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Preservation of Mesoproterozoic age deep burial fluid signatures, NW Scotland

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ABSTRACT

Bedding-parallel fibrous calcite is a widely developed feature of mudrock successions, reflecting conditions of fluid overpressure (Stoneley, 1983; Parnell et al., 2000; Cobbold et al., 2013). The calcite preserves signatures of fluids developed during deep burial, including hydrocarbons. Most studied examples are of Phanerozoic (<540 Ma) age. This study reports well-preserved fibrous calcite in the Mesoproterozoic (~1180 Ma) Stoer Group, NW Scotland. The fibrous calcite occurs immediately above a unit of carbonaceous black shale. If hydrocarbons were generated from the black shales, they could have contributed to the development of fluid overpressure, but there is no direct evidence for this. The calcite reflects the original deep burial fluid, rather than a later overprint, because (i) it has a distribution related to stratigraphy, (ii) the bedding-parallel fibres have not been recrystallized, and (iii) later veining is at high angles to bedding. The calcite contains fluid inclusions, and has yielded stable isotope and entrained volatile data, indicating the potential to record diagenetic processes over one billion years ago.

1. Introduction

Bedding-parallel veins of fibrous calcite, the so-called ‘beef’ veins of some literature (Rodrigues et al., 2009; Cobbold et al., 2013), are a widespread phenomenon in shales, especially carbonaceous shales. Characteristically, the veins are millimeter-scale to centimeter-scale (bedding-normal), and have up to metre-scale lateral (bedding-parallel) extent. They are commonly antitaxial, i.e. they developed by growth on two planes between the vein and the wall rock. The veins have been attributed a range of origins, including force of crystallization, burial and unloading, hydrothermal fluid circulation and tectonic activity, but a consensus is developing around a model of mineral precipitation under conditions of high pore fluid pressure and vertical gradients in overpressure (Stoneley, 1983; Cobbold and Rodrigues 2007, Rodrigues et al., 2009; Cobbold et al., 2013). The possible causes of high fluid pressure include hydrocarbon generation, consistent with the common occurrence of the veins in carbonaceous shales. This model implies that the calcite represents a potential source of information about the composition of diagenetic fluids. Accordingly, fibrous calcite has been analyzed for stable isotope composition (Al-Aasm et al., 1995; Fischer et al., 2005; Kowal-Linka, 2010), trace element composition (Marshall, 1982; Elburg et al., 2002), organic biomarkers (Kiriakoulakis et al., 2000) and fluid inclusion microthermometry (Parnell et al., 2000; Bons et al., 2009). The great majority of described bedding-parallel vein occurrences are from the Phanerozoic (Cobbold et al., 2013), but there are examples in Proterozoic shales (Bons et al., 2009; Turner and Kamber, 2012).

In this study we report extensively developed fibrous calcite in Mesoproterozoic rocks, and propose that they offer a rare opportunity to sample diagenetic fluids from deep geological time over one billion years ago. The objectives of the study were (i) to record the petrography of the fibrous calcite veins; and (ii) to demonstrate that they have the potential to yield fluid signatures.

1.1. Host succession; description

The fibrous calcite documented here is in the late Mesoproterozoic Stoer Group, Torridonian Supergroup, North West Scotland. The Stoer Group was deposited in a continental setting including alluvial fan, fluviatile and lacustrine environments (Stewart, 2002; Kinnaird et al., 2007). The succession includes a distinctive unit of

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about 100 m shale designated the Poll a' Mhuilt Member of the Bay of Stoer Formation (Fig. 1), interpreted as lacustrine (Stewart, 2002; Andrews et al., 2010). The shales are almost wholly red-coloured, but include a further distinctive unit of grey-black shale interpreted as the deposit of a permanent lake. The grey-black colour is due to organic matter, including algae and some of the earliest eukaryotic life (Cloud and Germs, 1971; Strother et al., 2011). This unit closely follows a meteorite impact deposit dated at 1.18 Ga (Parnell et al., 2011). The rocks have experienced low-grade regional metamorphism, but their sedimentary characteristics are perfectly preserved. The burial history of the Stoer Group is difficult to constrain, as only 1 km thickness of the group is preserved above the Bay of Stoer Formation, below an unconformity with the ~1.0 Ga Torridon Group (Stewart, 2002). However, clasts of Stoer Group sandstone in the basal Torridon Group were fully lithified and compacted (Lawson, 1976), the Stoer Group sandstone is conspicuously more indurated than the Torridon Group sandstone, and Stewart (2002) reports that pumpellyite veining (probably 200+ °C affect the Stoer Group but not the Torridon Group. If any hydrocarbons were generated from the Stoer Group, it is probable that this occurred during the ~200 Myr between Stoer Group deposition and Torridon Group deposition. The Stoer Group would formerly have been buried beneath the Cambro-Ordovician Durness Group, including limestones.

Samples were examined from a Stoer Group section on the north side of the Bay of Stoer (National Grid Reference NC 032285), described by Stewart (2002).

2. Methods

Fluid inclusion studies were performed on doubly polished wafers using a Linkam THMS-600 heating–freezing stage mounted on a Nikon Labophot transmission light microscope. The instrument equipped with a range of objective lenses including a 100× lens, was calibrated against synthetic H_2O (374.1 and 0.0 °C) and CO_2 (−56.6 °C) standards (Synthetic Fluid Inclusion Reference Set, Bubbles Inc., USA).

Entrapped gases were measured by the crush-fast scan (CFS) method (Blamey, 2012). Samples were analyzed by incremental cold-crush fast scan, or a bulk decrepitation/crush method under an ultra-high vacuum (approx. 10^{-8} Torr) using Pfeiffer Prisma quadrupole mass spectrometers operating in fast-scan, peak-hopping mode. Two to ten bursts of fluid (up to $\sim 2\ 10^{-11}$ l) were released per sample and analyzed for H_2, He, CH_4, H_2O, N_2, O_2, Ar and CO_2. Calibration was checked against commercial standard gas mixtures, atmospheric capillary tubes and three fluid-inclusion standards as described by Norman and Blamey (2001). Instrumental blanks were also analysed routinely. The amount of each species was calculated by proprietary software to provide a quantitative analysis, but crushing does not liberate all the entrapped gas from samples, so data are generated as molar percentages rather than moles. Data for entrapped gas are reported as oxygen/nitrogen and methane/carbon dioxide ratios, as a measure of whether the volatile components are dominated by oxidized or reduced species (see Wright et al., 2012; McMahon et al., 2012, 2013 for use of these ratios). In addition to measurement of fibrous vein samples, a sample of red calcite-cemented sandstone from the vein-bearing section was also sampled. Given former burial beneath Cambro-Ordovician limestone, a sample of the limestone from 30 km to the east was measured for comparison.

Samples were analysed for carbon and oxygen isotope compositions using an Analytical Precision AP2003 continuous-flow mass spectrometer at SUERC. Replicate measurements of the internal Mab2b standard, and international standards IAEA-CO1 and IAEA-NBS19, were made before and after sample analysis. External precision (1σ) was better than +/− 0.2‰ for both carbon and oxygen isotope compositions.

Petrographic studies were made on polished samples using an ISI ABT-55 scanning electron microscope, operated in backscattered imaging mode, and equipped with a Link Analytical 10/55S processor and ISS I-SCAN 2000 software.

3. Stoer Group bedding-parallel veins

3.1. Petrography

Bedding-parallel fibrous veins occur in the Poll a' Mhuilt Member in red shales immediately above the unit of grey-black shales (Fig. 2). The fibrous veins are calcitic, dolomitic, or mixed, but the calcite veins predominate and are the focus of this study. The veins are typically 1–2 mm thick, and up to 1 cm thick. The calcite is a deep red colour. Veins are generally horizontal, parallel to bedding, but may dip at up to 30° where they lie on sedimentary foreset surfaces (Fig. 2). The veins contain entrapped lenses of fully compacted red mudstone (Fig. 3). Some veins exhibit a median line typical of antitaxial crystal growth. Where a paragenetic

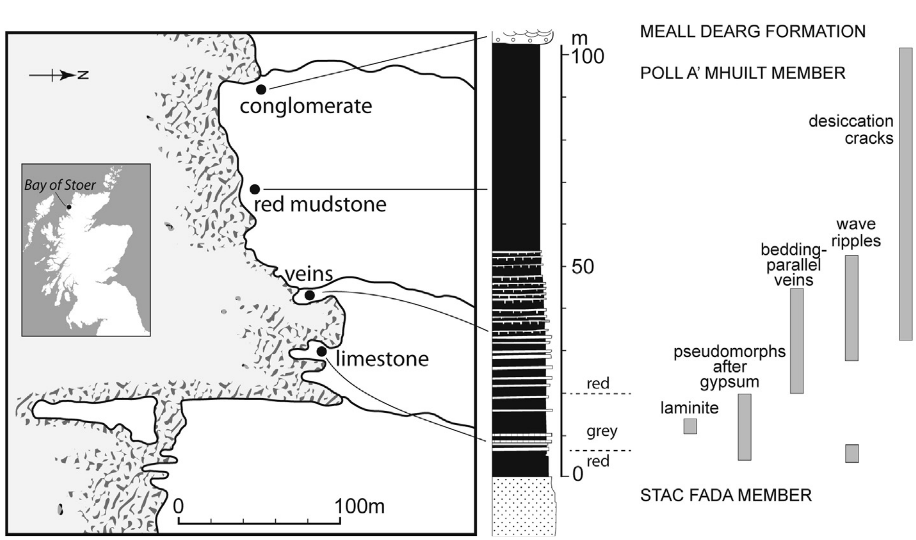

Figure 1. Location map for section containing fibrous veins, Bay of Stoer, Sutherlandshire, Scotland (modified from Stewart, 2002).

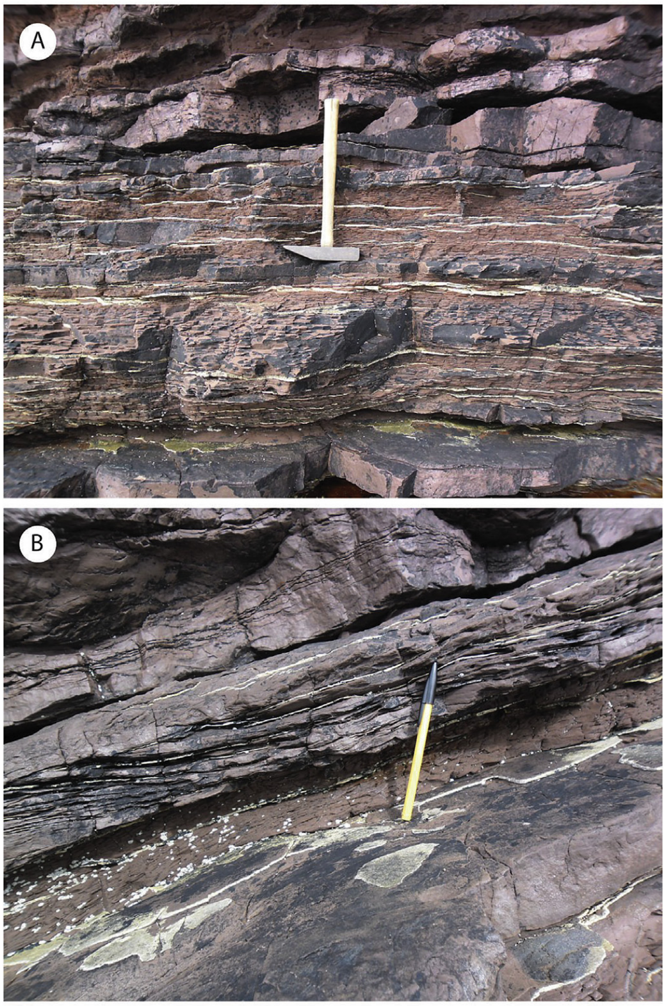

Figure 2. Occurrence of fibrous veins in Bay of Stoer Formation, Bay of Stoer. A, bedding-parallel veins (white) in mudrocks between blocky sandstone beds; B, veins (white) on foreset surfaces.

relationship between calcite and dolomite is evident, the dolomite occurs closer to the median line in antitaxial veins, indicating that it is younger. Locally, the fibres exhibit cone-in-cone structure (Fig. 4; parallel fibres represent cone-in-cone with an apical angle of 0°). In

Figure 3. Vein of fibrous dolomite, with encapsulated fragments of fully compacted mudrock. Vein is cross-cut by minor veinlet of younger dolomite.

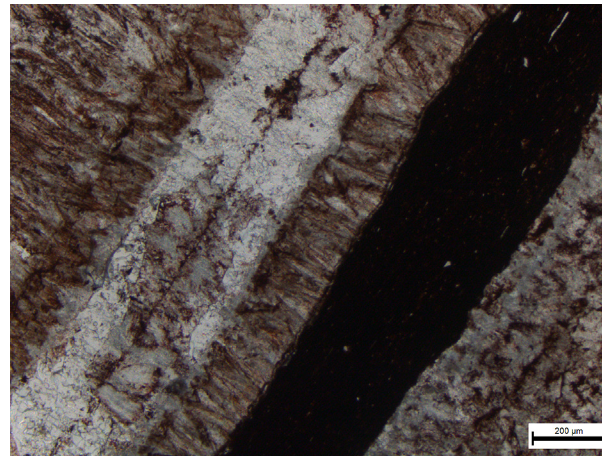

Figure 4. Photomicrograph of thin section of fibrous calcite vein, showing cone-in-cone structure outlined by haematite (dark) in layers in centre and upper left of vein.

addition, there are several minor authigenic mineralogical components: (i) quartz at the vein margins (ii) barite precipitated between calcite fibres, (iii) haematite, mixed with the calcite, conferring the red colour, (iv) rare earth element (REE) carbonates, and (v) apatite, mixed with the quartz (Fig. 5). The dolomite is monomineralic. A more limited development of bedding-parallel calcite occurs in red mudrocks below the Stac Fada Member.

3.2. Fluid inclusions

Fluid inclusions were observed in both dolomite and calcite crystals. The most abundant type of inclusion is monophase liquid and/or vapour (less than 5 microns in size) distributed along annealed fractures (secondary origin). Calcite crystals also host a number of two-phase (liquid + vapour) aqueous-rich inclusions with a high degree of fill ($F = 0.95$, measured on a 2-D screen image, although the accuracy of measurement is severely limited by small size; $F =$ vol. of liquid/[vol. of liquid + vapour]). Their size ranges from 1 to 5 microns length and they are rounded to elliptical in shape. They generally occur in trails along annealed fractures and are thus classified as secondary inclusions, but they can also occur in groups at the core of the crystal and these are interpreted as primary in origin (Fig. 6). The two-phase inclusions imply temperatures of trapping of at least 60 °C, as inclusions trapped at lower temperatures rarely exhibit a vapour bubble (Roedder, 1984). Homogenization temperatures were successfully measured in five two-phase fluid inclusions in calcite, at 74, 76, 79, 80 and 140 °C. Four of the values are closely grouped between 74 and 80 °C. The single higher value may represent a later, distinct fluid pulse. Calcite is susceptible to leakage from inclusions, but an apparently constant size of vapour bubble suggests that leakage has not occurred in these inclusions.

A single bedding-parallel calcite vein below the Stac Fada Member contains larger inclusions, which yield a mean homogenization temperature of 79 °C ($n = 13$), and ice melting temperatures equivalent to salinities in the range 5–8 wt% NaCl (Parnell et al., 2011). The homogenization temperatures near-identical to those for the fibrous calcite veins above the black shale strongly suggest that the occurrences represent a single episode of fluid migration.

3.3. Stable isotopes

The calcite and dolomite veins have yielded stable carbon and oxygen isotope data (Table 1, Fig. 7). Oxygen isotope values ($\delta^{18}O$)

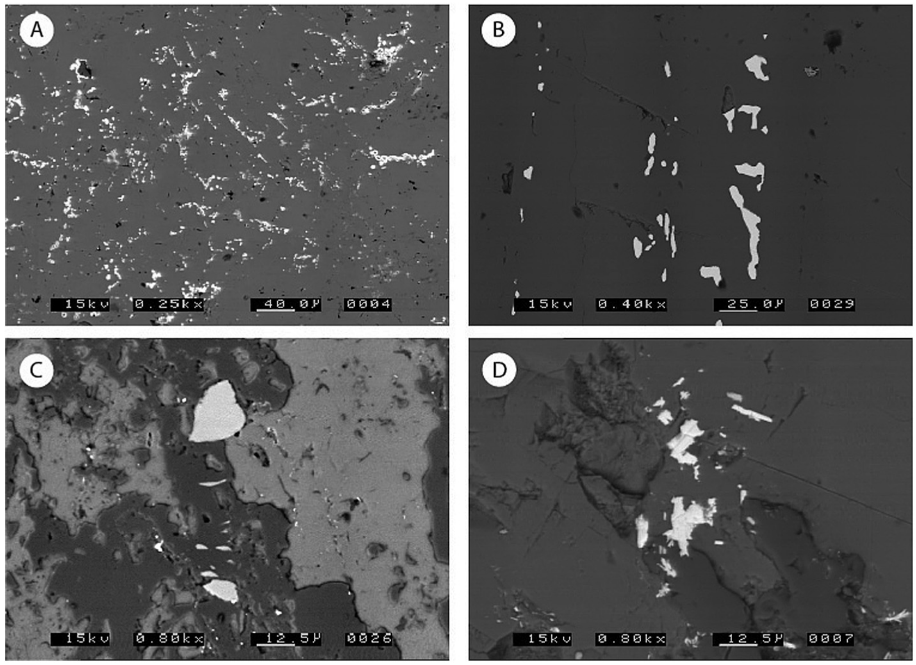

Figure 5. Backscattered electron micrographs of bedding-parallel fibrous calcite veins, showing diversity of subsidiary mineralogy, Bay of Stoer Formation, Bay of Stoer. A calcite (grey) with haematite (bright) between crystals; B, calcite (grey) with barite (bright) between crystals; C, calcite (light grey) intergrown with quartz (dark grey) and apatite (bright); D, calcite (grey) with REE carbonate (bright).

are around −10 to −13‰ VPDB and carbon isotope values ($\delta^{13}C$) are around −1‰ PDB. Data is also available for calcite in cemented sandstone in the vein-bearing section, and the limestone and black shale below it. All samples have carbon isotope values in a narrow range from 1 to −2‰ VPDB.

3.4. Entrapped volatiles

The calcite veins and dolomite veins yield distinct compositions of entrapped volatiles. The calcite has a higher O_2/N_2 ratio and lower CO_2/CH_4 ratio than the dolomite, and similar to the calcite-bearing sandstone (Fig. 8). However, both vein types contain higher O_2/N_2 and CO_2/CH_4 than the control Cambro-Ordovician limestone, i.e. the volatiles have a more oxidized composition than the younger sample.

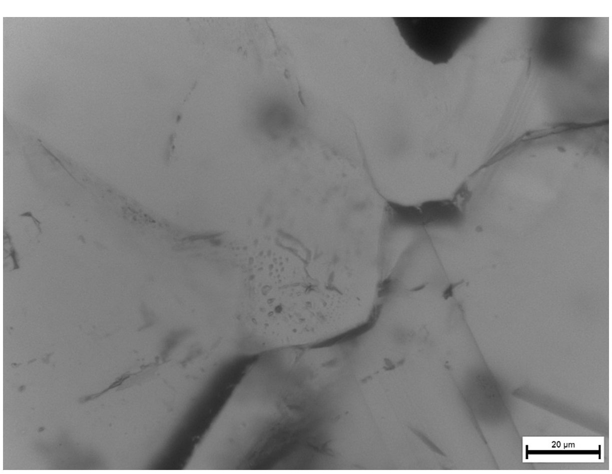

Figure 6. Primary fluid inclusions in fibrous calcite vein. High degree of fill indicates low (<100 °C) temperature of entrapment.

4. Discussion

4.1. Evidence for age

The veins exhibit typical features of similar veins in mudrock successions, including bedding-parallel form, antitaxial growth, and cone-in-cone structure in the fibres (Cobbold et al., 2013), and are therefore attributed a diagenetic origin. Cone-in-cone structure consists of interlocking stacked cones of calcite, grown during diagenesis, with the host siliciclastic matter displaced to the inter-cone boundaries (Gillman and Metzger, 1967). The entrapped lenses of compacted mudstone show that the veins formed during late diagenesis, like most bedding-parallel veins, and distinct from some occurrences of displacive fibrous calcite that grow during shallow burial and incorporate uncompacted sediment (e.g. Franks, 1969). The calcite is not related to metamorphism. Veining attributed to low-grade metamorphism in the region is characterized by quartz and pumpellyite (Hay et al., 1988; Stewart, 2002), and cuts the Stoer Group and underlying Lewisian basement in high-angle structures. The pumpellyite does not occur in the bedding-parallel fibrous veins, so these veins do not have a metamorphic signature. In addition, there is no feasible mechanism for the later metamorphic fluids to open fractures parallel to bedding.

Table 1
Stable isotope compositions of Mesoproterozoic carbonate samples, Bay of Stoer Formation.

Sample	$\delta^{13}C$ (‰VPDB)	$\delta^{18}O$ (‰ VPDB)	$\delta^{18}O$ (‰ VSMOW)
Fibrous calcite vein	−0.6	−11.8	18.7
Fibrous calcite vein	−0.8	−10.9	19.7
Fibrous dolomite vein	−0.4	−13.3	17.2
Calcite cemented sandstone	0.6	−15.1	15.3
Calcite cemented sandstone	0.8	−14.1	16.4
Grey limestone	−1.1	−15.0	15.4
Calcareous black shale	−2.0	−14.3	16.2

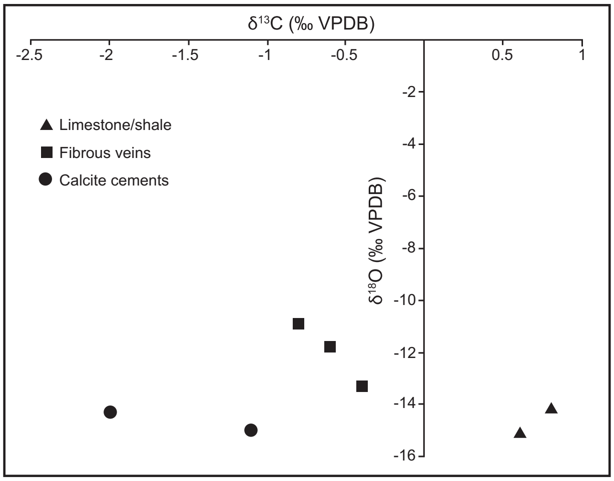

Figure 7. Cross-plot of carbon and oxygen stable isotope compositions for carbonate samples in Bay of Stoer Formation.

4.2. Fluid signature

It has been possible to observe and/or measure fluid inclusions, stable isotope compositions, and entrained volatiles in these bedding-parallel calcite veins. We therefore have the potential to interpret the composition of diagenetic fluids of over 1 billion years age. The detailed data set and interpretation will become available subsequently, but at this stage some preliminary remarks are possible.

The occurrence of two-phase fluid inclusions in the calcite implies temperatures of almost 80 °C, and hence burial depths of at least 2–3 km, for normal geothermal gradients of 25–30 °C/km. This indication of growth in the deep subsurface is consistent with the compacted nature of enclosed mudstone lenses, and temperature estimates for fibrous calcite veins in younger successions of 70–120 °C (Cobbold et al., 2013).

Within 10 m below the fibrous calcite, the meteorite impact deposit of the Stac Fada Member (Amor et al., 2008) preserves primary fluid inclusions in feldspar and calcite infilling degassing structures (Parnell et al., 2011). The fluid inclusions in the calcite in the Stac Fada Member yield a mean homogenization temperature of 76 °C, very similar to the values obtained from the fibrous calcite. This suggests that the two occurrences of calcite may represent a single episode of calcite precipitation, and gives us additional confidence that the calcite in the fibrous layers preserves an original fluid signature from the Mesoproterozoic.

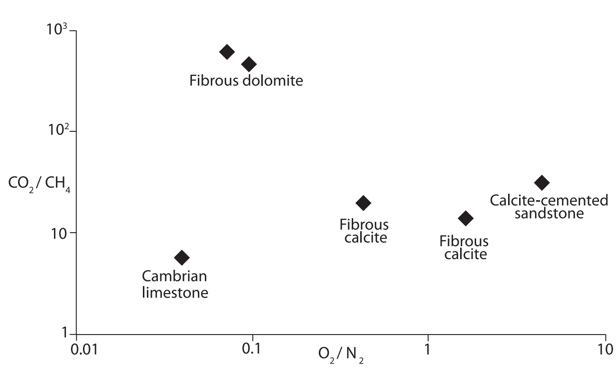

Figure 8. Cross-plot of O_2/N_2 against CO_2/CH_4 molar ratios for samples of fibrous veins and other samples for comparison, determined by crush-volatile technique (see text). Fibrous veins show high levels of oxidation.

Bedding-parallel fibrous layers containing quartz are less common than purely calcitic layers in the geological record, and are especially recorded in turbidites (Cobbold et al., 2013). In the Stoer Group below the section with fibrous veins, the Stac Fada Member, rich in impact glass, would have been an exceptional source of relatively soluble amorphous silica into diagenetic fluids. The temperature range over which quartz overgrowths precipitate in sandstones suggests that the silica can be mobile at temperatures as low as 70 °C (Walderhaug 1994).

The stable isotope compositions from continental successions are strongly dependent upon local conditions (Leng and Marshall, 2004). However, the light oxygen isotope values measured are more likely to reflect growth during burial than from depositional waters. Water-rock interaction tends to generate ^{18}O-depleted pore waters, especially from initially light meteoric waters, and comparable values have been recorded in younger fibrous calcite veins (Marshall, 1982; Al-Aasm et al., 1995). The $\delta^{13}C$ values for the calcite and dolomite veins, and also for the calcite cements in sandstones, are very similar to those of limestone beds within the black shale section (Table 1), indicating local derivation from them. The cement in the sandstone is sparry, post-dated an earlier grain-coating albite cement and was deposited when the sandstone porosity was about 10%, i.e. when the burial depth was probably less than 1 km, and so inferred to be earlier than the fibrous veins. The oxygen isotope values for the limestones are so light that they must reflect high altitude and or high latitude. As the latitude of deposition was probably less than 30° (Young, 1999; Buchan et al., 2001), the implication is for high altitude.

In other basins, fibrous calcite veins have been related to the maturation of organic matter and hydrocarbon generation at several kilometres depth (Rodrigues et al., 2009; Le Breton et al., 2013). This may explain why the veins occur directly above the unit of grey-black shales. These shales and associated limestones contain organic carbon of probable algal origin (Upfold, 1984; Stewart, 2002), and could have released hydrocarbons during deep burial. Although there is no direct evidence for hydrocarbons in the veins, the temperatures implied by the fluid inclusions are consistent with at least the early stages of hydrocarbon generation, which vary between basins but are typically above a threshold of 50–80 °C (Tissot and Welte, 1984). Many Precambrian successions of black shale, which must have generated hydrocarbons (Craig et al., 2013) do not show direct evidence for hydrocarbons, so their absence does not mean that they were not generated. In addition to hydrocarbon generation, similar conditions of thermal maturation can yield a pulse of water through dehydration of clay minerals, contributing to high pore fluid pressure (Osborne and Swarbrick, 2004).

The array of mineral phases recorded in the calcite veins has no parallel in previously described occurrences. However, almost all other reports are from black shale sequences, whose pore fluids would have had different Eh-pH characteristics and so precipitated different minerals, such as sulphides (Jowett, 1987). There is notably no evidence of albite in the fibrous veins, which is otherwise widespread as an authigenic precipitate in the Stoer Group, described as sodium metasomatism by Van de Kamp and Leake (1997). The albite formed early grain-coatings in sandstones, and clearly predated the fibrous veins.

4.3. Oxygenation

The mineralogy of the calcitic veins is informative. The haematite and barite are both precipitates of relatively oxidizing fluids. In a reducing environment, we would expect iron and sulphur to precipitate pyrite, but no sulphides were observed in the fibrous veins. This is consistent with fluids generated in a thick succession of continental red beds. Although haematite is stable in oxidizing conditions, iron is only present in alkaline fluids (implicated by the calcite and typical of continental environments) in low concentrations. Conceivably, the iron was mobilized from the underlying black shales, whose pore waters would have been more acidic, then precipitated out in the alkaline red beds. The sulphate (barite) could similarly have been derived from the black shales, which are rich in sulphides (Parnell et al., 2012). Barite is a typical red bed mineral, and can form near-surface evaporative cements, but in this case its late diagenetic context suggests precipitation from groundwaters that may have oxidized nearby sulphides. The barite occurs between calcite crystals, so must have precipitated at some stage subsequent to calcite precipitation. More generally, the occurrence of the mineralized veins close to the interface between black shale and red beds suggests that they are a variant on Eh-controlled red bed mineralization, which includes roll front deposits and metalliferous reduction spheroids (e.g. Northrop and Goldhaber, 1990; Hofmann, 1991). The precipitation of REE minerals, recorded in the calcite veins, also occurs in reduction spheroids in red beds (Hofmann, 1991). Metalliferous reduction spheroids do occur lower in the Bay of Stoer Formation (Spinks et al., 2010), confirming that Eh-controlled diagenesis was important in these rocks. The reduction spheroids developed post-compaction, so like the fibrous veins they represent diagenesis in the deep subsurface.

However, given that the oxygen content of the atmosphere was much lower (1–10% of present) in the Mesoproterozoic (Canfield, 2005; Campbell and Allen, 2008), the redox conditions at the surface and in the subsurface are uncertain and debated (Parnell et al. 2010, Kah and Bartley, 2011; Cumming et al., 2013; Stüeken, 2013). Red (fine-grained) haematite is normally assumed to be a product of oxidizing meteoric waters (Holland, 1984), i.e. groundwaters penetrating from the surface. Fibrous veins are attributed to the development of high pore fluid pressure in mudrocks which are hydraulically sealed (e.g. Cobbold et al., 2013), i.e. isolated from the surface. This implies that the groundwaters still contain dissolved oxygen inherited from the surface, at 2+ km burial after deposition. The oxygen content of the Mesoproterozoic atmosphere was much lower than today, but the major sink for oxygen in modern groundwaters of organic matter in the soil zone was lacking in the Mesoproterozoic, so oxygenation may have persisted to deep levels. The evidence from the Stoer Group indicates that oxidizing fluids could penetrate the deep subsurface at least 1 billion years ago.

High O_2/N_2 ratios are recorded in the calcite veins, which contain the oxidized mineral phases (haematite, barite). High O_2/N_2 ratios also occur in the adjacent red (haematite-bearing) sandstone. The CO_2/CH_4 ratios are also higher in the Stoer Group samples. These compositions are clearly distinct from that of the Cambro-Ordovician limestone. Both the O_2/N_2 and CO_2/CH_4 ratios increase with oxidation (McMahon et al., 2012, 2013). Elsewhere in the region, veins penetrate downwards from Phanerozoic rocks into Precambrian rocks (Hay et al., 1988; Parnell et al., 2004; Blumstein et al., 2005), allowing ingress of younger fluids, but there is no evidence for that in the Bay of Stoer. Although the Stoer Group samples are older, deposited when the oxygen content of the atmosphere was lower, they represent a greater level of oxygenation.

5. Conclusions

The fibrous calcite veins in the Stoer Group are comparable with those in younger successions, that have a diagenetic origin, and we propose that they therefore represent diagenetic fluids of Mesoproterozoic age. Preliminary observations and measurements show that the fluids can be characterized by techniques commonly applied to much younger, Phanerozoic, successions. As the Stoer Group rocks were deposited in a continental environment, studies utilizing these techniques will provide valuable evidence to the debate on the redox conditions pertaining in sedimentary rocks at a time of limited atmospheric oxygenation. In particular, evidence for the penetration of oxidizing fluids to the deep subsurface has implications for the history of a range of redox-dependent geochemical processes, including the development of secondary porosity, the weathering and beneficiation of ore deposits, and deep subsurface habitat for aerobic microbial life.

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