Evolution of fluid chemistry and fluid-flow pathways during folding and faulting: an example from Taemas, NSW, Australia

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Abstract: In the Taemas area, New South Wales, Australia, a swarm of hydrothermal calcite and quartz veins is hosted in upright, open to close folded limestones and shales. Overprinting relationships and vein geometries demonstrate that the vein swarm formed progressively during fold growth and associated reverse faulting. Textures preserved in veins reveal that veins formed via hundreds to thousands of individual dilation and mineral precipitation events. Bedding-parallel flexural slip during fold growth was associated with laminated vein development, and limb-parallel stretching during fold growth was associated with the formation of bedding-orthogonal extension veins. The presence of subhorizontal extension fractures and severely misoriented reverse faults imply that fluid pressures exceeded lithostatic levels, at least transiently, during the development of the vein swarm.

Vein δ18O compositions increase upwards through the Murrumbidgee Group in response to a progressive reaction of an externally derived, upwards-flowing low-δ18O fluid (of probable meteoric origin) with host limestones. Vein δ18O and 87Sr/86Sr compositions vary spatially and temporally within the same outcrop, and within individual veins. These variations are inferred to be caused by the ascent of packages of fluid along constantly changing flow pathways caused by multiple permeability creation–destruction cycles associated with fault slip and fault sealing. Vein trace and rare earth element (REE) concentrations are more variable, probably reflecting rapid rock buffering along fluid pathways on length scales of less than 10 m. Our results indicate that fluid-flow pathways change dynamically during crustal shortening, with pathways switching between states of low and high permeability during episodic fault slip and associated fracture development.

Supplementary material: Two appendices are available at http://www.geolsoc.org.uk/SUP18492.

Syntectonic veins record information on spatial and temporal variations in the composition of fluids migrating through the crust during progressive deformation and associated vein growth (e.g. Dietrich et al. 1983; Rye & Bradbury 1988). Exhumed vein systems potentially contain a record of where fluid flow was localized, how flow has influenced the mechanical behaviour of the crust, and the nature of chemical reactions between rocks and fluids along fluid-flow pathways. Vein chemistry may also provide constraints on the nature of fluid reservoirs contributing to fluid flow during crustal deformation.

An extensive fold- and fault-related vein network (hereafter called the 'Taemas Vein Swarm' or TVS) composed mainly of calcite veins is developed throughout much of an interbedded limestone and shale sequence (the Murrumbidgee Group) in the Taemas area of southeastern NSW. The vein swarm is localized mainly within an area of approximately 20 km². Vein development and folding were synchronous, with a variety of bedding-discardant fault veins, bedding-parallel fault veins and extension veins developed. Laminated veins related to bedding-parallel slip are common, particularly in thinly interbedded limestone–mudstone units. Bedding-discardant faults, fault-related extension veins and extension veins related to flexural flow and bedding-parallel stretching of fold limbs are also found (Cox 2007).

As externally sourced fluids react with rocks, they become progressively rock-buffered along fluid-flow pathways. Many studies have been carried out exploring how fluid flow and fluid–rock reaction processes may affect the chemical and isotopic composition of host rocks and hydrothermal veins (e.g. Bickle & McKenzie 1987; Lassey & Blattner 1988; Rye & Bradbury 1988; Bowman et al. 1994;
Gerdes et al. 1995; McCaig et al. 1995; DePaolo & Getty 1996; Abart & Sperb 1997; Eppel & Abart 1997; Steefel & Lichtner 1998; Abart & Pozzorini 2000; McCaig et al. 2000; Badertscher et al. 2002; Knoop et al. 2002; Matthäi 2003; Steefel et al. 2005; DePaolo 2006; Cox 2007; Zack & John 2007). Many of these studies have assumed ‘steady state’ or essentially continuous fluid flow, without considering the influence that dynamic changes in permeability, with both time and space, will have on resulting fluid and vein compositions.

In addition to isotopic compositions of calcite, we present trace element compositions from hydrothermal calcite veins. Calcite commonly contains appreciable concentrations of Mg, Mn and Fe, and lesser amounts of Sr and Ba (Deer et al. 1962, 1992; Mucci & Morse 1990). In general, there are little available experimental data addressing the trace element composition of calcite precipitated at temperatures above 50 °C. The concentration of trace elements in calcite will reflect a variety of factors in the fluid from which the calcite precipitated. These factors include the concentration of substituting elements in solution, temperature, pH, other aspects of fluid composition (e.g., concentrations of other species such as CO$_3^{2-}$) and oxidation state. The major factors controlling trace element partitioning between calcite and fluid are the size of the cation site and the ionic radius of the substituting element (Garrels & Christ 1982; Mucci & Morse 1990; Zhong & Mucci 1995). The reviews of Mucci & Morse (1983) and Wasylenki et al. (2005) found a strong temperature control on the incorporation of both Mg and Sr into calcite. Faster precipitation rates also lead to higher concentrations of both Sr and Mg in calcite (Mucci & Morse 1990). Fe and Mn concentrations in calcite are controlled by the concentration of Fe and Mn in solution, as well as the temperature and precipitation rate of calcite (Dromgoole & Walter 1990). In hydrothermal fluids, rare earth element (REE) fractionation is a function of: (a) sorption and desorption of REEs during migration of fluids along particle surfaces; and (b) coprecipitation (Bau & Moller 1992).

The aim of this chapter is to use spatial and temporal variations in vein isotopic and trace element composition to explore controls on fracturing, fluid flow, and fluid–rock reaction, in a fracture-controlled hydrothermal system that was active during progressive crustal shortening.

Geological setting of the Taemas
Vein Swarm

The Taemas area is located SW of Yass, in the Eastern Belt of the Lachlan Orogen, in southeastern New South Wales, Australia (Glen 1992). Here, a major fold triplet (Wee Jasper Syncline, Narrangullen Anticline and Taemas Synclinorium) forms the larger Black Range Synclinorium (c. 180 km long × 25 km wide). The Taemas Synclinorium is a doubly-plunging synclinorial structure approximately 5 km wide (Cramsie et al. 1975) (Fig. 1). Within the Taemas Synclinorium, sedimentary rocks of the Murrumbidgee Group (Table 1) have been folded into upright, open to close folds (wave-lengths varying from tens-of-metres to kilometre-scale), which have a predominant NNW trend, and steep axial surfaces (Fig. 2). The synclinorium is to the west of the major, steeply-dipping, Warroo and Deakin–Devil’s Pass Fault System. Here, Silurian volcanics overthrust the Murrumbidgee Group sediments (Cramsie et al. 1975). Within the Taemas Synclinorium, the Murrumbidgee Group is approximately 1 km thick, and is composed of several limestone and shale formations that were deposited during the Early Devonian (Browne 1958) (see Table 1 for stratigraphy and formation name abbreviations).

At the base of the sedimentary sequence (in the Sugarloaf Creek Formation, SLC and the underlying volcanic basement) bedding dips are low (typically <20°) and bedding is gently folded, with fold wavelengths of the order of hundreds of metres to more than 1 km. Higher in the sequence, particularly in the Cavan Bluff Limestone (CBL), Spirifer yassen-sis Limestone (SYL) and Bloomfield Limestone (BFL), close to tight folds occur, with shorter fold wavelengths (from tens to hundreds of metres: see Figs 2 & 3). The shorter fold wavelength in the interbedded limestone–shale units (SYL and BFL), compared with the thicker, more competent underlying and overlying units (Majurgong Formation (MJJ) and Receptaculites Limestone, RCL) reflects a strong control of thickness of competent stratigraphical units on fold wavelength. The changes in fold wavelength and strains accommodated by folding through the Murrumbidgee Group require detachment accommodated by faulting where major changes in fold wavelength occur.

Cleavage is strongly developed in the MJF, and in shale-rich beds in the SYL and BFL. Within sandstone beds in the MJF, cleavage fans strongly around outcrop-scale folds, and is typically at a high angle to bedding. This implies that layer-parallel shortening occurred early during fold growth, with the subsequent buckling of bedding (Ramsay & Huber 1987). In general, shales have a penetrative slaty cleavage, whereas limestone beds are internally relatively unstrained or contain a weak pressure-solution cleavage. Total strain, calculated using bed lengths of internally unstrained limestone sequences, is in the range of 20–50%. Given geological strain rates of the order of 10$^{-14}$–10$^{-15}$ s$^{-1}$ (Pfiffner & Ramsay 1982;
Fig. 1. Simplified geological map of the Taemas area (modified from Cox 2007), showing representative bedding orientations and major outcrop locations (locality numbers in parentheses) documented in this chapter. Map grid is Australian Geodetic Datum (1984). Figure 4 is at locality 2, Figure 5 is at locality 1. Other locations are noted in text. Cross sections (a–a', b–b', c–c', d–d', e–e') are shown in Figure 2.
Mueller et al. 2000), this would imply that folding occurred over a period of 0.5–15 Ma.

The Taemas Vein Swarm

Veins occur as:

• fault veins – veins that form as dilatant zones within faults, which cut across and displace bedding;
• bedding-parallel veins (BPV) – veins that are concordant to bedding and show evidence of shear, such as laminations and slickenfibres;
• extension veins – veins that have no evidence of shear displacement.

Fault veins

Shear veins, occurring as both bedding-discordant and bedding-parallel structures, are found throughout the Taemas Vein Swarm. Fault veins cross-cut and displace bedding, and are found in several outcrops. Fault veins are dominantly calcite, with minor quartz and rare fluorite. Extension veins are common around bedding-discordant faults. Nearly all fault veins are hosted by reverse faults that, with respect to the inferred stress field at the time of faulting, range from optimally oriented to severely misoriented (cf. Sibson 1985). In addition, some minor subvertical, apparently late, strike-slip faults cut bedding. Displaced marker beds and the size of dilational jogs indicate that the majority of fault veins have net slip of the order of centimetres to a few metres. Within the Murrumbidgee Group, only four mapped faults have displacements larger than a few tens of metres.

Commonly, bedding-parallel and bedding-discordant fault veins are connected. Some of the thickest calcite veins found to date in the TVS occur where a bedding-parallel fault becomes bedding-discordant and displaces two anticlines against one another, generating a dilatant jog with a strike length of several tens of metres (Fig. 1, locality 2; see the detailed outcrop photograph in

Table 1. Stratigraphy and brief description of host rocks for the Taemas Vein Swarm*

| Group               | Formations                                                                 | Members                                                                 |
|---------------------|---------------------------------------------------------------------------|------------------------------------------------------------------------|
| Murrumbidgee Group  | Taemas Formation: massive to interbedded limestones, shale, shaly limestones, variably fossiliferous | Crinoidal Limestone: calcarenite with prominent crinoid ossicles         |
|                     |                                                                           | Warroo Limestone: shaly, thinly bedded, very fossiliferous limestone     |
|                     |                                                                           | Receptaculites Limestone (RCL): Massive, grey limestone with similar appearance to Currajong Limestone |
|                     |                                                                           | Bloomfield Limestone (BFL): thinly interbedded limestone and shale      |
|                     |                                                                           | Currajong Limestone (CJL): Massive, grey lst, prominently outcropping   |
|                     |                                                                           | Spirifer yassensis Limestone (SYL): thinly interbedded limestone and shale |
|                     | Majurgong Formation (MJF): thin to well-bedded red sandstone beds, thin-interbedded limestones at bottom and top of formation. |
|                     | Cavan Bluff Limestone (CBL): thinly bedded flaggy limestones with interbedded shale |
| Black Range Group   | Sugarloaf Creek Formation (SLC): tuff, shale, tuffaceous silstone, rhyolite, agglomerate |                                                                   |
|                     | Rhyolite, andesite, dacite, agglomerate, tuff                            |                                                                      |

*Note the abbreviations for host rocks used in the text. See Browne (1958) and Cransie et al. (1975) for further details.
Fig. 2. Cross-sections constructed from field mapping, aerial photographs and pre-dawn infrared images, showing the fold style in the Black Range and Murrumbidgee groups. Fold wavelengths tend to be longer (c. km scale) in the Black Range Group, and decrease to wavelengths of 100 m or less in the Spirifer yassensis and Bloomfield members of the Taemas Limestone. For clarity, some units that do not crop out are not shown on sections. The equal-area stereonet shows poles to bedding (circles) and cleavage (squares) throughout the Taemas area. Plotted is a best-fit great circle, indicating a NNW–SSE trend for the Taemas Synclinorium, with a very gentle south plunge.
Bedding-parallel veins

Bedding-parallel veins commonly contain tens to hundreds of mesoscopic grey-brown laminations, which lie subparallel to the vein margins. Laminations are usually striated, with striations generally subperpendicular to the plunge of fold hinges. However, the trend of striations on low-angle bedding-parallel veins at Shark’s Mouth Peninsula (Fig. 2, locality 4) varied over 55° on different laminae in the same vein. Most veins have dips of 40°–60°.

The laminated, bedding-parallel veins are analogous to those described previously, where slickenfibres and slickenlines found on laminations in the bedding-parallel veins record the slip vector (Gaviglio 1986; Tanner 1989; Jessell et al. 1994; Fowler 1996 and references therein). Some BPV may be traced around fold hinges. The presence of BPV in fold-hinge zones, and asymmetrically folded laminations within BPV on fold limbs, suggest that ongoing fold growth post-dated initial flexural slip. It seems likely that during the initial stages of folding, significant strain was accommodated via slip along bedding. However, as bedding dips increased during folding, frictional lock-up occurred (Ramsay 1974). During ongoing fold thickening, new bedding-discordant faults have formed. The occurrence of small saddle reefs indicates that dilation occurred at some fold hinges during fold amplification by flexural slip.

Extension veins

Fold limbs rotated into steep orientations have undergone limb-parallel stretching, resulting in incipient bedding boudinage and formation of associated subhorizontal extension veins (Fig. 5). Extension veining of this type is most prevalent in the CJL. This is likely owing to the high competence of this unit relative to the surrounding interbedded limestone–shale of the SYL and BFL.

Generally, extension veins overprint cleavage development and are generally later than bedding-parallel slip veins. At locality 3 in Figure 1, calcite extension veins cut cleavage at a high angle on fold limbs. A bedding-parallel vein between the two anticlines is cut by extension veins, which dip east (342°/37°E). The bedding-parallel vein is interpreted to be the result of flexural slip during folding. The high angle of calcite extension veins to cleavage within folds is consistent with some veins formed as beds deformed via flexural flow (Ramsay & Huber 1987). Extension veins crosscutting the bedding-parallel vein imply that strain may be accommodated via flexural-flow folding after bedding-parallel slip ceases due to the frictional lock-up of beds (Ramsay 1974). It is noted that en echelon arrays of veins related to flexural flow form only in semi-competent and incompetent beds, and do not form within more competent massive limestone beds.

Extension veins can also show mutually overprinting relationships with cleavage (in shale-rich beds) and stylolites (in more massive limestones), and folded veins are rare. This implies that extension vein formation and folding were contemporaneous. Extension veins sometimes show mutually overprinting relationships (Fig. 5c, e), implying that the orientation of σ3 (at least sometimes) changed dynamically over time.

In summary, various vein types formed throughout crustal shortening. Thus, vein chemistry may be used to track variations in fluid composition.
Vein textures

Veins dominantly have fibrous (Fig. 6a), massive (Fig. 6b), laminated (Fig. 6c) and fibrous (Fig. 6d) textures, with elongate-blocky and crustiform textures also occurring (Bons 2000; Oliver & Bons 2001). Bedding-parallel and discordant fault veins have massive and laminated textures, with fibrous textures preserved in some parts of fault and bedding-parallel veins (Fig. 6b). Conversely, extension veins have massive, elongate-blocky or fibrous textures (Fig. 6a, d). It is emphasized here that the particular textures are not isolated to specific host lithologies, and textural variations are present among veins within the same outcrop, as well as within individual veins (Fig. 6b). Notably, veins may contain both fibrous and massive calcite; massive and fibrous extension veins also show mutually overprinting relations (Fig. 6b).

Laminated textures in bedding-parallel slip veins have been classified according to the terminology of Koehn & Passchier (2000). Inclusion bands are thin, dark bands parallel to the vein margins. Crack–seal bands are thin, dark bands between parallel inclusion bands, which, in this study, are typically inclined at angles of 20°–35° to inclusion bands (Figs 6c & 7). Crack–seal bands are typically separated by distances of 100 μm–2 mm in laminated veins (Fig. 6c), and hundreds of crack–seal bands may occur in an interval of around 10 cm along one calcite lamina (Fig. 6c). Crack–seal bands are inferred to have formed along dilational

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**Fig. 4.** Faults and veins within the Cavan Bluff Limestone at a fault–fold complex at location 2 in Figure 1. The top panel is a cross-section through the outcrop shown in the photograph in the lower panel. On the photograph white lines mark bedding, black lines mark faults. Shown are O and Sr isotope compositions for different vein types (numbered below) contained within the outcrop: (1) bed-parallel vein; (2) saddle-reef; (3) bed-parallel vein; (4) hinge extension vein; (5) flexural-flow extension vein; (6) laminated fault vein; and (7) fault vein dilatant jog. Inset graph shows the relationship between δ18O and 87Sr/86Sr (± 2 SE) for different veins. (SE, standard error.)

(δ18O, 87Sr/86Sr, trace and rare earth elements), not just during growth of individual veins but also as the TVS evolved from early fold growth to later fold tightening, cleavage development and associated reverse faulting.

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Fig. 5. (a) Photograph of Currajong Limestone with extension veins in subvertical bedding at ‘Kangaroo Flat’ on the eastern side of Taemas Peninsula (locality 1 in Fig. 1, and locality 5 in Fig. 3). (b) Interpretative sketch of (a). Bedding is dashed black, calcite veins are red. Representative fault and bedding orientations are shown. Equal-area stereonet shows the average orientation of bedding (great circle) and poles to veins (note the higher density of veins at approximately 90° to bedding). The outcrop is approximately 10 m wide. (c) Photograph of calcite extension veins from limestone on the right-hand side of photograph (a). Pencil tip (10 cm) for scale. (d) Interpretative sketch of (c). Note that vein sets (ν₀ and νₓ) with similar orientations show mutually overprinting relations. Styolites are approximately parallel to bedding. Some veins cross-cut styolites, while other veins are truncated against styolites. (e) Boudinaged limestone beds and extension veins on the upper transition of CJL to BFL. Note the pencil (15 cm) for scale.
sites during slip along laminations on the BPV (Koehn & Passchier 2000).

**Geochemical methods**

**Sample collection**

The position and structural relationships of veins were recorded in the field prior to sample collection (see Supplementary material SUP18492 for sampling locations and complete analytical results). Unaltered host rock (at distances of more than 50 m from any visible veins) was collected from the Cavan Bluff, Spirifer yassensis, Currajong, Bloomfield and Receptaculites limestones.

**Stable isotope analysis**

Oxygen and carbon isotope ratios for carbonates were measured on a Finnigan MAT251 mass...
Carbonate powder was dissolved in 103% H$_3$PO$_4$ at 90 °C in an automated carbonate (Kiel) device. Carbon isotope ratios are reported relative to Vienna Peedee Belemnite (VPDB). Oxygen isotope results are reported relative to Vienna Standard Mean Ocean Water (VSMOW), and were converted from VPDB values, where:

$$
\delta^{18}O_{\text{VSMOW}} = 1.03091 \times \delta^{18}O_{\text{VPDB}} + 30.91.
$$

(Coplen et al. 1983).

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

$$
\text{NBS} - 19 \delta^{18}O_{\text{VPDB}} = -2.20\%e;
$$

$$
\delta^{18}O_{\text{OSMOW}} = +28.64\%e \text{ and } \delta^{13}C_{\text{VPDB}} = +1.95\%e;
$$

$$
\text{NBS} - 18 \delta^{18}O_{\text{VPDB}} = -23.0\%e;
$$

$$
\delta^{18}O_{\text{OSMOW}} = +7.2\%e \text{ and } \delta^{13}C_{\text{VPDB}} = -5.0\%e.
$$

The standard deviation (2σ) for the 50 replicate NBS-19 standards used during the analysis of these samples was 0.02‰ for δ$^{13}$C and 0.06‰ for δ$^{18}$O.

Quartz oxygen isotope ratios were measured at the University of New Mexico. Quartz samples were separated from calcite (the calcite was stored for oxygen isotope analysis, as outlined earlier), and the quartz chips were placed into a 1 M HCl solution until all effervescence had ceased and calcite was removed.

The resulting quartz separates were examined using a binocular microscope, and clear quartz pieces were selected for analysis by laser fluorination (following the method of Sharp 1990). An internal laboratory standard (Lausanne-1) was analysed to determine the reproducibility of analyses (±0.2‰).

**Strontium isotope analyses**

**Host rock.** Sr isotope compositions of host-rock carbonate were measured by thermal ionizing mass spectrometry (TIMS). Approximately 1 kg of each of two samples from each limestone member (10 samples in total) was crushed using a tungsten carbide swing mill. Around 0.06–0.11 g of rock powder was placed into a clean Teflon® screw-cap vial. To separate only the carbonate component of the limestones, 1 ml of distilled 1 M acetic acid was added to each beaker, resulting in immediate, gentle effervescence. The beakers were allowed to rest for 2 h at room temperature, and a further 1 ml of acetic acid was added, after which effervescence ceased. The resulting mixture of solution and sediment was centrifuged in clean tubes, and the liquid was drawn off and dried on hot plates. The samples were then taken up in HNO$_3$ for loading onto cation-exchange columns, where Sr was separated from other matrix elements. Rubidium was not collected or analysed as Rb concentrations in carbonate are generally very low (Faure & Powell 1972), and were confirmed to be very low (<1 ppm) by laser ablation multi-collector inductively coupled plasma mass spectrometry (LA-MC-ICP-MS) analyses (see later).

Purified Sr was loaded in H$_3$PO$_4$ on Ta filaments and analysed on a Finnigan Mat261 mass spectrometer. All filaments were out-gassed for 30 min prior to loading. Sr isotope values were normalized to $^{86}$Sr/$^{88}$Sr = 0.1194. The NIST SRM-987 Sr isotope standard analysed had a $^{87}$Sr/$^{86}$Sr value of 0.71023 ± 0.00001.

**Carbonate veins.** Sr isotope compositions of vein calcite were analysed on the same samples on which trace element analyses were conducted. Analyses were made using in situ LA-MC-ICP-MS, and the results of the vein analyses are reported in Supplementary material SUP18492. 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). Analyses were performed using a single-spot approach (with a laser spot diameter of 137–233 µm). Laser pulse rates of 5 Hz in combination with a laser fluence of 5 J cm$^{-1}$, short laser wavelength ($\lambda$ = 193 nm) and aperture imaging optics were used to attain controlled calcite ablation (c. 1 µm s$^{-1}$) in a He ablation medium (Eggins et al. 1998).

The gas flow and electrostatic lens settings were optimized for maximum Sr sensitivity and peak shape while ablating a modern *Tridacna* clam shell, which has a measured $^{87}$Sr/$^{86}$Sr value of 0.709143 ± 15 (Woodhead et al. 2005). *Tridacna* was additionally used to monitor instrument reproducibility and accuracy. For 22 analyses of *Tridacna*, the average $^{87}$Sr/$^{86}$Sr ratio was 0.709149 ± 38 (2σ). Further details of analytical procedures are given in Barker et al. (2006).

**Trace element analyses**

**Host rock.** The trace element compositions of the carbonate component of limestone host rocks were measured by solution collector inductively coupled plasma mass spectrometry (ICP-MS). A known amount of approximately 50–60 mg of rock powder was placed into a clean Teflon® screw-cap vial. To separate only the carbonate component of the limestones, 1 ml of distilled 1 M acetic acid
was added to each beaker resulting in immediate, gentle effervescence. The beakers were allowed to rest for 2 h at room temperature, and a further 1 ml of acetic acid was added, after which effervescence ceased. The resulting mixture of solution and sediment was centrifuged in clean tubes, and the liquid was drawn off, dried on hot plates and taken up in around 100 ml of 2% HNO₃ for analysis. Trace elements were measured using a quadrupole ICP-MS (Agilent 7500s) running in solution mode. Multiple major and trace elements (Be, Na, Mg, Si, P, Sc, Mn, Fe, As, Rb, Sr, Y, In, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, Lu, Re, Pb, Bi, Th, U) were analysed during laser sampling in the mode. Multiple major and trace elements (Be, As, In, Re, Bi) to monitor instrument performance and drift. Carbonate veins. Veins were analysed for trace element compositions using a multiple-spot analysis, laser ablation ICP-MS approach. Samples were pre-cleaned with ethanol. Every vein sample was analysed using a pulsed ArF Excimer laser (λ = 193 nm) and a quadrupole ICP-MS (Agilent 7500s; Eggins et al. 1998). Samples were pre-cleaned with ethanol. Every vein sample was analysed by repeated, rapid sequential peak hopping, with a rate of 5 Hz in combination with a laser fluence of 5 J cm⁻², short laser wavelength (λ = 193 nm) and aperture imaging optics were used to attain controlled calcite ablation (c. 1 μm s⁻¹) in a He ablation medium (Eggins et al. 1998).

Vein and wall-rock chemistry

Characterizing the isotopic and trace element composition of a heterogeneous host rock is a challenging problem. For example, it is difficult to determine the overall oxygen or strontium isotope composition of a calcareous shale because small variations in the proportion of carbonate:silicate minerals may cause significant changes in Sr or O isotopic ratios. In addition, it is not feasible to characterize each individual bed in an interbedded limestone–shale unit and then produce an ‘average’ isotopic composition. The majority of veins in the Taemas Vein Swarm are calcite, with minor quartz. Cox (2007) found that the siliciclastic Majurong Formation had no affect on the oxygen isotopic composition of fluids migrating through this unit. Therefore, it was decided to characterize only the carbonate component of host rocks via weak acid extraction of carbonate. In particular, extracting only the Rb-poor carbonate component of host rocks means that no age correction is required to determine ⁸⁷Sr/⁸⁶Sr values at the time of hydrothermal vein growth (Faure & Powell 1972).

Distal limestone samples (more than 50 m from significant veinining) have δ¹⁸O values between 0.70815 and 0.70828 (Table 2), which are consistent with sea-water values for the Early Devonian (Veizer et al. 1999). Host rocks measured within about 1 mm–1 cm of vein margins have a broader range of δ¹⁸O, varying between 14 and 24‰ (Cox 2007). Depleted δ¹⁸O margins are usually a few centimetres wide, except around a fault zone at the bottom of the Cavan Bluff Limestone (Fig. 4), where δ¹⁸O-depleted zones are several metres wide (Cox 2007).

A few veins (less than 10) have δ¹³C values up to 11‰ lower than is typical for the unaltered host rocks. Vein carbonate δ¹⁸O values have significant variation, from roughly 0 to 25‰, ⁸⁷Sr/⁸⁶Sr ratios of 0.70815 and 0.70828 (Table 2), which are consistent with sea-water values for the Early Devonian (Veizer et al. 1999). Host rocks measured within about 1 mm–1 cm of vein margins have a broader range of δ¹⁸O, varying between 14 and 24‰ (Cox 2007). Depleted δ¹⁸O margins are usually a few centimetres wide, except around a fault zone at the bottom of the Cavan Bluff Limestone (Fig. 4), where δ¹⁸O-depleted zones are several metres wide (Cox 2007).

Table 2. Host-rock carbonate Sr isotope ratios (and associated errors) as measured by TMS

| Sample                  | ⁸⁷Sr/⁸⁶Sr | ±2σ  |
|-------------------------|----------|------|
| Cavan Bluff host rock 1 | 0.70828  | 0.00003 |
| Cavan Bluff host rock 2 | 0.70828  | 0.00002 |
| Spirifer yassensis host rock 1 | 0.70826 | 0.00005 |
| Spirifer yassensis host rock 2 | 0.70826 | 0.00001 |
| Currajong host rock 1   | 0.70821  | 0.00002 |
| Currajong host rock 2   | 0.70815  | 0.00003 |
| Bloomfield host rock 1  | 0.70825  | 0.00002 |
| Bloomfield host rock 2  | 0.70826  | 0.00003 |
| Receptaculites host rock 1 | 0.70821 | 0.00002 |
| Receptaculites host rock 2 | 0.70819 | 0.00001 |
values, although, in individual localities, correlations are observed between $\delta^{18}$O and Sr isotope ratios (Fig. 4).

Oxygen isotope compositions from calcite and quartz inferred to have grown in equilibrium (i.e. intergrown fibrous quartz and calcite) suggest fluid temperatures of between 100 and 250 °C (Table 3 and Fig. 9) (thermometer of Zheng 1993).

Host-rock carbonates have variable Mg concentrations, particularly in the Cavan Bluff Limestone (see Table 4 for calcite trace element compositions in host rocks). In general, the CBL has higher concentrations of Mg, Mn, Sc, Y and the REEs. Sr concentrations are relatively constant throughout the Murrumbidgee Group (1000–2000 ppm). The massive Currajong and Receptaculites limestones generally have lower concentrations of most trace elements in comparison to the interbedded limestone–shale members (Cavan Bluff, Spirifer yassensis and Bloomfield limestones). Host-rock REE, Y and Sc concentrations, and REE patterns, are similar to those measured in Devonian limestones by Nothdurft et al. (2004).

Vein calcites have Mn concentrations (50–800 ppm) that are similar to those of host limestone calcite (50–900), whereas Sr concentrations (1000–15 000 ppm) are generally higher than those of host-rock carbonates, particularly for veins within

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**Table 3. Oxygen isotope ratios ($\delta^{18}$O, VSMOW) for coexisting quartz and calcite fibres from two different samples**

| Sample  | Qtz $\delta^{18}$O (VSMOW) | Cct $\delta^{18}$O (VSMOW) |
|---------|-----------------|-----------------|
| CL12-7  | 26.8            | 24.1            |
| CL12-5  | 27.1            | 23.8            |
| CL12-4  | 25.8            | 24.0            |
| Cjcrk-C3| 26.0            | 23.8            |
| Cjcrk-C4| 26.1            | 23.8            |
| Cjcrk-C5| 26.9            | 23.9            |
| Cjcrk-C6| 27.1            | 23.8            |
| Cjcrk-C7| 26.9            | 25.0            |
| Cjcrk-J1| 27.1            | 23.9            |
| Cjcrk-J2| 25.5            | 23.9            |
| Cjcrk-Ka| 26.1            | 23.6            |
| Cjcrk-Kb| 27.1            | 23.6            |

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**Fig. 8.** Graph of Sr v. oxygen isotope compositions for veins in different stratigraphical units. The striped box represents the compositional range of the host-rock carbonate.

**Fig. 9.** Quartz–calcite oxygen isotope pairs ($\delta^{18}$O, relative to VSMOW) plotted on temperature contours derived from Zheng (1993). Black squares are data from Cox (2007); grey squares are data from this study.
Vein carbonate has highly variable Sc, Y and REE concentrations.

**Chemical variations in vein composition with stratigraphical position**

Vein δ¹⁸O increases with stratigraphical height through the Murrumbidgee Group (Fig. 10). However, variations in vein δ¹⁸O values are seen at any one stratigraphical level, with veins (exceptionally) having approximately 10‰ δ¹⁸O variation. Veins in the Currajong Limestone have slightly lower ⁸⁷Sr/⁸⁶Sr ratios than veins in the interbedded limestone–shale units (Fig. 10). Below the Cavan Bluff Limestone, vein carbonate ⁸⁷Sr/⁸⁶Sr is slightly lower than CBL ⁸⁷Sr/⁸⁶Sr host-rock carbonate compositions. However, within the CBL, vein carbonate is slightly higher, or in equilibrium with, the host-rock carbonate with respect to ⁸⁷Sr/⁸⁶Sr.

Within the SYL, veins have higher ⁸⁷Sr/⁸⁶Sr (0.7083–0.7086) than host-rock carbonate (0.70826). ⁸⁷Sr/⁸⁶Sr decreases with increasing stratigraphical height towards the Currajong Limestone. Within the CJL, vein calcites have ⁸⁷Sr/⁸⁶Sr ratios (0.70817–0.7083) that are generally close to equilibrium with those of host-rock carbonate (⁸⁷Sr/⁸⁶Sr = 0.70815–0.70821). However, veins in the interbedded limestones and shales of the immediately overlying Bloomfield Limestone have calcite ⁸⁷Sr/⁸⁶Sr values (0.7083–0.7087) elevated above those of host-rock carbonate (⁸⁷Sr/⁸⁶Sr = 0.70825).

In the interbedded limestone–shale lithologies, veins have the most variable trace element concentrations, particularly in the Cavan Bluff Limestone (Fig. 11). Generally, trace element concentrations in vein carbonate decrease with increasing stratigraphical height (except for Mg). Vein carbonate Sr concentrations are generally significantly higher (around 2000–10 000 ppm) than host-rock carbonate Sr concentrations (c. 1000–3000 ppm). Pb concentrations in veins are consistently lower than Pb concentrations in host-rock carbonate. Sc, Y and heavy REE (HREE) concentrations are generally similar, or lower, than host-rock carbonate. Light REE (LREE) concentrations decrease with increasing stratigraphical height, whereas the HREEs show a more limited concentration decrease with increasing stratigraphical height. Chondrite-normalized (values of McDonough & Sun 1995) REE patterns in Cavan Bluff veins are generally LREE-enriched, whereas veins higher in

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**Table 4. Host-rock carbonate trace element composition for selected trace elements (concentrations given in parts per million, ppm)**

| Element | CBHR1 | CBHR2 | SP1  | SP2  | CJ1 | CJ2 | BL1 | BL2 | RCP1 | RCP2 |
|---------|-------|-------|------|------|-----|-----|-----|-----|------|------|
| Mg      | 57783 | 9767  | 7165 | 4931 | 3395| 5821| 2526| 1921| 2529 | 1848 |
| Sc      | 4.29  | 2.67  | 1.47 | 1.59 | 0.61| 0.40| 1.72| 1.50| 1.28 | 0.90 |
| Mn      | 1026  | 821   | 312  | 118  | 63  | 47  | 284 | 476 | 154  | 160  |
| Fe      | 1264  | 1805  | 2500 | 3500 | 2105| 2014| 2326| 2183| 1848 | 1593 |
| Rb      | 1.10  | 0.54  | 0.60 | 0.63 | 0.13| 0.15| 0.63| 0.52| 0.50 | 0.42 |
| Sr      | 1556  | 1478  | 1123 | 1647 | 1078| 2182| 1805| 1808| 1057 | 910  |
| Y       | 20.13 | 19.34 | 5.77 | 3.86 | 2.40| 1.09| 5.31| 6.17| 2.93 | 2.36 |
| Ba      | 39.21 | 38.13 | 10.21| 8.18 | 6.10| 6.61| 9.51| 8.70| 6.81 | 5.81 |
| La      | 16.86 | 19.43 | 5.43 | 3.93 | 1.46| 1.00| 4.94| 4.18| 3.10 | 2.25 |
| Ce      | 37.63 | 42.39 | 12.33| 8.95 | 3.33| 1.98| 11.17|10.56| 6.71 | 4.93 |
| Pr      | 4.04  | 4.48  | 1.51 | 1.12 | 0.36| 0.21| 1.46| 1.47| 0.79 | 0.59 |
| Nd      | 16.99 | 18.08 | 6.19 | 4.57 | 1.48| 0.84| 6.19| 6.70| 3.19 | 2.36 |
| Sm      | 4.02  | 3.94  | 1.32 | 0.91 | 0.33| 0.19| 1.27| 1.50| 0.62 | 0.47 |
| Eu      | 0.98  | 0.89  | 0.29 | 0.20 | 0.08| 0.04| 0.36| 0.62| 0.16 | 0.11 |
| Gd      | 4.17  | 4.01  | 1.26 | 0.83 | 0.38| 0.18| 1.16| 1.38| 0.58 | 0.45 |
| Tb      | 0.65  | 0.61  | 0.19 | 0.12 | 0.06| 0.03| 0.17| 0.20| 0.09 | 0.07 |
| Dy      | 3.88  | 3.55  | 1.09 | 0.69 | 0.37| 0.17| 0.97| 1.12| 0.50 | 0.41 |
| Ho      | 0.77  | 0.70  | 0.21 | 0.13 | 0.08| 0.04| 0.20| 0.21| 0.10 | 0.08 |
| Er      | 2.03  | 1.83  | 0.54 | 0.35 | 0.21| 0.09| 0.49| 0.51| 0.27 | 0.21 |
| Yb      | 1.69  | 1.40  | 0.42 | 0.30 | 0.18| 0.08| 0.41| 0.37| 0.21 | 0.18 |
| Lu      | 0.23  | 0.20  | 0.06 | 0.04 | 0.03| 0.01| 0.06| 0.05| 0.03 | 0.02 |
| Pb      | 3.79  | 2.81  | 1.23 | 0.89 | 0.75| 0.24| 1.06| 1.26| 0.66 | 0.62 |
| Th      | 1.24  | 1.56  | 0.62 | 0.83 | 0.31| 0.15| 0.71| 0.89| 0.34 | 0.25 |
| U       | 0.38  | 0.64  | 1.99 | 1.38 | 1.51| 0.75| 0.49| 0.24| 0.62 | 1.12 |

CBHR, Cavan Bluff Limestone; SP1 and SP2, Spirifer yassensis Limestone; CJ1 and CJ2, Currajong Limestone; BL1 and BL2, Bloomfield Limestone; RCP1 and RCP2, Receptaculites Limestone.
stratigraphy in the SYL and CJL become relatively depleted in LREE.

**Chemical variations within and between outcrops**

Veins were assessed on an outcrop-by-outcrop, as well as within-outcrop, scale to examine how fluid–rock reaction varies between veins in a similar host rock. Figure 4 shows the location, vein type and isotopic compositions of different veins (fault, bedding-parallel and extension) from a fold–fault complex in the CBL. Notable is that δ¹⁸O varies by approximately 5‰, and ⁸⁷Sr/⁸⁶Sr varies between 0.70825 and 0.70846. A small extension vein isolated within a single limestone bed (probably formed during flexural flow) shows higher ⁸⁷Sr/⁸⁶Sr and δ¹⁸O, whereas bedding-parallel and fault veins show some of the lowest δ¹⁸O values and ⁸⁷Sr/⁸⁶Sr ratios.

Figure 12a, b illustrates the structural setting, and Sr and O isotope ratios, of veins from distinct but closely spaced outcrops of folded Spirifer yassensis Limestone at Kangaroo Flat (locality 1 in Fig. 1, which is also shown in Fig. 3). These outcrops represent one of the few locations in which the chemistry of veins from the same stratigraphical level, but different structural settings, may be compared (see highlighted regions in Fig. 3). Site A (Fig. 12a) has a bedding-parallel vein developed within an asymmetrical syncline–anticline pair.

![Graph showing δ¹⁸O and ⁸⁷Sr/⁸⁶Sr values with stratigraphical height through the Murrumbidgee Group](image-url)
Site B (Fig. 12b) is at the hinge zone of an upright, close fold containing predominantly bedding-parallel veins, with several small dilational jogs and late bedding-perpendicular extension veins inferred to be related to limb-parallel stretching.

Within both outcrops, vein carbonate δ¹⁸O varies between 20 and 25‰ for most veins (except for a late strike-slip fault vein: 14.7‰), and vein δ¹⁸O values for the two outcrops are statistically indistinguishable at the 95% confidence level (P value = 0.63, Mann–Whitney test). However, the vein cluster at ‘Site A’ (Fig. 12a) has consistently lower ⁸⁷Sr/⁸⁶Sr ratios than the ‘Site B’ (Fig. 12b) vein cluster (⁸⁷Sr/⁸⁶Sr P value = 0.016) (Fig. 13). These two different vein clusters also have significantly different concentrations of Mn, Fe, Sr and Eu. Veins at ‘Site A’ have higher Mn, Fe and Eu concentrations, and lower Sr concentrations (P values for Mann–Whitney test: Mn = <0.0001, Fe = <0.0001, Sr = 0.0009, Eu = 0.0133) (Fig. 13). For normalized REE patterns, both outcrops have LREE-enriched patterns, with veins at ‘Site A’ having a more positive Eu anomaly than veins at ‘Site B’.

**Vein-type variations**

Approximately 80 different bedding-parallel, extension and fault veins were analysed from the Spirifer yassensis and Currajong limestones. Within the SYL, δ¹⁸O in vein calcite varies between 14.7 and 25.2‰, with the majority of veins having δ¹⁸O values of between 22 and 25‰. There is no apparent relationship between O isotope composition and vein type. Strontium isotope values (⁸⁷Sr/⁸⁶Sr) show no relationship to the vein type (Fig. 14). Similarly, all veins within the CJL have δ¹⁸O values of 20–25‰, with the majority of values clustering between 22 and 25‰. However, ⁸⁷Sr/⁸⁶Sr values systematically vary according to vein type, with extension veins having lower ⁸⁷Sr/⁸⁶Sr values than most fault or bedding-parallel veins (Fig. 14).

Similar trends are observed for trace elements, with veins in the SYL having a broad range of trace element compositions, with no relationship observed between vein type and trace element concentration (Fig. 15). In comparison, extension veins within the CJL have lower concentrations of most
trace elements compared to fault or bedding-parallel veins (Fig. 16). In particular, REE concentrations are lower in extension veins than in bedding-parallel or fault veins.

Extension veins in the Currajong Limestone have Sr isotope and trace element compositions that are most similar to host-rock carbonate compositions. In comparison, all veins in the SYL have a broad range of Sr isotope ratios and trace element concentrations, which are generally elevated above host-rock carbonate compositions. Many extension veins in the CJL are related to fold limb-parallel stretching. In comparison, most extension veins in the Spirifer yassensis Limestone are associated with bedding-discordant fault zones. The fluid that migrated through late extension veins in the CJL was apparently significantly more influenced by local host rock than the fluid from which fault veins or bedding-parallel veins formed.

Discussion

The isotopic and trace element composition of hydrothermal calcite veins found within fault–fracture systems will reflect a variety of factors, including changes in fluid source, fluid-flow pathways, and the intensity of fluid–rock reaction in both time and space. The veins of the Taemas Vein Swarm record spatial and temporal variations in the composition of hydrothermal fluids responsible for the formation of the vein swarm.

Fluid sources

If it is assumed that calcite precipitated in equilibrium with the parent fluid, and the fluid temperature can be estimated, then the δ18O of vein calcite may be used to determine the isotopic composition of the parent fluid. Quartz–calcite oxygen isotope pairs (see Fig. 10) (Cox 2007) suggest fluid
temperatures of 100–250 °C, with the presence of illite implying temperatures of less than 200 °C (Cox 2007). Minimum δ18O values measured in veins at the base of the Cavan Bluff Limestone are about 0 to +2‰ (Cox 2007). At temperatures of 100–200 °C, this implies that fluid δ18O was between −14 and −8‰ (Zheng 1999). Such low δ18O values are consistent with a meteoric fluid source (Sheppard 1986). To form a meteoric fluid with these low δ18O values, the meteoric fluid must have been sourced at either high latitude (c. 50–60°), or significant altitude (2–4 km) (Bowen & Wilkinson 2002).

Several veins, or sections, of individual veins have unusual 87Sr/86Sr and δ13C values compared to the majority of veins in the TVS (e.g. sample C2a; see Supplementary material SUP18492). Barker et al. (2006) and Cox (2007) attributed localized negative-δ13C values to the oxidation of organic matter during fluid–rock reaction. The coupling of elevated 87Sr/86Sr and depleted δ18O values implies that a second fluid ‘source’ may have been present. This fluid may have been a residual interstitial pore fluid, which underwent enhanced fluid–rock reaction with iron oxides (causing oxidation of organic carbon) and 87Sr-enriched clay minerals (i.e. Majurgong Formation or the SYL) prior to mixing with the invading meteoric fluid.

**Implications of isotopic and trace element data for fluid flow**

Assuming that calcite deposition in veins was an equilibrium process, then the δ18O of vein carbonate changes in response to the δ18O of pore fluid, as pore fluid and wall rock undergo progressive reaction (Fig. 17). The conceptual model presented in Figure 17 emphasizes that veins within the same outcrop could have considerably different isotopic compositions (compare vein pair 1 and 3, and vein pair 6 and 7 in Fig. 4), depending on the length of the pathways along which those fluids flow. If a fluid migrates along a tortuous (i.e. long) fluid-flow pathway, then it will have greater opportunity to react with the country rock than fluids that migrate along more direct (i.e. shorter) fluid-flow pathways (see Fig. 17). In addition, fluid-flow pathways may change during deformation as permeability is created and destroyed. Variations in the isotopic composition of different vein types within the same outcrop in the Currajong Limestone indicate that fluids that precipitated calcite in fault and bedding-parallel veins underwent less interaction with host rocks than fluids forming extension veins. This is probably related to the length of fluid-flow pathways, with fault and bedding-parallel veins having (relatively) short flow pathways, causing fluids to undergo less reaction with host rock than fluids that formed extension veins (see Figs 16 & 17). This suggests that bedding-parallel and fault veins act as high-permeability pathways along which fluid could migrate.

The transition from the SYL to CJL is marked by a change from mixed shale–limestone lithology to only limestone, and a coincident decrease in vein 87Sr/86Sr ratio. The carbonate content of SYL limestone determined in the laboratory (estimated from loss of weight after acetic acid leaching) is
85–90% carbonate, while CJL limestones are 97–98% carbonate. The decrease in $^{87}\text{Sr}/^{86}\text{Sr}$ from the SYL to the CJL is interpreted to be a result of decreasing amounts of other minerals being available for fluid–rock reaction (i.e. increasing amounts of carbonate to buffer fluids). As in the SYL, calcite veins in the Bloomfield Limestone (interbedded limestone–shale immediately above the Currajong Limestone) have $^{87}\text{Sr}/^{86}\text{Sr}$ values elevated significantly above host-rock calcite, even as little as about 10 m stratigraphically above the Currajong Limestone. This implies that fluids have scavenged trace elements from the surface of other minerals such as layer silicates, and/or feldspars, over relatively short reactive path lengths during fluid flow. The lack of mineral specific Sr isotope data, and the uncertainty regarding the timing of hydrothermal activity (see Barker et al. 2009), make this hypothesis difficult to test further.

During this study a relatively small number of host rocks were analysed. In particular, analyses of shales were not carried out during this study. The consistent isotopic and trace element composition of limestone carbonate throughout the stratigraphical sequence suggests that average carbonate compositions do not vary by a significant degree (except, perhaps, for Mg concentrations), particularly compared to the degree of variation in trace element concentrations in veins. The study of Cox (2007) demonstrated that fluids dominantly

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**Fig. 14.** $\delta^{18}\text{O}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ isotope composition of extension, bedding-parallel and fault vein in the Currajong and Spirifer Yassensis Limestones. Sr isotope analyses are $\pm 2$ SE. Rectangles show range of host rock compositions.
interacted with carbonate with respect to $\delta^{18}$O. Thus, comparing only vein calcite with only host-rock carbonate minerals allows other controls on vein chemistry (such as the interaction with other minerals and changes in physiochemical conditions) to be assessed.

Trace element concentrations in hydrothermal calcite veins may be affected by several factors, including (Lassey & Blattner 1988; Moller et al. 1991; Bau & Moller 1992; DePaolo & Getty 1996; Steefel & Lichtner 1998; Hecht et al. 1999; DePaolo 2006):

- spatial and temporal variations in the composition of infiltrating (source) fluid;
- interaction of infiltrating fluid with matrix fluid;
- dissolution of host-rock minerals, releasing lattice-bound trace and minor elements; that is, host carbonate being dissolved;
- scavenging by fluids of trace elements loosely bound to mineral surfaces, particularly layer silicates, releasing adsorbed elements. In addition, shales generally have well-developed cleavages, indicating that layer silicates have deformed and recrystallized, implying that chemical species associated with these minerals would be available for infiltrating fluids during deformation;
- precipitation of hydrothermal minerals (e.g. calcite) leading to coprecipitation of other trace elements, removing those elements from solution;
- sorption of trace elements onto mineral surfaces during fluid migration, removing trace elements from fluids;
- changes in physicochemical conditions (e.g. temperature, pressure, pH, complexing species), which may affect trace element fractionation fluids and vein-forming minerals.

Fig. 15. Trace element composition of extension (grey squares), bedding-parallel (black circles) and fault veins (black diamonds) in the Spirifer yassensis Limestone. Rectangles show range of host rock compositions.
Steefel & Lichtner (1998) and DePaolo (2006) provided models addressing the chemical interaction of host rock, ‘matrix fluid’ and ‘fracture fluid’ during fracture-controlled fluid flow. As fluid migrates through a fracture, diffusion of trace elements occurs between that fluid and the rock matrix. The position of alteration fronts will be dependent on the temperature, fluid-flow rate, diffusion rate, kinetics of reactions and the reactive surface area of minerals. Along any one fracture, these factors will change depending on the fracture aperture, fracture roughness and wall-rock composition. For example, a small cataclastic fault zone, containing pulverized host rock with a high reactive surface area, will react in a different manner to a smooth-sided extension fracture through the same host rock.

Trace element concentrations are highest in veins in the lowest stratigraphical units; that is, those contained within the Cavan Bluff Limestone. This implies that the fluid which infiltrated the base of the Murrumbidgee Group was already enriched in trace elements. Presumably, the trace element composition of fluids infiltrating the base of the CBF reflects fluid–rock interaction that occurred with underlying rocks (i.e. volcanic sediments of the Black Range Group). Notable in some veins within the Cavan Bluff Limestone are elevated Sr concentrations, and veins with extremely positive Eu anomalies that could be produced by the dissolution of Ca-feldspar, which has appreciable concentrations of both Sr and Eu (Schnetzler & Philpotts 1970).

![Diagram](image-url)

**Fig. 16.** Trace element composition of extension (grey squares), bedding-parallel (black circles) and fault veins (black diamonds) in the Currajong Limestone. Labelled rectangles show range of host rock compositions.
When vein REE concentrations are normalized to chondrite values, it is apparent that REE patterns in Cavan Bluff veins are generally LREE-enriched, whereas veins higher in stratigraphy in the SYL and CJL become gradually depleted in LREE (Figs 11, 15 & 16). In hydrothermal fluids, REE fractionation is a function of: (a) sorption and desorption of REEs during the migration of fluids along particle surfaces; and (b) co-precipitation (Bau & Moller 1992). Carbonate and hydroxyl ligands form stronger complexes with HREEs than LREEs (Bau & Moller 1992). In carbonate-dominated hydrothermal solutions (such as those that would be expected in limestones), calcite precipitating from solutions with relatively low $\text{CO}_3^{2-}$ concentrations will have flatter chondrite-normalized REE patterns than

Fig. 17. Schematic diagrams showing evolution of vein $\delta^{18}$O compositions with time and space during progressive fluid–rock reaction (modified after Cox 2007). (a) Fluid from a fluid reservoir with a depleted $\delta^{18}$O composition advects through a rock sequence with a less depleted $\delta^{18}$O composition. (b) Evolution of vein $\delta^{18}$O compositions with time ($t_0, t_1, t_2, t_3$) as a low $\delta^{18}$O advect through the rock mass. (c) Illustration of how a vein at the same distance along a fluid-flow pathway could have a markedly different $\delta^{18}$O composition depending on the fluid flow and/or reaction rate between the rock and fluid. (d) Evolution of the $\delta^{18}$O composition of a vein with time at a single point ‘$\alpha$’ in (a), depending on the fluid–rock reaction rate. With a more rapid reaction rate, fluid becomes more rapidly buffered by the host-rock carbonate.
calcite precipitating from a solution with higher CO$_3^{2-}$ concentrations, which will be relatively enriched in the LREEs. This is because in carbonate-poor solutions there will be little difference in the complexing of the light and heavy REEs (Bau 1991; Bau & Moller 1992). If this interpretation is correct, it is suggested that [CO$_3^{2-}$] decreased as fluids migrated upwards through the Murrumbidgee Group, consistent with decreasing fluid pressure as fluids ascended.

**Implications for fluid-flow pathways and vein development during crustal shortening**

Important conclusions that may be drawn from this study, and the previous studies of the Taemas vein swarm (Barker et al. 2006; Cox 2007; Barker et al. 2009), are:

- veins formed over an extended period, from early folding until after fold lock-up and cleavage development;
- depleted $\Delta^{18}$O ratios in vein carbonate relative to host-rock carbonate indicate that fluid was derived externally to the host rocks;
- reactive transport modelling of oxygen isotope variations by Cox (2007) demonstrate that the systematic increase in vein $\delta^{18}$O and marked O-isotope alteration front in the Taemas Vein Swarm was the result of the buffering of an infiltrating low-$\delta^{18}$O fluid by progressive fluid–rock reaction. Fluid flow was restricted largely to fractures with no substantial lateral fluid flow into vein sidewalls;
- analyses of vein $\delta^{18}$O and $^{87}$Sr/$^{86}$Sr conducted during this study, and results reported in Barker et al. (2006) and Cox (2007), reveal that fluid-flow pathways, path lengths, and/or fluid-flow and fluid–rock reaction rates changed dynamically during the growth of individual veins, and between different veins in the same outcrop. This is probably related to the creation and destruction of permeability during repeated fracture opening and sealing events.

Dynamic switches in fluid-flow pathways are interpreted in terms of fluid flow through a fault–fracture mesh (Hill 1977; Sibson 2001). In such a mesh, it is predicted that fractures will be transiently permeable after fracturing (promoting rapid migration of fluids) and then this permeability will be destroyed (i.e. via hydrothermal mineral deposition), thus creating a dynamic fluid-flow environment.

According to the conditions for tensile failure, fluid pressure must exceed the least compressive stress and the tensile strength of the rock to cause extension fractures to form. In a contractional (i.e. reverse) faulting regime, gently dipping extension veins imply that: (a) the least compressive stress was approximately vertical; and (b) that the fluid pressure (at least transiently) exceeded the lithostatic pressure (i.e. $\lambda_1 > 1.0$: Sibson 2001). Additional evidence for transiently high fluid pressures is provided by steeply dipping bedding-parallel slip veins, and severely misoriented bedding-discordant reverse faults. The presence of folded and unfolded laminations in some of these veins suggests that slip continued on these veins throughout fold growth, with some vein dips exceeding $70^\circ$.

For slip to continue at severe misorientation on incohesive reverse faults requires that fluid pressures exceed supralithostatic levels (Sibson 1985). This constraint must also be met for cohesive faults (Cox 2010). These factors indicate that the formation of the Taemas Vein Swarm was driven by overpressured fluids (cf. Cox 2007).

Differential stress levels must have varied significantly during deformation (at least on a local scale). Parts of the stratigraphy must have had low differential stress levels at the time of vein formation to form extension fractures. Mutually overprinting relationships between shear and extension fractures indicate that differential stress values oscillated between $(\sigma_1 - \sigma_2) < 4T$ and $(\sigma_1 - \sigma_3) > 5.66T$, where $T$ is the tensile strength of the rock (Secor 1965; Hancock 1985). Such differential stress variations could be related to the loading and stress release associated with repeated seismic slip events (Sibson 1989).

In active fold-and-thrust belts, strain is accommodated in sedimentary rocks by a combination of folding and thrust faulting (e.g. Shaw & Suppe 1994). Seismic reflection profiles and surface mapping suggest that actively growing folds are intimately related to seismically active faults (e.g. Namson & Davis 1988; Davis et al. 1989; Shaw & Suppe 1994). In the Taemas Vein Swarm, timing relationships between bedding-parallel slip veins and overprinting flexural flow and extension veins indicate that early during folding strain was accommodated via flexural-slip folding with associated fluid flow along bedding surfaces. Crack–seal textures in bedding-parallel veins at Taemas indicate that bedding-parallel slip was episodic, suggesting that fold growth occurred episodically. Episodic fold growth and associated faulting probably generate significant fracture permeability in actively deforming fold-thrust belts (Finkbeiner et al. 1997). Later in folding, once fold lock-up occurred, fluid flow may have localized more along bedding-discordant faults and extension vein networks associated with fold limb stretching, rather than being isolated along bedding planes. Where bedding-parallel veins linked with discordant fault veins (i.e. thrust faults cutting through fold hinges), it is likely that
some bedding-parallel veins remained active as faults, even though fold tightening had essentially ceased.

Conclusions

The Taemas Vein Swarm preserves evidence of hydrothermal vein growth during fold growth. Vein formation was intimately related to space created during folding, with vein growth active from the early to the latest stages of fold growth. Mutually cross-cutting relationships between veins indicate that vein growth was intermittent, and that veins formed as localized stress fields underwent significant changes in both orientation and magnitude.

Subhorizontal extension fractures and severely misoriented faults indicate that fluid pressures intermittently exceeded lithostatic levels over (at least) local regions of the deforming crust. Individual veins grew incrementally and preserve a variety of textures (fibrous, massive and laminated), and indicate that vein opening and mineral deposition rates varied significantly. Mutually cross-cutting veins and incrementally developed vein textures imply that high-permeability fluid-flow pathways varied dynamically through time and space.

A progressive increase in vein δ¹⁸O with increasing height through the Murrumbidgee Group is attributed to progressive buffering of ¹⁸O-depleted fluids by reaction with host-rock carbonate. Vein δ¹⁸O values imply that the invading fluid had δ¹⁸O compositions consistent with a meteoric fluid source. The isotopic and trace element composition of hydrothermal veins is variable across stratigraphy, between outcrops, within individual outcrops and within individual hydrothermal veins. Variability in O and Sr isotope ratios within and between veins is attributed to variable fluid–rock reaction along dynamically changing fluid-flow pathways, caused by episodic failure, permeability enhancement and transitory fluid flow accompanying episodic slip events within a fault–fracture mesh.

The isotopic and trace element composition of syntectonic veins reflect different rates of fluid–rock reaction for different elements and isotopic systems during hydrothermal fluid flow. Strontium isotope ratios (⁸⁷Sr/⁸⁶Sr) indicate that fluids react with host-rock carbonate, but also scavenge Sr from Sr-enriched minerals (e.g. illite), within shale beds over short reactive path lengths. Trace element concentrations generally decrease with increasing stratigraphical height. Rare earth element concentrations and patterns are influenced by progressive calcite precipitation and sorption along fluid-flow pathways, and changes in REE complexation in solution.

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