and trace element compositions of antitaxial fibrous veins.
Figure 6.18: Laser ablation ICP-MS results from crustiform vein thick section (W56). Traverse is over approximately the same location as strontium isotope results, and show Sr, Mg, Fe and La concentrations. Sr and Mg results (grey line is 20 µm data) have been smoothed (black line) using a 300 µm moving average. 'α' marks a black band, and ‘zonal’ marks the region of zonal texture.
Figure 6.19: Laser ablation ICP-MS results from crustiform vein thin section (W56). Traverse is over the red line, and show Sr, Mg, Fe and La concentrations. Sr results (grey line is 20 µm data) have been smoothed using a 300 µm moving average (black line). ‘α’ marks a black band, and ‘zonal’ marks the region of zonal texture.
in South Australia. Figure 2g of their study documents $^{87}\text{Sr}/^{86}\text{Sr}$ variations through different regions of a fibrous vein. This figure clearly indicates that the $^{87}\text{Sr}/^{86}\text{Sr}$ signatures change as calcite fibres grow, demonstrating that the intravein Sr isotope variations documented in this study are not isolated to a particular location, and may be a common phenomenon.

The $\delta^{18}\text{O}$ values of the vein are more depleted than the surrounding host rocks. This indicates that the fluid from which the vein formed was out of equilibrium with the host rocks, and was externally derived. In addition, the asymmetry in the evolution of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ on either side of the median line implies a variation in vein growth rate, or asynchronous growth of TZs 4 and 5. In textural zones 1, 2, 4 and 5, $\delta^{18}\text{O}$ values become closer to wall-rock values with decreasing age. The progressively increasing $\delta^{18}\text{O}$ values could be explained by a temperature decrease during calcite growth. A temperature decrease of approximately 15–20 $^\circ\text{C}$ during the growth of TZ 5 would be sufficient to explain the change in $\delta^{18}\text{O}$ (Kim and O'Neil 1997). If the increase in $\delta^{18}\text{O}$ was due to decreasing temperature, then a slight positive increase in $\delta^{13}\text{C}$ (approximately 0.06 permil) would also be anticipated (Deines et al. 1974). Instead, $\delta^{13}\text{C}$ decreases by approximately 0.5 permil.

It is suggested that an initially isotopically depleted fluid entered the vein site, and began precipitating calcite at the median line. Progressively increasing $\delta^{18}\text{O}$ with time indicates that the fluid $\delta^{18}\text{O}$ became progressively more rock-buffered with time. This could be caused by an increase in reactive path length, or a decrease in fluid flow rate (causing enhanced fluid-rock reaction).

6.7.2 Distinguishing extrinsic and intrinsic controls on mineral chemistry in hydrothermal veins

An important question in the chemical study of any geological sample is to what extent original variations may have been affected by later recrystallisation, diffusion or other factors. For example, in the laminated vein SM1, one grain boundary (GB1 in Figs. 6.11 and 6.12) is marked by a subtle change in Sr, Mg and Fe concentrations. In comparison, a second grain boundary (GB2 in Figs. 6.11 and 6.12) is not marked by any abrupt variation in trace element concentrations. Sections of the sample SM1 examined here have clearly been affected by secondary dissolution and precipitation of calcite, with white calcite crosscutting older inclusion bands. This raises the question as to what extent other parts of this vein may have been altered and/or affected by recrystallisation.

The large size of calcite crystals in sample SM1 implies that either (a) nucleation of new crystals is extremely difficult during vein growth, and, during each crack-seal event, precipitating calcite overgrew pre-existing crystals or (b) that recrystallisation and grain growth has occurred, which has not affected inclusion or crack-seal bands.

Recent experimental work by McCaig et al. (2007) suggests that grain boundary migration may cause complex chemical zoning in calcite crystals. However, considering the low temperatures suggested for the TVS (100–200 $^\circ\text{C}$), it seems unlikely that lattice diffusion or grain boundary migration have significantly influenced mineral chemistry in the veins examined in this study. I suggest that trace element variations preserved in these veins closely mirror the original vein chemistry.
One key result of the high-spatial resolution trace element analyses are the significant fine-scale (sub-millimetre) variations observed (a) parallel to vein fibres in vein TS-20, (b) within and between crack-seal layers in samples SM1 and BPS, and (c) within and between individual growth layers in the crustiform-banded vein. If these changes reflect fluctuations in bulk fluid chemistry then this would have significant implications, perhaps reflecting some cyclic variation in crustal permeability during vein growth.

The traverse along a single fibre in sample TS-20 (Fig. 6.5b) indicates that the fine-scale variations occur along individual fibres, and are not a sampling artifact caused by multiple fibres being crossed during laser ablation traverses. The fine-scale trace element variations could be caused by some form of supersaturation-nucleation-depletion (SND) disequilibrium cycle (Ortoleva et al., 1987).

Alternatively, variations in trace element concentrations could be explained by the growth-entrapment model of Watson (1996; 2004), which was examined in §3.3. In this model, changes in crystal growth rates and trace element diffusion rates cause fine-scale chemical zoning in crystals. Experimental results presented in §3.4.3 (Fig. 3.9) revealed that crystals grown from solutions with approximately constant chemistry had significant variations in trace element composition over distances of < 100 μm. This result suggests that the fine-scale (< 100 μm) trace element concentration changes observed in natural veins (e.g., Wogelius et al., 1997; Barker et al., 2006; Allan and Yardley, 2007) are strongly influenced by crystal growth processes. Variations in trace element concentrations likely result from both changes in extrinsic fluid composition, as well as crystal growth effects.

### Variations in rare earth elements

The enrichment of heavy REEs observed in TZ 1 in sample TS-20 (the antitaxial fibrous vein, Fig. 6.7) is accompanied by increased concentrations of Mg, Fe and Sr, more rock-buffered O isotope compositions, and lighter C isotope compositions (Fig. 6.4). These changes are probably due to the influx of a fluid with a chemical composition distinct from the fluids from which TZs 2–5 formed. The trace elements support the Sr and O isotope evidence, which suggests that this vein formed from fluids whose chemistry varied distinctly with time. These chemical variations could potentially arise from chemical changes in fluid reservoirs, or from the variable nature of fluid-rock interaction along changing flow paths.

In hydrothermal fluids, REE fractionation is a function of (a) sorption and desorption of REEs during migration of fluids along particle surfaces, and (b) coprecipitation (Bau and Moller, 1992). Carbonate and OH\(^-\) ligands form stronger complexes with HREEs than LREEs. In carbonate-dominated hydrothermal solutions (such as those which would be expected in limestones), solutions with low CO\(_3\)^2\(^-\) concentrations will have flatter chondrite normalised REE patterns than solutions rich in CO\(_3\)^2\(^-\) (see Figure 3.1; Bau and Moller, 1992). This is because in CO\(_3\)^2\(^-\) poor solutions there will be little difference in the complexing of the light and heavy REEs. Figure 6.7 shows the variation in REE normalised patterns with distance across the antitaxial fibrous vein, and illustrates which parts of the vein are relatively enriched in the light or heavy REEs. Notable in this graph are the high frequency oscilla-
6. Temporal changes in fluid-rock reaction using vein chemistry

These oscillations are similar to those previously noted for trace elements, and may be caused by changes in bulk fluid chemistry, or the SND cycles discussed above. Relative enrichment or depletion of CO$_3^{2-}$ during vein growth could cause changes in the absolute concentration, and relative enrichment of light or heavy REEs in calcite. There is the potential to use REEs to trace changes in carbonate concentrations in fluids from which fault and vein-filling calcite precipitated. Further experimental work is needed to explore this.

6.7.3 Records of fluid oxidation in syntectonic veins

In TZ 1–3 of sample TS-20, δ$^{13}$C signatures become depleted (up to 5‰) compared to the δ$^{13}$C in the rest of the vein. One mechanism to create depleted δ$^{13}$C values is by fluid oxidation. Organic matter (e.g. CH$_4$) is heavily depleted in the heavier $^{13}$C isotope. At low temperatures, isotopic equilibration between CO$_2$ and CH$_4$ (and other organic species) is very slow (estimated at 10$^{10}$ years at 200°C; Ohmoto and Goldhaber, 1997). Hence, the organic carbon species must be oxidised so that the isotopically light carbon can be incorporated into carbonate. One simple oxidation mechanism is:

$$RCH_2O + FeOOH + 8H^+ = 4Fe^{2+} + CO_2 + 7H_2O + R$$

(6.1)

where R refers to organic matter which did not react (Ohmoto and Goldhaber, 1997).

The depleted δ$^{13}$C signatures found in TZ 1–3 record the influx of fluids containing $^{13}$C depleted species which have been oxidised. This oxidation could have occurred in red bed sandstones, which occur stratigraphically above and below the Cavan Bluff Limestone.

Further evidence for changes in the degree of fluid oxidation during vein growth is shown by the Ce/Ce* ratios (Fig. 6.6). Cerium occurs as both a trivalent and tetravalent ion, depending on its oxidation state. In a fluid where all the Ce occurs in the $^{3+}$ valency, with initially chondritic REE ratios, then Ce$_{CN}$ should fall on the same trend in a normalised REE pattern as its immediate neighbours (La$_{CN}$ and Pr$_{CN}$). However, if some Ce becomes oxidised into the $^{4+}$ valency, it is possible that a Ce anomaly may occur in calcite precipitated from that fluid.

Eu anomalies are likely controlled by the Eu content of the host rocks with which fluids are reacting, as well as the oxidation state of the fluid. The host rock Eu content is likely to be controlled by the presence/absence of Ca-plagioclase (Schnetzler and Philpotts, 1970). Accordingly, variations in Eu/Eu* in the vein calcite precipitating from a fluid will be dependent on both the location and degree of fluid-rock reaction, as well as the oxidation state of the fluid.

Higher Ce/Ce* values occur over the same region as δ$^{13}$C decreases. Over the same region, the lowest values of Eu/Eu* are measured. Bau and Moller (1992) suggest that the generation of a Ce and Eu anomaly in the same physico-chemical environment is impossible (i.e. changing only the fluid oxidation state cannot cause both a negative Eu anomaly and positive Ce anomaly). Thus, we suggest that the covariance in Eu and Ce anomalies observed in this study is caused by enhanced fluid-rock reaction with a Eu-depleted host rock (causing a negative Eu anomaly),
coupled with a change in fluid oxidation state (generating a positive Ce anomaly). This generated a fluid with depleted Eu/Eu*, lower $\delta^{13}$C, and higher Ce/Ce*. Significant Ce/Ce* and (particularly) Eu/Eu* anomalies were reported for sample SM1 (Fig. 6.12). Eu/Eu* anomalies fluctuate considerably more than Ce/Ce* anomalies. During analysis of synthetic calcite crystals (§3.4.3), no significant Eu or Ce anomalies were detected. This suggests that the Eu and Ce anomalies reported for these natural veins reflect changes in the bulk composition of the fluid from which veins precipitated.

6.7.4 Constraints on the formation of antitaxial fibrous veins

Five texturally distinct zones occur within the fibrous, antitaxial growth vein examined in this chapter. Adjacent textural zones (TZ 1–4) have different $^{87}$Sr/$^{86}$Sr ratios. These changes indicate that the intensity and/or style of fluid-rock reaction changed during the growth of each textural zone. This change in fluid-rock interaction likely reflects changes in fluid flow pathways or the chemistry of fluid reservoirs.

Textural zones 4 and 5 may have grown broadly contemporaneously on either side of the median line. However, asymmetry in the evolution of $\delta^{18}$O and $\delta^{13}$C indicate that vein growth occurred at different rates on either side of the median line. In addition, aspects of the chemical evolution of TZ 4 are not mirrored in TZ 5 (e.g. Fe, Sr, Eu/Eu*). Accordingly, incremental calcite growth events on either side of the median line must have been asynchronous for a substantial part of the growth history of TZs 4 and 5.

Textural zones 1–3 have markedly depleted $\delta^{13}$C signatures, which are probably the result of the influx of more oxidised fluids in the later stages of vein growth. Cerium and Eu anomalies in calcite veins may provide a record of fluid oxidation state and fluid-rock reaction, and warrant further investigation, particularly in veins where a growth history may be determined from textural observations.

From textural observations and chemical information collected from this fibrous vein, it is suggested that:

1. Calcite in the vein precipitated from fluid derived externally to the host rocks. This is demonstrated by the depleted $\delta^{18}$O signature of the vein calcite compared to the surrounding host rocks. Therefore, this fluid was sourced from an external fluid reservoir.

2. Coarse-scale (several mm) textural zonation in the vein indicates a minimum of four different stages in the growth history of this antitaxial vein.

3. Asymmetry in the chemical and stable isotope zonation in TZ 4 and 5 on either side of the median line indicate asynchronous, incremental vein growth and different growth rates on either side of the median line.

4. Each textural zone is characterised by a different suite of trace element, REE and isotopic compositions. It is suggested that these changes are due to variations in fluid chemistry during vein growth, most probably caused by variations in fluid-rock reaction along changing flow pathways.
The high spatial-resolution chemical profiles presented in §6.4.2 clearly demonstrate asymmetry about the median line of the antitaxial vein. The variations in Sr, C and O isotope ratios, and changes in trace and REE concentrations across the textural zones indicate that different stages of vein growth were accompanied by the influx of fluids that had undergone varying fluid-rock reaction. Changes in the intensity of fluid-rock interaction could be caused by changes in fluid pathways and reactive path lengths (Fig. 6.20). Alternatively, these changes could be caused by chemical “armouring” of pathways, with fluid chemistry changing as a result of variable fluid velocities and fluid-rock reaction along these pathways. Changes in reactive path lengths can be driven by ‘toggle-switch’ permeability changes (Miller and Nur, 2000), whereby local permeabilities may change over very short periods of time. Such rapid permeability changes could be caused by periodic cycles of vein opening and sealing, related to hydrofracturing and fault rupture during earthquake slip.

The broad scale chemical changes (between different textural zones) are modulated by submillimetre scale fluctuations within textural zones. These fluctuations may be due to crystal growth processes previously discussed. Alternatively, the high-spatial resolution variations may be caused by changes in the bulk fluid composition, possibly due to multiple pulses of chemically distinct fluid flowing through the vein. If the variations are due to multiple fluid pulses, this could imply that a fine-scale crack-seal process was involved in forming the vein, similar to the mechanism described by Ramsay (1980).

The formation of a fibrous texture requires extremely limited growth competition between adjacent crystals, so that the growth of grains is not occluded by more rapidly growing neighbours (Cox, 1987). Such limited growth competition may be caused by a very small vein aperture (Hilgers and Urai, 2002). Following the laboratory work of Means and Li (2001), some authors (e.g. Wiltschko and Morse, 2001; Oliver and Bons, 2001) have suggested that fibrous veins grow purely by pervasive, grain-scale diffusional processes, without the need for fracture formation. The observations and analyses outlined for sample TS-20 are not consistent with models for antitaxial fibrous vein formation which suggest that vein growth occurs continuously, as a result of pervasive (grain-scale) fluid flow through the surrounding rocks. Furthermore, local scale diffusion of material from the surrounding wall rocks cannot explain the variations in C, O and Sr isotope compositions. My observations are consistent only with vein growth in a discontinuous flow regime, in which calcite precipitated from fluid which migrated along episodically changing pathways.

### 6.7.5 Fluid flow during flexural-slip

In sample SM1, small, but significant variations in $^{87}\text{Sr}/^{86}\text{Sr}$ occur between adjacent crack-seal layers. However, significant variations in $\delta^{18}\text{O}$ values were not detected between adjacent crack-seal layers. The growth of bedding-parallel veins during flexural-slip folding and links between seismicity and bedding-parallel slip was explored in §4.5.1. More specifically, it was suggested that crack-seal layers were developed during small magnitude earthquakes which occurred between bedding-planes during flexural-slip fold growth.
The small variations in $^{87}\text{Sr}/^{86}\text{Sr}$, with little or no change in $\delta^{18}\text{O}$ are a function of both the stratigraphic position of SM1, as well as the proposed mechanism for bedding-parallel vein growth. Within the Spirifer yassensis Limestone, $\delta^{18}\text{O}$ values typically lie between 22 and 24 ‰ (relative to VSMOW, Fig. 5.4), and, at this level in the Murrumbidgee Group, oxygen isotope ratios in vein calcite have been essentially buffered by host limestones. Therefore, little change in oxygen isotope ratios would be predicted for a vein at this stratigraphic height, unless a substantial change in reactive path length, or fluid flow rate occurred (see discussion in §5.1, Fig. 5.1 and Cox 2007). However, within the SYL, $^{87}\text{Sr}/^{86}\text{Sr}$ shows considerable variation (between 0.7083 and 0.7086), which was attributed to variable scavenging of $^{87}\text{Sr}$ from clays and micas within shale layers.

It was inferred that the earthquakes which produced crack-seal layers within
bedding-parallel veins had somewhat similar ruptures lengths, of up to $\sim 200$ m. Therefore, there would be little opportunity to substantially increase the reactive path length during flexural slip episodes. Hence, there would be little change in the oxygen isotope ratio of migrating fluids during each rupture event, as the degree of fluid-rock reaction would be approximately the same. However, small changes in the reactive surface area of a fault could cause changes in $^{87}$Sr/$^{86}$Sr, by changing the amount of clay and/or mica on fault surfaces.

### 6.7.6 Origin of the crustiform vein

This thesis, and the study of Cox (2007) demonstrate that veins in the Murrumbidgee Group were formed from externally-derived, upwardly migrating fluids. These fluids underwent progressive fluid-rock reaction, leaving an isotopic record of an fluid infiltration front. The isotopic signature of a vein formed from an isotopically uniform source, under isothermal conditions, is controlled by the degree of fluid-rock reaction during fluid flow. The degree of fluid-rock reaction is affected by the length of reactive fluid flow pathway, fluid flow rate and rate of fluid-rock reaction.

Oxygen isotope values determined for the crustiform vein ($\delta^{18}$O = $-1$‰ to $+5$‰ VSMOW) are significantly depleted compared to unaltered host rocks, and have considerably lower $\delta^{18}$O values than other veins at a comparable stratigraphic height within the Murrumbidgee Group (this study, and Cox, 2007). This fault vein is the only one containing crustiform textures located to date in the Taemas area. This vein also has unusually low concentrations of rare earth elements and Fe compared with other veins. I suggest two possible causes of the unusual isotopic and trace element characteristics of this vein.

The vein may have formed from fluid which migrated through the Murrumbidgee Group while undergoing very little fluid-rock reaction, in a similar manner to other veins contained within the Taemas Vein Swarm (Cox, 2007). This is unlikely, as depleted veins forming at the base of the Murrumbidgee Group have higher Sr and REE concentrations, which generally decrease with progressive fluid-rock reaction through the Murrumbidgee Group. Hence, if this vein formed from the same fluid source, much higher REE and Sr concentrations would be anticipated.

Alternatively, the vein may have formed from fluid of a different source, or from fluid which migrated along a very different flow pathway. The extremely low $\delta^{18}$O of this vein (as low as $-1$‰, VSMOW) implies that calcite grew from a fluid with extremely low $\delta^{18}$O values ($-14$‰ at $150^\circ$C; $-11$‰ at $200^\circ$C; Zheng, 1999).

The crustiform vein lies adjacent to the Warroo Fault Zone (WFZ). It is possible that this vein may have formed from meteoric fluid which migrated from the WFZ. Several veins collected from near and within the WFZ have low $\delta^{18}$O ($+4$ to $+6$‰, VSMOW; Cox, 2007), suggesting that fluids contained within the WFZ had depleted $\delta^{18}$O values.

Crustiform textures imply that this vein formed by precipitation of calcite from fluids with varying isotopic (and possibly trace element) composition. Calcite precipitation occurred into open space, allowing the growth of large (cm-scale) euhedral calcite crystals, which developed a zonal texture. Zonal textures (see Adams, 1920)
are confined to crystals that grow directly from a hydrothermal fluid, requiring the fluid to be only slightly supersaturated with respect to the precipitating mineral. The zonal texture is caused by mildly fluctuating chemical conditions during crystal growth (Fournier 1985; Dong et al. 1995).

The variation in oxygen isotope ratios coincident with different calcite bands implies that each episode of calcite precipitation occurred from a fluid with different oxygen isotope compositions, likely related to varying fluid-rock reaction, fluid source or fluid temperature. Small but significant variations in Sr isotope ratios (which are unlikely to show any significant fractionation due to temperature changes) imply that changes in oxygen isotope ratios are most likely related to varying fluid-rock reaction. Periodic changes in fluid-source and/or fluid pathways are likely due to the creation and destruction of permeability, possibly related to seismic activity on the nearby Warroo Fault.

6.8 Conclusions

Textural observations combined with high-spatial resolution chemical analyses of veins provide a record of changes in fluid chemistry and evidence for changes in fluid flow pathways during vein growth. The analyses reveal millimetre to submillimetre scale variations in the trace element and isotopic composition of vein calcite.

Changes in calcite mineral chemistry in syntectonic veins are influenced by changes in the ‘bulk’ composition of hydrothermal fluids (‘extrinsic’ controls), as well as variations in mineral growth (‘intrinsic’ controls). Integration of textural observations with measurements of isotopic ratios, particularly Sr isotope ratios, allow extrinsic and intrinsic controls to be differentiated. In particular, Sr and O isotope ratios change with time during vein growth. These variations are inferred to be due to changes in fluid flow pathways and reactive path lengths, caused by permeability creation and destruction.

The collection of high-spatial resolution isotopic and trace element data from syntectonic veins is an exciting field of research. Application of these techniques to fracture-hosted ore deposits may allow the chemical conditions conducive to high-grade ore formation to be discerned. Interpretation of trace element variations in veins could be improved substantially by further experimental investigation of controls on trace and rare earth element incorporation into calcite.