Sm–Nd, Sr, C and O isotope systematics in hydrothermal calcite–fluorite veins: Implications for fluid–rock reaction and geochronology

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ABSTRACT

The ^{147}Sm – ^{143}Nd isotope system may be used to determine the age of hydrothermal vein growth for single veins, or sets of veins, providing that the minerals in these veins formed from a hydrothermal fluid with initially homogeneous $^{143}\text{Nd}/^{144}\text{Nd}$. In this study, we determined the ^{147}Sm – ^{143}Nd , $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotopic composition of 9 calcite and fluorite veins (comprising 12 samples in total) that form part of a low-temperature (100–200 °C) fault and fracture hosted hydrothermal system, in the eastern Lachlan Fold Belt, Australia. The vein swarm is hosted by mid-Devonian limestones, which were folded around 350–325 Ma, with vein growth occurring during folding.

The veins chosen for analysis yield homogeneous Sr isotopic compositions ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70851 \pm 0.00003$) and $\delta^{18}\text{O}$ isotope values ($22.5 \pm 0.1\text{‰}$), which are similar to those of the host limestones. The homogeneity of Sr and O isotope compositions is attributed to the progressive reaction of fluids with host rock, with sufficient reaction occurring along discrete fluid flow pathways to fully equilibrate the fluids for these isotope systems. By contrast, $^{143}\text{Nd}/^{144}\text{Nd}$ isotope compositions for the same samples show more variation ($^{143}\text{Nd}/^{144}\text{Nd} = 0.51259$ – 0.51199), which significantly exceeds analytical error. In addition, calcite and fluorite from within the same vein have distinctly different age-corrected Nd isotope compositions. Accordingly, it is likely that fluorite and calcite precipitated from different fluids.

This study indicates that apparently synchronous vein-forming fluids, as suggested by structural relationships, may have diverse isotopic characteristics even over relatively small scales, reflecting variable equilibration of the fluids with the host-rocks. Incomplete equilibration or mixing, resulting in a range of initial $^{143}\text{Nd}/^{144}\text{Nd}$ compositions, is likely to be a common characteristic of fracture-hosted hydrothermal systems, compromising attempts to determine ages using Sm–Nd isochrons. The formation of veins with essentially identical Sr and O isotope compositions, yet diverse initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios, means that Sr and O isotopes cannot be used to identify suitable samples for Sm–Nd geochronological studies.

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1. Introduction

Several studies have explored the application of Sm–Nd isotopes to hydrothermal systems, in order to characterise the source of hydrothermal fluids, and, in particular, to determine the age of hydrothermal mineral deposition (Chesley et al., 1991, 1994; Nagler et al., 1995; Relvas et al., 2001; Bau et al., 2003; Marks et al., 2003; Peng et al., 2003; Xu et al., 2003; Munoz et al., 2005; Sanchez et al., 2006; Su et al., 2009). As is the general case for age determinations

using the isochron approach, the Sm–Nd system will only define an accurate and precise age for hydrothermal mineral growth if the samples selected for analysis formed from solutions with homogeneous $^{143}\text{Nd}/^{144}\text{Nd}$ and there is sufficient spread in the Sm/Nd ratios among the phases. As isochrons for hydrothermal systems are often based on limited sample sets, distinguishing mixing lines from isochrons can be particularly difficult.

The measured Sr and Nd isotopic composition of hydrothermal minerals will be dependent on the age of the vein, and the initial isotopic composition of the fluid when the vein formed. The composition of the fluid will be determined by the composition of the fluid source, the isotopic composition of the rocks along the fluid flow path, and the extent of isotopic exchange between the rock and the fluid. Hydrothermal calcite veins usually contain insignificant Rb compared to Sr, meaning that an age correction usually is not required to compare directly the Sr isotope composition of different calcite veins, but making the Rb–Sr system generally unsuitable for age determinations.

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Sm/Nd ratios in hydrothermal calcite veins, however, can be much more variable and providing the samples selected for analysis are coeval and precipitated from an isotopically homogeneous fluid, the Sm–Nd isochron method can, in principle, be used to determine the age of hydrothermal vein formation. If reactive path lengths change dynamically in a hydrothermal system, the fluids migrating through this hydrothermal system may be affected by different degrees of fluid–rock reaction (expressed as variable isotope ratios) in different veins at the same location (Fig. 1). Variations in reactive path lengths experienced by a parcel of hydrothermal fluid during its migration through the crust could, therefore, have potentially significant implications for the use of isochron dating techniques in hydrothermal systems.

As externally-sourced fluids react with rocks, they progressively become rock-buffered along fluid flow pathways (Rye and Bradbury, 1988; DePaolo and Getty, 1996). As a parcel of fluid moves along a flow path, the fluid will gradually becoming equilibrated with the host rock via dissolution–precipitation and exchange reactions. The extent of equilibration for a particular isotopic system (i.e., $^{87}\text{Sr}/^{86}\text{Sr}$) will depend on the concentration of the element in the fluid, the concentration of the element in different minerals in the wall rocks, the kinetics of reactions between the fluid and mineral phases along the flow paths, and the efficiency of mixing within the fluid. Rock-buffering is reflected in isotope systems such as O, Sr and Nd where the $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ or $^{143}\text{Nd}/^{144}\text{Nd}$ ratio should be the same for both veins and host rocks. During fracture-controlled fluid flow, where fluid pathways change dynami-

cally due to permeability creation and destruction during multiple fault rupture events (Sibson, 2001; Cox, 2005, 2007), multiple fluid ‘batches’ will migrate along different flow pathways. Such discontinuous fluid flow events will lead to changes in reactive path length, as fluids exploit different fluid flow pathways (Fig. 1).

In order to better understand the sources of vein-forming fluids during a compressional tectonic event, and identify suitable veins to determine the age of the hydrothermal system using Sm–Nd isochrons veins, we have measured the ^{147}Sm – ^{143}Nd , $^{87}\text{Sr}/^{86}\text{Sr}$, $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ isotope compositions of hydrothermal calcite and associated fluorite from a low-temperature hydrothermal vein swarm found on the Taemas property, New South Wales, Australia.

2. Geological setting and sample description

An extensive fault–fracture network (hereafter called the ‘Taemas Vein Swarm’, or TVS; Barker et al., 2006; Cox, 2007) is developed in the Taemas Synclinorium, in the Eastern Belt of the Lachlan Orogen, eastern New South Wales, Australia (Glen, 1992). The vein swarm consists of calcite and/or quartz veins (with accessory fluorite and barite) hosted in a network of faults and fractures that were developed within a folded limestone–shale sequence (the Murrumbidgee Group; Browne, 1958; Cramsie et al., 1975). Fossil Acanthodian fish remains indicate a Lower Devonian age for the base of the Murrumbidgee Group (Lindley, 2000). The Murrumbidgee Group is underlain by the Black Range Group, which in turn overlies lower Paleozoic basement (Hood and Durney, 2002). The Berridale Batholith, which forms an extensive suite of I- and S-type granitic rocks (White et al., 1974), is exposed approximately 100 km to the south of the Taemas area and provides a comparison for potential sources of granite-derived fluids that may have traversed the field area (McCulloch and Chappell, 1982). Volcanic rocks underlying the Taemas area have Sr and Nd isotopic compositions similar to the S-type granites measured by McCulloch and Chappell (1982).

Cox (2007) demonstrated that veins in the TVS formed from overpressured, evolved meteoric fluid, which migrated upwards through the Murrumbidgee Group along episodically changing fluid flow pathways, and that fluid flow was restricted largely to macroscopic fractures rather than occurring via porous flow. Oxygen isotope thermometry in fibrous quartz–calcite veins suggests that veins formed at temperatures of 100–200 °C, which, for reasonable geothermal gradients, may have been at depths of 5–8 km (Barker, 2007; Cox, 2007).

Within the Taemas Synclinorium, sedimentary rocks of the Murrumbidgee Group have been folded into upright, open to close folds. Mutually crosscutting relationships between veins and cleavage indicate that vein growth and folding were synchronous, with a variety of fault-related veins, bedding-parallel slip veins and extension veins developed. Total shortening strain in the sedimentary sequence is in the range of 20–50% (Cox, 2007). Typical strain rates of 10^{-14} s^{-1} to 10^{-15} s^{-1} (Pfiffner and Ramsay, 1982; Mueller et al., 2000) imply that folding occurred over a period of 0.5 Ma to 15 Ma.

The age of fold, fault and vein formation at Taemas is poorly constrained. Stratigraphic relationships between the Murrumbidgee Group and the overlying Middle Devonian Hatchery Creek Formation (30 km west of Taemas) are uncertain. Possible conformable relationships between these units imply that regional deformation may have occurred during the Kanimblan Orogeny (early Carboniferous age, approximately 325 Ma; Hood and Durney, 2002), younger than the mid-late Devonian age for folding proposed by Browne (1958).

The isotopic composition of limestones associated with the Taemas Vein Swarm have been documented by Barker et al. (2006), Barker (2007) and Cox (2007). The carbonate component of the limestones in which these veins are hosted has $\delta^{18}\text{O}$ compositions of 22–25‰, $\delta^{13}\text{C}$ compositions of -1 to $+2$ ‰, and $^{87}\text{Sr}/^{86}\text{Sr}$ of 0.70815 to 0.70830. These values are typical for mid-Devonian marine

Fig. 1. (a) Illustration of fluid migration upwards from a fluid reservoir through a set of fractures and faults in a host rock along two different fluid flow pathways (paths '1' and '2', shown by dashed lines), each of which will have different reactive path lengths, (b) Sketch of fluid flowing from a reservoir into a host rock, (c) Sketch of how the isotopic composition of a vein will change with distance as fluid reacts with a host rock. Different reactive path lengths will result in two veins forming at the same point in space, 'x', having different isotopic compositions depending on whether fluid migrated along 'path 1' (more rock buffered) or 'path 2' (less rock buffered; after Cox, 2007).

limestones (Veizer et al., 1999). As yet, no Nd isotopic study has been carried out on host limestones.

The structural and textural characteristics of veins analysed in this study were carefully documented prior to sample analysis. Six bedding-parallel, massive textured calcite veins from the same outcrop (hereafter called the ‘vein cluster’) of *Spirifer yassensis* Limestone (Browne, 1958) were selected for analysis. The setting of these veins is shown in Fig. 2. In this anticline, veins lie both parallel to bedding (inferred to have formed via bedding-parallel slip during flexural slip fold growth), and orthogonal to bedding (extension veins formed during limb-parallel stretching). All of the analysed samples were from different bedding-parallel veins. These samples were collected with the aim of evaluating the isotopic homogeneity of veins occurring in the same structural setting, at the same outcrop location.

In addition to the 6 veins sampled from the same outcrop, veins containing both calcite and fluorite were collected from an outcrop of Currajong Limestone (Browne, 1958) approximately 100 m away from the ‘vein cluster’, with the goal of investigating Sm–Nd systematics between coexisting calcite and fluorite. This allows an evaluation of fluid sources for calcite and fluorite, and potentially the calculation of ages from mineral isochrons. In these three veins, fluorite occurs as isolated grains set in a matrix of massive calcite (Fig. 3a) and is interpreted to have grown at the same time as calcite. In contrast, one vein had a layer of fibrous calcite immediately adjacent to the wall rock, which was overgrown by larger, euhedral fluorite crystals (Fig. 3b). This vein was not chosen for analysis, because the calcite and fluorite appear to have been deposited during two different intervals of vein growth. A vein displaying intergrown elongate calcite and fluorite fibres was located, but unfortunately, the sample was not large enough to yield sufficient fluorite for Sm–Nd isotope analysis.

The selected veins all preserve massive textures, and show no evidence for significant recrystallisation or dissolution/precipitation after formation. Observations made with cold cathodoluminescence do not reveal regular zonation or banding within these calcite veins.

Fig. 3. Images of calcite–fluorite veins found in the Currajong Limestone (Browne, 1958) (a) solitary fluorite grain (Fl) set in a matrix of massive calcite within a fault vein. Note pencil tip (1 cm long) for scale, (b) photomicrograph of an extension vein with fibrous calcite at the vein margin immediately adjacent to the wall rock (WR), and larger, euhedral fluorite crystals in the vein interior. The overgrowth of larger fluorite crystals suggests that the calcite and fluorite were deposited in two separate vein growth events (NB: this vein was not analyzed during this study).

Fig. 2. Photo of the ‘vein cluster’ hosted in an anticline within the *Spirifer yassensis* Limestone, showing the location of veins collected for this study. Listed are the $\delta^{18}\text{O}$ (relative to VSMOW), $\delta^{13}\text{C}$ (relative to VPDB) and Sr isotope values for the different veins. Bedding is defined by layering between limestone (grey beds) and shales (dark grey to black beds). Cleavage is approximately axial planar and vertical down the photograph.

The occurrence of Sm and Nd within vein calcite (rather than within other trace mineral phases) was confirmed by *in situ* trace element analyses of vein calcite carried out using laser ablation quadrupole inductively coupled plasma mass spectrometry. Considering the very slow rates of REE diffusion in calcite at temperatures of ~200 °C (Cherniak, 1998), it is unlikely that Sm–Nd isotope ratios have been disturbed significantly after deposition of these veins.

3. Methods

In the previous studies of Cox (2007) and Barker (2007) the Sr, O and C isotope composition of host rock were determined by carrying out a weak acid leach (either acetic or phosphoric acid) to dissolve only the calcite component of the host rock, which is composed of 70–99% carbonate. This means that O and Sr isotope ratios would not be influenced by small variations in the proportion of detrital minerals in host rocks. Host rock carbonate is Rb-poor (concentrations of <1 ppm), as are hydrothermal veins, meaning that no age correction is required to compare the $^{87}\text{Sr}/^{86}\text{Sr}$ of host rock carbonate and hydrothermal veins (Barker, 2007).

3.1. Strontium isotope methods

Strontium isotope compositions were analysed *in situ* by laser ablation multi-collector inductively-coupled plasma mass spectrometry (LA-MC-ICPMS) on individual chips of vein calcite, as part of a larger study of Sr isotope compositions of veins throughout the TVS (Barker, 2007). Analyses were carried out at the Australian National University, using a HelEx ArF excimer laser ablation system, interfaced to a Finnigan MAT Neptune MC-ICPMS (see Eggins et al., 1998, 2005, for details). Laser pulse rates of 5 Hz in combination with a laser fluence of 5 J/cm², short laser wavelength ($\lambda = 193$ nm), and aperture imaging optics were used to attain controlled calcite ablation (~1 μm per second). Laser spot sizes were varied according to Sr concentrations in the calcite to obtain an ^{87}Sr intensity of ~0.7 V during analysis, with spots varying between 100 and 200 μm in diameter (method is described previously in Barker et al., 2006).

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

3.2. Stable isotope methods

Clean chips of vein calcite were crushed using an agate mortar and pestle, and the resulting fine powder was used for analysis of carbon and oxygen isotope ratios on a Finnigan MAT 251 mass spectrometer. For each sample, 200 ± 20 μg of powder was dissolved in 103% H_3PO_4 at 90 °C in an automated carbonate (Kiel) device. Carbon isotope ratios are reported relative to Vienna Pee Dee Belemnite (VPDB). Oxygen isotope results are reported relative to VSMOW, and were converted from VPDB values, where $\delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \cdot \delta^{18}\text{O}_{\text{VPDB}} + 30.91$ (Coplen et al., 1983).

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

$$\text{NBS} - 19 \delta^{18}\text{O}_{\text{VPDB}} = -2.20\%; \delta^{18}\text{O}_{\text{SMOW}} = +28.64\% \text{ and } \delta^{13}\text{C}_{\text{VPDB}} = +1.95\%$$

$$\text{NBS} - 18 \delta^{18}\text{O}_{\text{VPDB}} = -23.0\%; \delta^{18}\text{O}_{\text{SMOW}} = +7.2\% \text{ and } \delta^{13}\text{C}_{\text{VPDB}} = +5.0\%$$

The standard deviation (2 σ) for the 10 replicate NBS-19 standards used during the analysis of these samples was $\pm 0.04\%$ for $\delta^{13}\text{C}$ and $\pm 0.12\%$ for $\delta^{18}\text{O}$.

3.3. Trace element analyses

Concentrations of trace elements were measured *in situ* by LA-ICP-MS. Samples were analysed using a pulsed ArF Excimer laser ($\lambda = 193$ nm) and a quadrupole ICP-MS (Agilent 7500s). Multiple major and trace elements (^{24}Mg , ^{43}Ca , ^{44}Ca , ^{45}Sc , ^{49}Mn , ^{57}Fe , ^{85}Rb , ^{88}Sr , ^{89}Y , ^{138}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{147}Sm , ^{153}Eu , ^{158}Gd , ^{163}Dy , ^{166}Er , ^{174}Yb , ^{208}Pb) were measured in a single analysis 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), with NIST 612 standard (values of Pearce et al., 1997), analyzed before and after every 6 samples. Individual crystals were analysed by using a 65 μm spot size at 5 laser pulses per second with a moderately low laser fluence (5 J cm⁻²). Internal standardisation is carried out using ^{43}Ca , assuming stoichiometric CaCO_3 . Rb and Sr concentrations are shown in Table 1, other trace element concentrations are in the supplementary data set. Analytical precision is typically $\leq 5\%$ relative (1 σ), with detection limits calculated after Longerich et al. (1996).

3.4. Sm–Nd methods

Samarium and Nd isotope measurements were carried out at the Research School of Earth Sciences, The Australian National University. Clean reagents were used for all procedures, utilizing distilled acids and deionised water (>18 M Ω resistance). All Teflon ware that came in contact with samples was acid-cleaned, and all chemical procedures were carried out in HEPA-filtered clean air stations. Veins were coarsely crushed (9 veins total), and clean calcite and fluorite samples of ~5 g were handpicked. Calcite and fluorite was rinsed in deionised (DI) water, and then coarsely crushed by hand using an agate mortar and pestle. The fluorite samples were then rinsed in 0.2 M HCl to remove any calcite dust. Calcite samples were submerged in 0.2 M HCl for 10 s to clean the surface. From these clean samples, 100–300 mg of sample was weighed into clean screw-top Teflon vials and a weighed aliquot of 'ANU-1', a mixed ^{147}Sm – ^{150}Nd enriched isotope solution was added.

Clean calcite samples were then dissolved at room temperature in 0.5 M HCl. Fluorite samples were refluxed with 16 M HNO_3 , 8 M HCl and HClO_4 on a 170 °C hot plate. Following dissolution, rare earth elements (REEs) were separated from matrix elements by cation-exchange chromatography, using a REE-specific resin (Rehkamper et al., 1996). Neodymium and Sm were further purified using chromatography columns loaded with HDEHP-coated Teflon powder (Richard et al., 1976).

Isotope ratios were measured by thermal ionisation mass spectrometry using a Finnigan MAT261 for Sm concentration determinations, and a Thermo-Finnigan Triton TI for determination of Nd concentrations and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Neodymium and Sm were loaded onto separate filaments in HNO_3 and dilute H_3PO_4 , and run on Ta (evaporation)–Re (ionisation) double filaments. Filaments were outgassed at 4A for 30 min prior to sample loading. Nd analyses consisted of 150 measurement cycles in static mode using 8.4 s integrations; Sm concentrations were determined using shorter (30 cycles) runs in static mode. Nd samples were monitored for possible Ce and Sm interferences, which were in all cases negligible. La Jolla and the in-house AMES nNd-1 standards were run to monitor external reproducibility, with the sample data adjusted to yield a value for La Jolla of 0.511860. A procedural blank yielded 85 pg of Nd, which is negligible compared to the total quantity of Nd in the samples. Mass fractionation was corrected to

Table 1

Mineral type (Min; cct = calcite, fl = fluorite), sample identifier (ID), stable isotope ($\delta^{18}\text{O}$ relative to VSMOW, $\delta^{13}\text{C}$ relative to VPDB) and Sm–Nd isotopic and concentration data (Rb and Sr, determined by LA-Q-ICPMS, Sm and Nd determined by TIMS; bdl = below detection limit) for bedding-parallel calcite veins from a 'vein cluster' in the Spirifer yassensis Limestone (samples SP101, SP102, SP103, SP105, SP110) and calcite–fluorite vein pairs from the Currajong Limestone (CJ201, CJ2-2, SMF1).

Min	Longitude	Lat	ID	$\delta^{18}\text{O}$	$\delta^{13}\text{C}$	$^{87}\text{Sr}/^{86}\text{Sr}$	$\pm 2\text{se}$	Rb (ppm)	Sr (ppm)	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$\pm 2\text{se}$ 10^{-6}	$^{143}\text{Nd}/^{144}\text{Nd}$	$\pm 2\text{se}$ 10^{-6}	ϵNd	ϵNd (325 Ma)
Cct	148°48'10.54"E	34°56'48.82"S	SP101	22.4	0.96	0.70852	0.00002	0.1	1952	0.43	1.68	0.1553	12	0.512113	10	−10.2	−8.5
Cct	148°48'10.54"E	34°56'48.82"S	SP102	22.6	0.69	0.70852	0.00001	0.02	3963	2.27	11.71	0.1172	10	0.511990	8	−12.6	−9.4
Cct	148°48'10.54"E	34°56'48.82"S	SP103	22.5	0.94	0.70852	0.00002	bdl	2967	0.68	3.20	0.1293	9	0.512069	10	−11.1	−8.3
Cct	148°48'10.54"E	34°56'48.82"S	SP104	22.5	0.8	0.70849	0.00002	0.04	3288	1.15	5.38	0.1287	13	0.512076	9	−11.0	−8.1
Cct	148°48'10.54"E	34°56'48.82"S	SP105	22.5	0.76	0.70851	0.00002	0.02	3751	3.64	14.15	0.1553	18	0.512087	12	−10.8	−9.0
Cct	148°48'10.54"E	34°56'48.82"S	SP110	22.4	0.74	0.70854	0.00002	0.03	3066	0.90	4.26	0.1274	8	0.512069	9	−11.1	−8.2
Fl	148°48'11.22"E	34°56'47.40"S	CJ201-fl	N/A	N/A	N/A	N/A	N/A	N/A	0.06	0.24	0.1639	27	0.512242	21	−7.7	−6.4
Cct	148°48'11.22"E	34°56'47.40"S	CJ201-cct	N/A	N/A	0.70826	0.000021	bdl	2593	0.53	2.91	0.1105	9	0.512007	13	−12.3	−8.7
Fl	148°48'11.22"E	34°56'47.40"S	CJ202-fl	N/A	N/A	N/A	N/A	N/A	N/A	0.04	0.18	0.1469	38	0.512389	18	−4.9	−2.8
Cct	148°49'1.38"E	34°58'1.03"S	CJ202-cct	N/A	N/A	0.70827	0.000017	bdl	3426	0.28	1.50	0.1112	12	0.512034	11	−11.8	−8.2
Fl	148°48'10.54"E	34°56'48.82"S	SMF1-fl	N/A	N/A	N/A	N/A	N/A	N/A	0.13	0.26	0.2864	45	0.512589	33	−1.0	−4.7
Cct	148°48'10.54"E	34°56'48.82"S	SMF1-cct	N/A	N/A	N/A	N/A	N/A	N/A	0.21	0.93	0.1359	18	0.512328	29	−6.1	−3.5

$^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$. Nd isotopic compositions are reported as ϵNd :

$$\epsilon\text{Nd} = \left(\frac{^{143}\text{Nd}/^{144}\text{Nd}_{\text{sample}}}{^{143}\text{Nd}/^{144}\text{Nd}_{\text{CHUR}}} - 1 \right) * 10,000$$

where the present day $^{143}\text{Nd}/^{144}\text{Nd}$ CHUR composition is 0.512638. Values are shown for the measured $\epsilon\text{Nd}_{(0)}$, and the initial $\epsilon\text{Nd}_{(T)}$ calculated at 325 Ma (Table 1), that is, the most likely age of regional deformation (see above). External precision for $^{143}\text{Nd}/^{144}\text{Nd}$ based on repeat analyses on the Ames standard on the ANU Triton TIMS instrument from 2002 to 2006 ($n = 22$) is ± 30 ppm (2 SD).

4. Results

The $\delta^{13}\text{C}$, $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$, $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ values for calcite in the bedding-parallel veins occurring within the 'vein cluster' are shown in Fig. 2 and Table 1. These calcites have very similar $\delta^{18}\text{O}$ ($22.5 \pm 0.1\text{‰}$) and $^{87}\text{Sr}/^{86}\text{Sr}$ (0.70851 ± 0.00003) values, with slightly more variable $\delta^{13}\text{C}$ ($0.7\text{--}1.0\text{‰}$). The veins contained within the vein cluster have slightly lower $\delta^{18}\text{O}$ than unaltered wall rock.

In situ LA-ICP-MS analyses demonstrate that calcite veins have Rb concentrations of <1 ppm, and Nd and Sm concentrations of 1 to 15 ppm (Table 1, supplementary data set). Lanthanum concentrations vary between 0.6 and 9.3 ppm in vein calcite, with concentrations of other REEs similarly variable. Isotope dilution-TIMS data reveal that calcites are light REE enriched, with $^{147}\text{Sm}/^{144}\text{Nd}$ varying between 0.11 and 0.16. Calcite contained within veins that also have apparently coeval fluorite have $^{147}\text{Sm}/^{144}\text{Nd}$ ratios (0.11–0.14) similar to calcites contained within the vein cluster, described above (Table 1). The fluorite samples range from slightly light REE enriched ($^{147}\text{Sm}/^{144}\text{Nd} = 0.147\text{--}0.164$) to strongly light REE depleted ($^{147}\text{Sm}/^{144}\text{Nd} = 0.286$). The 3 fluorite samples have $\epsilon\text{Nd}_{(0)}$ of -1.0 to -7.7 , and coexisting calcite samples $\epsilon\text{Nd}_{(0)}$ range between -3.5 and -8.5 , whereas calcites from the vein swarm have $\epsilon\text{Nd}_{(0)}$ compositions between -10.0 and -12.6 (Table 1).

5. Discussion

Veins in the 'vein cluster' have $\delta^{13}\text{C}$ values between $+0.69$ and $+0.96\text{‰}$ (VPDB). This range in $\delta^{13}\text{C}$ is entirely within the range of host rock samples determined by Barker et al. (2006) and Cox (2007), and is typical for Devonian marine limestones (Veizer et al., 1999). It is possible that the $\delta^{13}\text{C}$ variations in veins could be caused by small variations in temperature. However, changes in $\delta^{13}\text{C}$ values do not correlate with changes in $\delta^{18}\text{O}$, so this possibility is discounted. Alternatively, small changes in $\delta^{13}\text{C}$ may be related to slight variations in the fluid oxidation state.

If small amounts of organic matter in shales, or small amounts of methane (or other organic compound) in the fluid become oxidized to $[\text{HCO}_3^-]$, then this could cause small variations in the $\delta^{13}\text{C}$ value of resulting veins. (Ohmoto and Goldhaber, 1997). Vein strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) ratios in the 'vein swarm' (and indeed throughout the Taemas Vein Swarm; Barker, 2007) are generally slightly elevated about host rock carbonate values, excepting veins hosted in nearly pure limestones (99–100% calcite). Oxygen isotope ratios of host rocks and veins in the Taemas Vein Swarm (Cox, 2007) suggest that silicate minerals did not undergo significant reaction with infiltrating fluid, with oxygen isotope values in veins apparently reflecting only reaction with carbonate-rich host rocks. Therefore, in this study, we analyzed only the calcite component of host limestones, via an acetic acid leach. The analyses of host limestones yielded $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.70815 to 0.70830 (Barker, 2007), typical for mid-Devonian limestones (Veizer et al., 1999). However, these analyses did not take into account the influence of more radiogenic minerals, such as potassium-rich illites, known to occur within the shale units (Cox, 2007). We attribute elevated $^{87}\text{Sr}/^{86}\text{Sr}$ in carbonate veins relative to host rocks to this contribution from clay and other silicate minerals.

In order to evaluate the possibility that the Taemas veins formed from a single, isotopically homogeneous fluid, we examined the Sm–Nd isotope data using conventional isochron diagrams of $^{147}\text{Sm}/^{144}\text{Nd}$ vs $^{143}\text{Nd}/^{144}\text{Nd}$ for the 'vein cluster' (Fig. 4) and calcite–fluorite pairs from individual veins (Fig. 5). The vein data do not define a straight line, therefore the Sm–Nd isotope data carry no age significance. The three calcite–fluorite veins define three 2-point lines with significantly different slopes (Fig. 5). The ages defined by these slopes have no geologic significance, as two of these ages (1510 ± 86 Ma and 671 ± 68 Ma), are older than the limestone in which the veins are hosted, while the younger age (265 ± 40 Ma) significantly postdates the proposed Carboniferous age for folding (Hood and Durney, 2002). In contrast, field relationships between the veins, folds, axial plane foliations and fold-related faults, all indicate that fold growth and vein formation were contemporaneous and that all of the veins formed at approximately the same geological time. A possible explanation for the Nd isotopic heterogeneity could be the presence of REE rich trace phases within the calcites. Thin section observations of calcite veins indicate that the calcite is clear with minimal solid mineral inclusions. Time-resolved REE/Ca ratios measured during laser ablation analyses with a $65\text{ }\mu\text{m}$ spot are homogeneous, or show only monotonic variation during analysis, and do not display sharp fluctuations over short time intervals as might be expected if inclusions were contributing significantly to the signal. Additionally the calcite samples were dissolved in dilute HCl and centrifuged prior to chemical separation effectively isolating any silicate inclusions.

Partitioning of rare earth elements (REEs) between calcite and fluid is highly dependent on pressure, temperature and the concentration of complexing species in hydrothermal solutions (Bau, 1991; Bau and Moller, 1992). Partition coefficients for rare earth elements between calcite and fluid are poorly constrained for hydrothermal calcite. Zhong and Mucci (1995) found that partition coefficients for calcite and fluids of seawater composition at low temperature (25 °C) were on the order of 10^2 for heavy REE and 10^3 for light rare earth elements. Rare earth concentrations in vein calcite reported in this study vary between 0.03 ppm (Yb) and 25 ppm (La). Assuming that the partition coefficients of Zhong and Mucci are relevant to the calcite veins analyzed in this study, REE concentrations in the fluids from which the calcite veins precipitated were on the order of 0.1 to 10 ppb. These inferred REE concentrations in fluids are lower than the concentrations reported for high-temperature hydrothermal fluids trapped in fluid inclusions (e.g., Norman et al, 1989), but are somewhat higher or similar to REE concentrations reported in cooler waters from hydrothermal wells (Aggarwal et al., 1996). The evidence presented above is consistent with rare earth element concentrations and isotopic ratios in calcite veins analysed in this study being controlled by primary incorporation of REEs into the calcite mineral lattice, rather than controlled by incorporation of REEs in other mineral phases or into fluid inclusions.

Textural relationships preserved in calcite–fluorite veins (i.e., intergrown calcite and fluorite fibers, massive crystals with sharp contacts) indicate that calcite and fluorite grew contemporaneously. Therefore, it seems reasonable to expect that fluorite and calcite crystals grew from a single parent fluid, with a homogeneous initial isotope composition. Thus, we conclude that these veins formed from fluids that were isotopically heterogeneous with a range of initial $^{143}\text{Nd}/^{144}\text{Nd}$ values, but isotopically homogenous with respect to oxygen and strontium isotope compositions.

The negative $\varepsilon\text{Nd}_{(0)}$ compositions of calcite from the ‘vein cluster’ of -10.0 and -12.6 , indicate a crustal (low Sm/Nd) source for the Sm and Nd found in these fluids (e.g., DePaolo and Wasserburg, 1976). In the case where precipitation ages for veins cannot be calculated from isochrons, but the age of hydrothermal vein formation can be independently constrained, then the initial εNd at the time of precipitation (here reported as $\varepsilon\text{Nd}_{325}$) can be used to infer information about the sources of rare earth elements in these hydrothermal fluids. Fig. 6 shows εNd compositions calculated for veins at 325 Ma, plotted with the range of εNd values determined for I-type and S-type granites in the Berridale Batholith (McCulloch and Chappell, 1982), recalculated to an age of 325 Ma. The Nd isotopic

Fig. 4. Graph showing $^{147}\text{Sm}/^{144}\text{Nd}$ plotted against measured $^{143}\text{Nd}/^{144}\text{Nd}$ for samples from the calcite vein swarm (SP samples). The 2σ error bars for each sample are shown. Note that the range of sample values does not define a linear trend (that is they do not define an isochron).

Fig. 5. Sm–Nd two point ‘isochrons’, showing $^{147}\text{Sm}/^{144}\text{Nd}$ plotted against $^{143}\text{Nd}/^{144}\text{Nd}$, for different calcite–fluorite vein pairs calculated using ISOPLLOT (Ludwig, 2003).

compositions of the calcite veins are entirely consistent with Nd in the veins being derived from similar regional granites, or their protoliths. In contrast, the three fluorite samples, and one calcite sample (SMF1) have εNd compositions that are distinctly different from the vein cluster. This implies that these samples formed from a fluid with a distinct source.

The implication of our results is that the assumption that adjacent mineral phases in massive textured hydrothermal veins were deposited at the same time, from similar compositions fluids, may not be valid. One method to obtain hydrothermal minerals that were deposited from the same fluid may be to collect samples that have

Fig. 6. Measured (open symbols) and initial ϵ_{Nd} values (closed symbols) for calcite (circles) and fluorite (squares) samples analyzed in this study. Also shown are the range of ϵ_{Nd} for I- and S-type granites from the regionally extensive Berridale Batholith (McCulloch and Chappell, 1982), which represents potential fluid endmember compositions. All ϵ_{Nd} values are calculated at 325 Ma. The veins show a large compositional variation at their likely age of formation, overlapping with granites from the Berridale Batholith (see text for further discussion).

equilibrium growth textures, i.e., vein material collected from the same growth band of polyminerals fibrous veins (Fisher and Brantley, 1992).

Mixing of fluids from multiple sources and variable fluid–rock reaction during fluid migration (thus producing variable initial $^{143}\text{Nd}/^{144}\text{Nd}$) are likely to be common processes in hydrothermal systems. Previous studies by Nagler et al. (1995) and Bau et al. (2003) have raised doubts about the applicability of Sm–Nd isochrons to hydrothermal systems. Peng et al. (2003) and Su et al. (2009) report high-precision Sm–Nd isochron ages for calcite veins hosted in predominantly carbonate rocks. However, Sr isotope measurements on veins on which Nd isotopes were also measured (Peng et al., 2003; Su et al., 2009) reveal a large range in $^{87}\text{Sr}/^{86}\text{Sr}$, despite the low Rb in these samples; that is, the $^{87}\text{Sr}/^{86}\text{Sr}$ cannot be attributed to radiogenic ingrowth. This suggests that calcite samples analyzed in the studies of Peng et al. (2003) and Su et al. (2009) may have formed from fluids with heterogeneous initial $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$.

The contrasting behavior of Sr and O isotopes (homogeneous between veins) compared to Nd isotopes, may relate to the precipitation of these veins in a carbonate host rock. Measured Nd/Sr ratios for the host limestones at Taemas are low (Barker, 2007), which are typical for sedimentary carbonates (Veizer, 1983). Therefore, it is likely that a much higher degree of fluid rock reaction is required to equilibrate Nd to rock values as compared to Sr. We suggest that the range in Nd isotope compositions inferred for the parental fluids may reflect different compositions in the fluid source and/or changes in length of fluid flow paths, whereas C, O and Sr isotopes show little variation because they were readily buffered by the host rocks. This is similar to the results of Voicu et al. (2000), who found that Nd isotope compositions within a gold deposit hosted in granitoid rocks (with surrounding andesites and basalts) reflected the source of the mineralising fluid, while Sr isotopes had become rock buffered. In comparison, Jamtveit et al. (1997) found that a skarn hosted in limestones and shales showed significant Sr isotope variation, yet little Nd isotope variation. It is likely that different hydrothermal systems will have different transport characteristics for Sr and Nd, depending on the composition of host rocks, and the composition and complexa-

tion of Sr and Nd in the hydrothermal fluid (Gammons et al., 1996; DePaolo and Getty, 1996; DePaolo, 2006).

Fig. 7 provides a hypothetical illustration of how different isotope systems could become equilibrated over different distances, (i.e., at different rates, see also Abart and Pozzorini, 2000) during the migration of an externally-derived fluid through a volume of rock. For example, at point 'α' in Fig. 7, the fluid remains fluid-buffered with respect to Nd, but has become partially rock-buffered with respect to O, and has become rock-buffered with respect to Sr isotopes. As fluid–rock reaction proceeds, at point 'β', the fluid has become totally rock-buffered with respect to both Sr and O, but only partially rock-buffered with respect to Nd. Fig. 7 demonstrates that as reactive path length changes, different isotope systems could be influenced in different ways.

The equilibration rate of a specific isotope system is likely controlled by the relative concentrations of the element in the rock compared to the fluid (DePaolo, 2006). In addition, changes in both mineralogy and/or reactive surface area along fluid flow pathways could influence how rapidly a fluid becomes rock-buffered with respect to different chemical species. For example, a fault zone containing significant pulverised material (i.e., cataclasite) might have considerably higher reactive surface area than a fracture network consisting of relatively smooth sided extension fractures.

Reactive path lengths could be changed by different segments of a fluid percolation network becoming active fluid flow pathways during multiple episodes of fault reactivation (see Fig. 1 and also Miller and Nur, 2000; Cox, 2007). Fracture generation (perhaps caused by seismic rupture) and fracture sealing by hydrothermal mineral precipitation will cause fluid flow pathways to evolve dynamically in both time and space. This will lead to changes in fluid flow pathways, as well as reactive path lengths. Additionally, changes in fluid flow rates and fluid fluxes in fracture-controlled hydrothermal systems will also influence the extent of rock buffering (Cox, 2007). Given this scenario, it would not be surprising if aspects of fluid chemistry varied during progressive vein growth, especially if fracture networks episodically breach different fluid reservoirs. In addition, repeatedly switching flow pathways exposes migrating, reactive fluids to variable wall-rock chemistries. In the Taemas Vein Swarm it appears that high O, C and Sr concentrations in the host rock sequence led to efficient rock buffering of O, C and Sr isotopic compositions. However, Sm–Nd isotopic compositions were not so strongly buffered by the immediate host-rocks.

Fig. 7. Schematic diagram showing how different isotopes could become equilibrated over different path lengths during progressive fluid–rock reaction. It is important to note that every fluid–rock system will behave differently for different tracers, depending on the composition of rocks and fluid, and will be dependent on the concentration of tracers in rock and fluid, as well as the isotopic values of these different tracers. Point 'α' marks the point at which Sr has become equilibrated with the host rock, but O and Nd have not yet become equilibrated. At point 'β' only Nd is not rock-buffered. Any change in reactive path length beyond point 'β' will change the Nd isotope ratio, but will not affect Sr or O isotope values.

6. Conclusions

The veins yield homogeneous Sr ($^{87}\text{Sr}/^{86}\text{Sr} = 0.70851 \pm 0.00003$) and $\delta^{18}\text{O}$ isotope values ($+22.5 \pm 0.1\text{‰}$), which are similar to host rock limestones. The homogeneity of Sr and O isotope compositions is attributed to progressive reaction of fluids with host rock limestones, with sufficient reaction occurring along fluid flow pathways to equilibrate the fluids with host rock limestones. However, Sm–Nd isotope values show significant variation, which is attributed to incomplete equilibration of Sm–Nd isotopes with host limestones during migration of fluids and/or changes in fluid source. This phenomenon is most likely applicable to carbonate-hosted vein systems, where the low Nd/Sr composition of host rocks will promote more rapid equilibration of Sr in comparison to Nd. In addition, calcite and fluorite within the same vein have been shown to have deposited from separate or compositionally heterogeneous fluids, with distinct Nd isotope compositions. Accordingly, it is likely that fluorite and calcite precipitated at different stages of vein growth or that the fluids were poorly mixed.

The calcite–fluorite pairs from individual veins do not produce geologically reasonable Sm–Nd isochrons. The erroneous isochron ages are attributed to vein minerals precipitating from multiple fluids or poorly mixed fluids, which had distinct $^{143}\text{Nd}/^{144}\text{Nd}$ compositions. This study indicates that veins that formed in apparent synchrony may deposit from solutions that have a diverse range of initial isotope ratios. High-precision ages for hydrothermal mineralisation obtained via Sm–Nd isochrons should be evaluated carefully for artifacts introduced by fluid heterogeneity.

Furthermore, vein fluids may have essentially identical Sr and O isotope ratios, yet diverse initial $^{143}\text{Nd}/^{144}\text{Nd}$, suggesting that Sr and O isotopes cannot be used to ‘fingerprint’ veins with the same initial $^{143}\text{Nd}/^{144}\text{Nd}$ for geochronological studies. Instead, independent criteria (such as equilibrium growth textures) are required to establish equilibrium between vein minerals.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.chemgeo.2009.07.009](https://doi.org/10.1016/j.chemgeo.2009.07.009).

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