Neoproterozoic microbial processes in chemical sediment diagenesis: evidence from the Aberfeldy barite deposits

Moles, Norman R.
School of Environment and Technology, University of Brighton, UK. Email: n.moles@brighton.ac.uk

Boyce, Adrian J.
Scottish Universities Environmental Research Centre (SUERC), University of Glasgow, UK

Abstract. Microbial- and diffusion-controlled diagenetic processes were significant in the formation of sulfide-, sulfate- and carbonate-rich stratiform mineralization hosted by Neoproterozoic graphitic metasediments near Aberfeldy in Perthshire, Scotland. In 1-10m thick beds of barite rock, barite $\delta^{34}S$ of +36 ±1.5 ‰ represents the isotopic composition of contemporaneous seawater sulfate. Pronounced vertical variations in $\delta^{34}S$ (+30 to +41 ‰) and $\delta^{18}O$ (+8 to +21 ‰) occur on a decimetre-scale at bed margins. These excursions are attributed to early diagenetic alteration, while the barite sediment was fine-grained and porous, due to pulsed infiltration of isotopically diverse porefluids into the marginal barite. Fluid-mediated transfer of barium and sulfate into adjacent sediments contributed to barium enrichment and growth of millimetric sulfate crystals cross-cutting sedimentary lamination. Witherite, barytocalcite and norsethite occur only as small inclusions within crystals of pyrite. Barium carbonate formation is ascribed to early diagenetic processes that generated very low sulfate activity in pore waters. Subsequently, sulfidation reactions produced secondary barite + non-barium carbonates in the rock matrix. Comparatively low $\delta^{34}S$ (+16 to +22 ‰) in secondary barite indicate sulfur derived from reduced sulfide. Similar sulfide $\delta^{34}S$ ratios in the host sediments are consistent with microbial reduction of seawater/ porewater sulfate.

1 Introduction

In modern and Phanerozoic shallow marine sediments, diagenetic processes are typically affected by bioturbation occurring within 0.1–0.4 m of the sediment–water interface and sometimes to depths of >1 m. This mixing speeds up reactions which would otherwise be limited by diffusion rates and homogenises light isotope compositions in the upper sediment layer (Goldhaber, 2003). In Precambrian marine sediments, the absence of burrowing organisms precluded mixing, consequently diffusion through pore water and pore water advection were the main processes affecting ionic concentration gradients and diagenetic mineralization.

Here we report evidence for microbial- and diffusion-controlled diagenetic processes in mid-Neoproterozoic sulfide-, sulfate- and carbonate-rich chemical sediments interbedded with organic-rich marine sediments.

2 Background

2.1 Barite deposition and diagenetic alteration

In modern ocean sediments, barite is not prone to diagenetic alteration after burial where oxic conditions prevail, but is soluble under reducing conditions especially in the presence of sulfate-reducing microbes and organic matter (e.g. Clark et al., 2004). Porewater sulfate reduction is ubiquitous in organic-rich sediments containing barite (e.g. Torres et al., 1996).

Some studies of sedimentary exhalative (sedex) barite deposits have proposed that barite precipitation occurred in the water column with finely crystalline barite deposited on the seabed (e.g. Lyons et al., 2006). However, in a study of non-hydrothermal sediment-hosted stratiform barite deposits worldwide, Johnson et al. (2009) found that many show marked isotopic variation with values far removed from that of contemporaneous seawater. They conclude that the $\delta^{18}O$ and $\delta^{34}S$ values in barite had been modified by exchange with porewater sulfate from adjoining sediments in which sulfate was consumed by oxidation of organic matter or anaerobic oxidation of methane. The isotopic profiles resemble those of pore water sulfate observed in modern ocean sediments.

Modern seafloor barite deposits, and ancient sedex deposits that have not been strongly metamorphosed, contain barium carbonates that are invariably diagenetic in origin, often replacing pre-existing mineral phases such as barite or celsian (e.g. Ansdell et al., 1989).

Magnall et al. (2016) report textural, mineralogical and isotopic evidence indicating that diagenetic replacement processes were dominant during barite and sulfide mineralization in the Tom and Jason shale-hosted massive sulfide (SHMS) deposits in the Selwyn Basin. They conclude that the interplay between biological activity, methanogenesis, seawater sulfate concentrations, and open system diagenesis are important to consider when interpreting $\delta^{34}S$ values in SHMS and barite deposits from the geologic record.
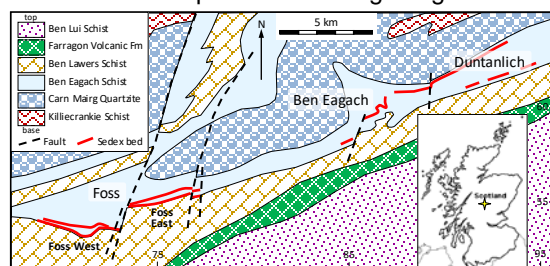

Figure 1. Bedrock geology in the vicinity of the barite deposits (map adapted from Coats et al., 1980 and Treagus, 2000). Inset map of Scotland with star indicating location of the area.

It should be noted that sulfides are a major component of mineralization at Tom and Jason, and barite rarely forms thick beds (Gardner and Hutcheon, 1985) whereas in the Aberfeldy deposits described here, barite commonly forms metre-scale beds (Fig. 2) of nearly monomineralic rock often with low sulfide content.

2.2 The Aberfeldy barite deposits

Located in the mountainous region of central Perthshire in the Grampian Highlands of Scotland (Fig. 1), the Aberfeldy ore deposits represent the UKs largest resource of industrial barite (Treagus, 2000). The orebodies were discovered in the 1970s by the British Geological Survey (then 'IGS'). Barite production by Dresser Minerals from the Foss Mine commenced in the 1980s and since then about 40,000 tonnes annually has been extracted by M-I SWACO, a Schlumberger company. Barite rock is also worked intermittently from a small quarry on Ben Eagach. In the nearby Duntanlich deposit, an unworked resource of at least 7.5 million tonnes of barite is reported (M-I SWACO, 2014) in a structurally simple, tabular orebody. In 2016, planning permission was granted for an under-ground mine at Duntanlich and development is currently ongoing.

The Duntanlich orebody is stratigraphically lower than the barite beds in the Foss deposit although both are hosted in the Neoproterozoic Ben Eagach Schist Formation. This comprises mainly graphitic quartz muscovite schists, the protoliths of which were organic-rich mudstone and siltstone, enriched in barium and base metals in the vicinity of the deposits (Hall, 1993). Locally the schists are calcareous with thin beds of graphitic dolostone. The stratigraphically overlying Ben Lawers Schist Formation is calcareous and non-sulfidic, and contains barite and chert mineralization only in the lowermost strata. The presence of mafic volcanic components together with the sedex mineralization has been interpreted as evidence of high heat flow and convective circulation of hydrothermal fluids in a passive continental margin rifting environment (Coats et al., 1980; Russell, 1985; Hall, 1993; Treagus, 2000).

Subsequently in mid-Ordovician Grampian Orogeny, the sedimentary beds were tilted and distorted by several phases of folding and faulting, and subjected to amphibolite facies regional metamorphism (Moles, 1985; Treagus, 2000; Treagus et al., 2013).

The hydrothermal exhalative activity that precipitated barite sediment occurred in relatively shallow water as evidenced by localised reworking to form barite conglomerate (Moles et al., 2015) and lateral facies and thickness variations. Cherty rocks rich in quartz and barium aluminosilicates (celsian, cymrite, barium-rich micas) envelope the barite beds and extend laterally further than the barite as they precipitated on the seafloor in deeper parts of the sedimentary basin where anoxic conditions prevailed near the sediment–water interface. In some parts of the deposits, carbonate and sulfide rocks (mainly pyrite with lesser sphalerite and galena) occur within the mineralized beds. Occasionally all of these components occur together forming laminated beds. Magnetite locally occurs in trace amounts instead of pyrite within thicker beds of barite. Pyrrhotite is a rare component of chert and carbonate rocks close to presumed hydrothermal vent sites (Hall, 1993).

The mineralized beds have sharp boundaries with the enclosing metasediments, and clastic sediments are seldom incorporated within the barite rock (Moles et al., 2015). These features suggest rapid deposition of the barite during hydrothermal exhalative episodes that were vigorous but short-lived and episodic. Seven such episodes are represented in the Foss deposit (labelled 1 to 7 in Fig. 2) although Foss Mine exploits just one barite bed, no. 5. Silicified, barium-enriched laminated sediment occurs locally in two contexts: stratigraphically below the mineralized beds, and as lateral equivalents located distal from the main locus of exhalative activity.
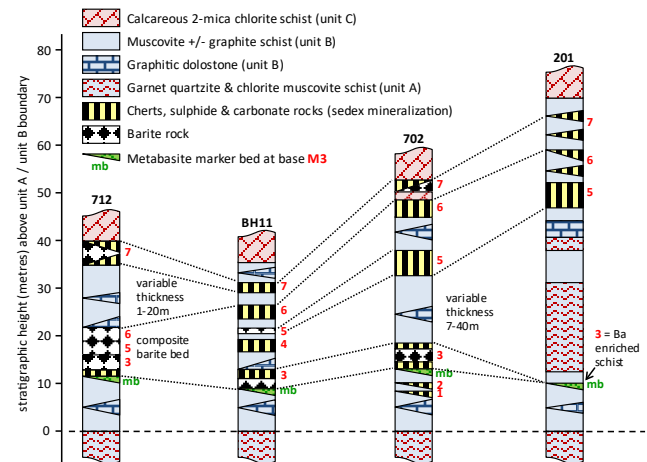

Figure 2. Representative vertical sections of mineralized beds illustrating the lateral variations across Foss East (Fig. 1). 3-digit numbers: Dresser Minerals boreholes. BH11: IGS borehole.

3 Mineralogical and isotopic evidence of diagenetic processes

3.1 Barium carbonates

Encapsulated within pyrite crystals in the bedded mineralization are small inclusions of sphalerite, barite and carbonates that have heterogeneous compositions in contrast with relatively homogeneous compositions of minerals in the rock matrix. The diverse composition of inclusions (Fig. 3a) suggests that due to encapsulation they were shielded from subsequent modification. We infer that these grains crystallized during the exhalative events and diagenesis of the chemical sediment.

The barium carbonates barytocalcite, norsethite and witherite occur only as tiny, pyrite-encapsulated grains within carbonate-bearing barite-sulfide rocks (Moles, 2015). They were initially identified by cold-source optical cathodoluminescence microscopy which revealed their distinctive luminescence colors (Fig. 3a). We infer that barium carbonates were formerly widespread within the chemical sediments and that later in the diagenetic / lithification sequence, matrix barium carbonate was replaced by barite + calcite or dolomite.
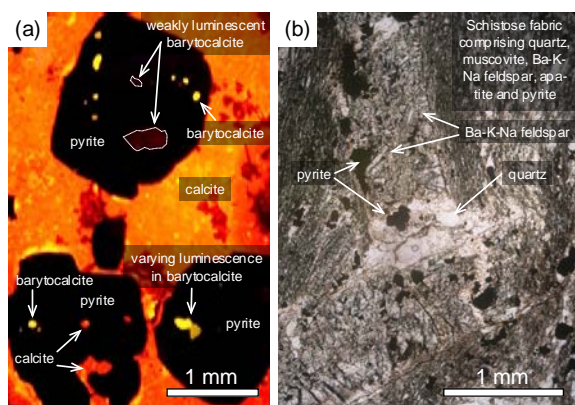
Figure 3 (a) Cathodoluminescence photomicrograph of pyrite-barite-calcite rock showing inclusions of yellow-luminescent barytocalcite within pyrite and orange-luminescent matrix calcite. Sample from DH105, western Foss East. **(b)** Photomicrograph of pseudomorphs after ~1 x 5 mm barite porphyrotopes in mineralized sediment underlying the lower (#3) barite bed in the Foss deposit. Sample N81-43c from near IGS BH3, eastern Foss East (Fig. 1).

3.2 Pseudomorphs of diagenetic barite crystals

Fortey and Beddoe-Stephens (1982) illustrate a silicified metasediment from IGS BH9 (Foss West) that contains bladed 'porphyroblasts' ~1 mm wide and 4–7 mm long of Ba-K-Na feldspars with complex internal structures and inclusions of pyrite and trace barite. They suggested that the tabular structures are pseudomorphs of barite crystals that formed in the sediments during diagenesis, comparable to diagenetic barite laths cross-cutting sedimentary lamination observed in bedded sulfide ores (e.g. Lyons et al., 2006, Figure 7D).

We have found further examples of these features, illustrated in Fig. 3b. The complex internal structure indicates replacement processes during which the original barite was dissolved and replaced by pyrite, quartz and Ba-K-Na feldspar, the crystals of which often show growth perpendicular to the long edges of the tabular shape. The host rocks range from graphitic quartz-mica-feldspar schists to cherts and quartz-carbonate rocks within the stratiform mineralization. The pseudomorphs appear to have survived metamorphism because they are hosted by quartz- and/or feldspar-rich rocks which resisted the deformation that caused mica-rich rocks to develop a penetrative cleavage.

We infer that, prior to metamorphism, diagenetic sulfate crystals were common within the sediments and within silica- and carbonate-rich sedex mineralization.

3.3 Isotopic composition of barite and sulfides

The sulfur isotopic composition of Aberfeldy barite and sulfides has been studied extensively with analyses published by Willan and Coleman (1983), Hall et al. (1991) and Moles et al. (2015). Based on analyses of 88 pure barite separates from the Aberfeldy deposits, Moles et al. (2015) showed that $\delta^{34}S$ values of +36.5 ±1‰ are typical across the entire geographical area and stratigraphic range. This is interpreted as the isotopic ratio of contemporaneous seawater sulfate which precipitated the Ba^{2+} exhaled in hydrothermal fluids.

However, upper and lower margins of barite beds show atypically low (+30 to +35 ‰) and high (+37 to +41 ‰) $\delta^{34}S$ values varying over distances of centimetres to tens of centimetres (Fig. 4). Barite $\delta^{18}O$ values scatter about a mean of +13.5 ±5 ‰ and display variations similar to those of $\delta^{34}S$ near bed margins. These features are attributed to post-depositional isotopic modification while the barite sediment was fine-grained and porous, i.e. diagenetic alteration.
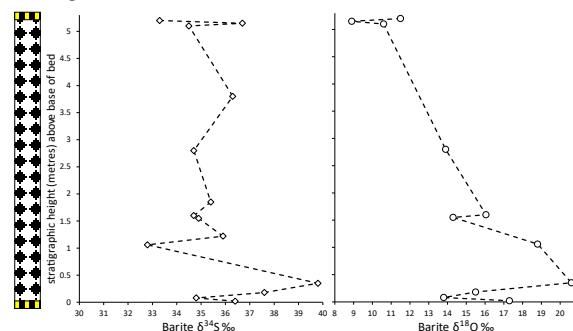

Figure 4. Stratigraphic profile through the barite bed intersected in Foss East DH424 showing pronounced marginal excursions in isotopic composition (from Moles et al. 2015).

In Fig. 5, sulfide samples derived from the meta-sediments and mineralized sediments (clastic sediment impregnated with Ba and Si derived from hydrothermal solutions) are distinguished from sulfide and barite in the stratiform mineralization. It is apparent that sulfide $\delta^{34}S$ values vary widely in both the metasediments and mineralization, contrary to the two-fold division proposed by Hall et al. (1991) of lower $\delta^{34}S$ values in the metasediments and higher values in the mineralization. Sulfide $\delta^{34}S$ values of +12 to +16 ‰ in some meta-sediments are consistent with microbial reduction of seawater sulfate involving fractionation of around +20 ±4 ‰. However, values range up to +23.5 ‰ suggesting that other sulfur sources or fractionation processes contributed to produce the wide range in compositions.

We obtained further $\delta^{34}S$ data by both conventional and laser ablation analyses of samples selected on the basis of preserved diagenetic features. Barite and pyrite were separated from a sample of carbonate-sulfide-barite rock (702-4B) in which pyrite crystals contain relatively abundant inclusions of barium carbonates. The barite has a $\delta^{34}S$ value of +14 to +16 ‰ which is comparable to the isotopic composition of sulfides in sediments and is exceptionally low compared to normal barite rock at Aberfeldy (Fig. 5). Conversely, pyrite in the same sample reports $\delta^{34}S$ values of +29 to +32 ‰ which is outside the range of previously reported sulfides from Aberfeldy but is within the range of primary barite ratios.

In a laminated pyritic chert rich in barium carbonate inclusions (sample 505-15), individual dispersed crystals of pyrite have $\delta^{34}S$ values (n=6) ranging from 21.1 to 26.8 ‰ within an area of <2 cm². This remarkably wide range confirms that sulfur isotope heterogeneity existed at this scale in the precursor sedimentary rock and survived regional metamorphism.

Pyrite in three samples of mineralized sediment gave $\delta^{34}S$ values of +27 to +29 ‰, at the upper end of the 'normal' range for Aberfeldy sulphides (Fig. 5).
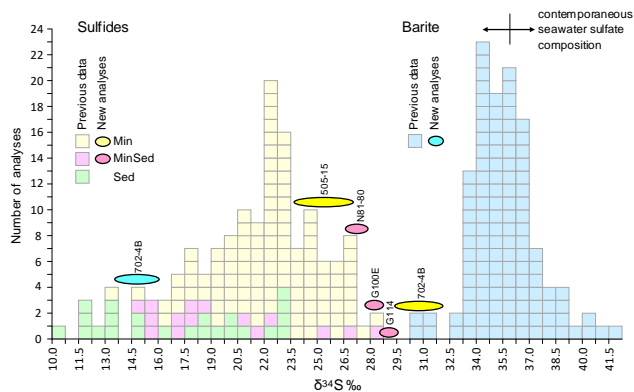
Figure 5. Histogram comparing $\delta^{34}S$ results for samples described here with previously published values from the Aberfeldy deposits. Min = sedex mineralization; MinSed = clastic sediment mineralized by hydrothermal material; Sed = metasedimentary host rock. Postulated seawater sulfate composition from Moles et al. (2015).

4 Summary of diagenetic processes

The barium carbonates and sulfate crystal porphyrotopes formed during diagenetic modification of the sediments prior to recrystallization during lithification and metamorphism. The barium carbonates precipitated within the sediments from porewaters that had very low sulfate ion activities due to microbial sulfate reduction. Under the highly reducing conditions, barium mobilised in the porewater infiltrated adjoining sediments where it was fixed by the precursors to barium muscovite and Ba-K-Na feldspars. Subsequent sulfidation reactions replaced the barium carbonates that were not encapsulated within inert crystals, and produced the matrix assemblage of calcite and/or dolomite plus secondary barite with an isotopic composition very different to primary barite that precipitated in the Neoproterozoic seawater. ^{34}S-rich secondary pyrite-sulfur was derived from reduction of pre-existing sulfate.

Fluxes of sulfate-bearing porewater derived from the organic-rich sediments diffused into the margins of the barite beds and modified the primary (seawater sulfate) isotope composition of the marginal barite. These fluxes had alternating enrichments in the light and heavy isotopes of sulfur and oxygen, creating layers of isotopically distinct barite rock parallel to bed margins. The isotopic perturbations preserve a record of the microbially-mediated porewater sulfate reduction and sulfate replacement processes that took place in the adjoining sediments. These are also evidenced by the growth in unconsolidated sediment of diagenetic sulfate porphyrotopes and their subsequent replacement by ^{34}S-rich sulfide-bearing pseudomorphs.

The barite bed-marginal isotopic excursions, and occurrences of sediment-hosted sulfate porphyrotopes, are not restricted to the base of barite beds but also occur at their tops. We infer that organic-rich clastic sediment was deposited soon after each exhalative event, before pore-sealing of the underlying chemical sediment, such that microbial activity in the overlying sediment generated isotopically diverse porewaters that infiltrated downwards into the barite sediment.

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