



Kilometre-scale compartmentalization of fluid sources to a fossil hydrothermal system



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ABSTRACT

The West Cumbria iron ore field exhibits kilometre-scale compartmentalization of fluid sources, as evidenced by sulphur isotope data. Barite accompanying haematite ore from 13 mines in an along-strike width of 5 km has $\delta^{34}\text{S}_{(\text{VCDT})}$ isotopic compositions ranging from +7.9 to +23.6‰. The large variation is strongly controlled by NNW-SSE faulting, in which the heaviest compositions are to the north and lightest in the south. The heavy and light compositions are comparable with those of Carboniferous and Permian evaporites respectively, both of which occur in West Cumbria and are the assumed primary sources of the barite sulphur, though input from the oxidation of Carboniferous coal pyrite may have provided a minor component. The derivation of sulphur from stratigraphically distinct sources shows that faults isolated fluid flow in compartments on a local scale. Published data for barite from an adjacent fault block in a potential waste disposal site at Sellafield are further distinct, indicative of a primary pyrite source. These data emphasize that fluid sources can be highly compartmentalized in a faulted system and require supporting evidence to confirm if they can be correlated.

1. Introduction

Sulphur isotope compositions are widely used to help interpret the genesis of hydrothermal ore deposits (Rye and Ohmoto, 1974; Shanks, 2014). Within an ore field, variations in hydrothermal sulphur isotope signatures are commonly related to differences in source rock type and/or different stages/processes of mineralization. The main metal-bearing brine hydrothermal sulphur isotope signature is usually considered a weighted average of contributions from different sources in the protolith, effectively providing a natural mass balance from different reservoirs (e.g. Fallick et al., 2001; Boyce et al., 1993). In this study, we show that considerable variation, rather than homogenization, of hydrothermal sulphur isotope compositions may be exhibited in an ore field divided by cross-cutting faults, implying that the structure has imposed a compartmentalization of fluids, which might be undetected in a limited data set. Many ore fields globally are cross-cut by arrays of sub-parallel faults, conferring a marked heterogeneity to fluid flow in the fields (e.g. Achtziger-Zupančič et al., 2017; Fridovsky, 2018; Wang et al., 2019). This study provides insight into the complexities of hydrothermal fluid flow in faulted basins and demonstrates how detailed sampling and analysis can be effective in identifying deposit-scale heterogeneities.

A study of a compartmentalized ore field was carried out in the West Cumbria iron ore field, adjacent to the Irish Sea Basin, England (Fig. 1). The ore is haematite, consistently containing barite (Fig. 2), whose paragenesis overlaps the haematite (Trotter, 1945; Goldring and Greenwood, 1990; Shepherd and Goldring, 1993).

This ore field was selected because:

- (i) The ore field can be sampled on a sub-kilometre scale through over many separate mining deposits;
- (ii) The ore field is cross-cut by a closely spaced set of sub-parallel faults;
- (iii) The faults strongly influence modern groundwater flow (Gutmanis et al., 1998; Fraser Harris et al., 2015), and thus may have done so in the past;
- (iv) The barite has not experienced medium-high temperatures (> 120 °C) that might have modified the geochemistry (Akhurst et al., 1997; Young, 2012).

2. Geological Setting

Haematite ore deposits, with contemporaneous barite, quartz and calcite mineralization occur below the sub-Permian unconformity

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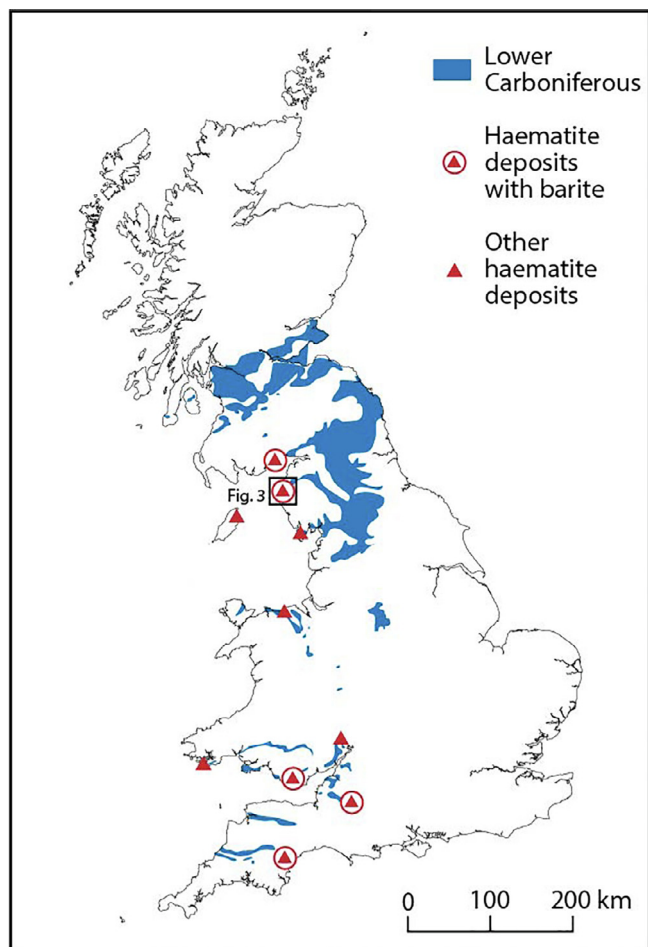


Fig. 1. Map of haematite deposits on the sub-Permian unconformity in Britain. Most deposits are on Carboniferous limestone (shown), but also on Devonian limestone in Devon or on basement rocks where the Carboniferous is now eroded away. Region of study (Fig. 3) shown.

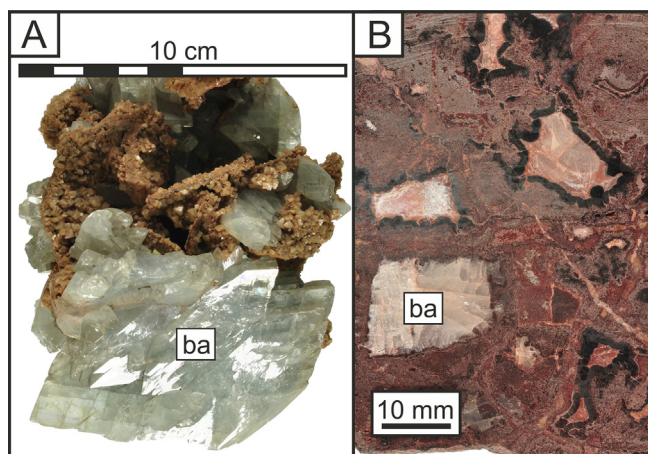


Fig. 2. Hand specimens of barite (ba), Cumbria. A, Large blue barite among dendritic haematite-quartz, Mowbray mine; B, Infill of porosity in colloform haematite, Winscale mine. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

across a large area of England and Wales. These ores are primarily hosted within Lower Carboniferous limestones and were formerly worked in Cumbria, South Wales, and SW England (Fig. 1). They represent a unique ore type, but despite their former importance to the

UK steel industry their origin is not completely understood. Petrographic, fluid inclusion and palaeomagnetic studies indicate ore mineralization occurred under moderate temperatures (up to 120 °C) from saline brines migrating along extensional faults during the Permo-Triassic (Shepherd and Goldring, 1993; Akhurst et al., 1997; Crowley et al., 2014). However, the origin of the iron, and accompanying trace elements, is uncertain. Circumstantial evidence suggests, in both Cumbria (Dunham, 1984) and South Wales (Rankin and Criddle, 1985), that the iron was stripped from overlying Permo-Triassic red beds, but alternative views advocate sources that are below the ore deposits either structurally (e.g. Irish Sea Basin) or stratigraphically (e.g. granites) (Rose and Dunham, 1977; Akhurst et al., 1997; Crowley et al., 2014).

In Cumbria, Lower Carboniferous marine limestones with associated haematite ore deposits occur at/near surface along a ~ 10 km wide NE-SW strike, immediately beneath Upper Carboniferous pyritic coals and shallow marine sedimentary units (Fig. 3). Deposition of Permo-Triassic red sandstone was preceded by basin inversion, sub-aerial exposure and erosion of the Carboniferous strata during the Variscan orogeny (Akhurst et al., 1997). This resulted in a variable thickness of Upper Carboniferous strata, with erosion and removal of Carboniferous sediments most pronounced to the SE of the region. Permo-Triassic sediments sit unconformably on top of these units, directly overlying Lower Carboniferous limestone in some areas. The Permian succession includes gypsum deposits from the St Bees Evaporites (Arthurton and Hemingway, 1973; Akhurst et al., 1997) and the Eden Shales Formation (Hughes, 2003). Haematite deposits hosted within these limestones in Cumbria, and elsewhere in the UK, occur in conjunction with extensive barite mineralization which formed during the same period of orogenesis (Young, 2012).

Across the Cumbrian ore field, extensive compressional faulting and erosion of overlying strata occurred prior to mineralization of the haematite + barite ores, which may have had an impact on fluid flow dynamics during the Permo-Triassic. During fluid-driven ore formation, it is important to consider potential barriers to mineralizing fluids, including faults and variations in stratigraphy, and their timing relative to ore-forming processes. In order to better understand the ambiguous sources of Fe-mineralization across the Cumbrian ore field, and the effect, if any, of fault compartmentalization, it is necessary to study the field on a sub-km scale. Comparison of sulphur isotopes from sources and barite deposits across the Cumbrian Fe-ore field may highlight variations in mineralization sources and fluid flow pathways during ore formation.

3. Samples & methods

3.1. Sampling

Sulphides and sulphates were sampled from haematite mines and several stratigraphic levels in Cumbria and the immediately surrounding areas:

- (i) Barite from 13 haematite mines in the West Cumbria iron ore field (Table 1; Fig. 2; Fig. 3).
- (ii) For comparison, 3 barite samples from haematite deposits in South Wales, 3 from haematite mines in Somerset and Devon, and 2 from a haematite mine in SW Scotland. These occurrences are, like Cumbria, in/near Carboniferous limestone, except in Devon in Devonian limestone.
- (iii) Gypsum from the Permian St. Bees Evaporites at Barrowmouth mine, Whitehaven, and the coeval Eden Shales Formation at Kirkby Thore.
- (iv) Pyrite from the Upper Carboniferous Coal Measures coal at former mines at Haig Colliery (Whitehaven), Pica Lake and the shore section at Parton Bay-Providence Bay.

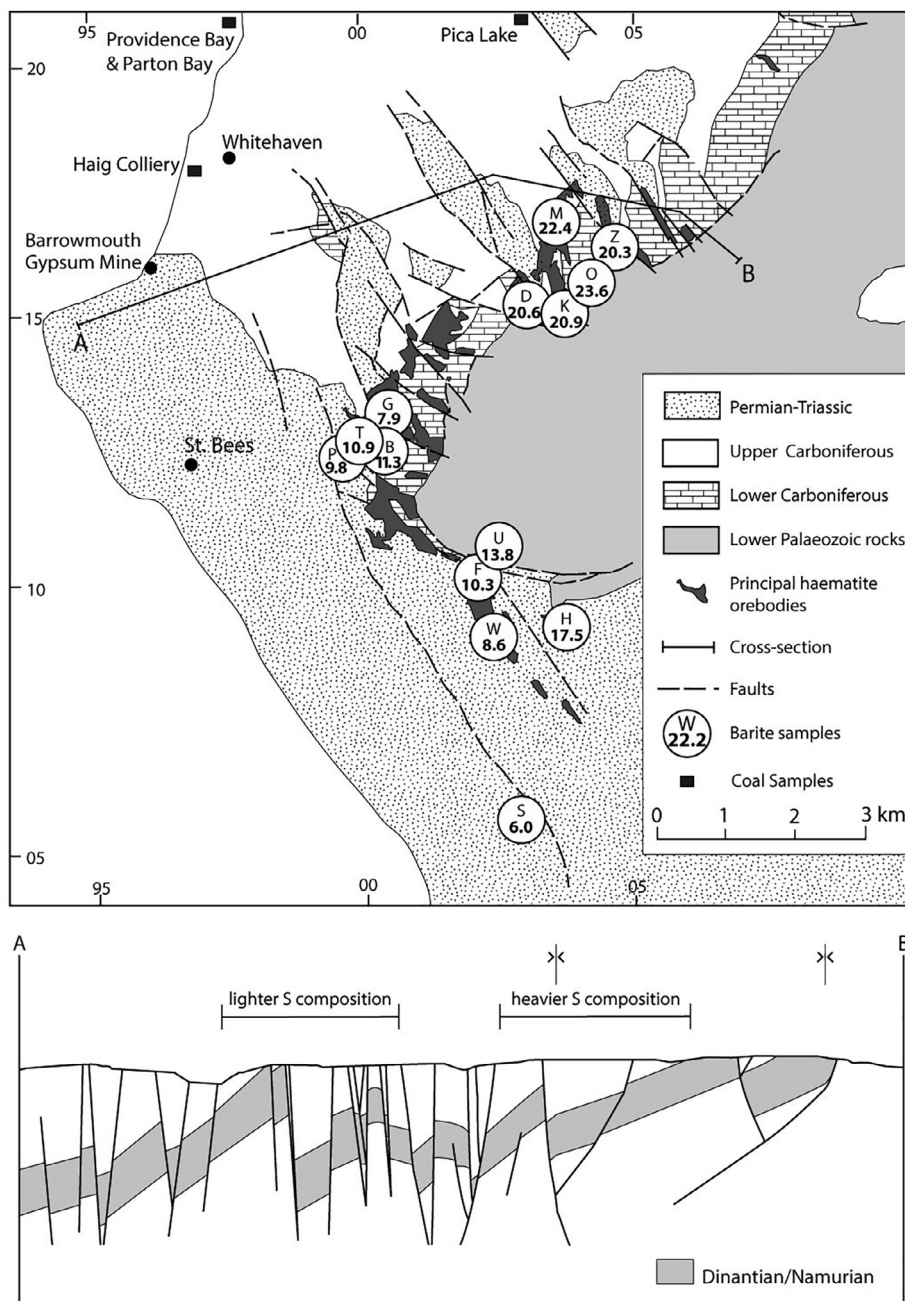


Fig. 3. Geological map of west Cumbria, after Akhurst et al. (1997). Barite deposits, annotated with S isotope composition: B, Bigrigg; D, Dalmellington; F, Florence; G, Gutterby Pit; H, Haile Moor; K, Parkside; M, Mowbray; O, Goose Green; P, Pallafiat; S, Sellafield; T, Southam; U, Ullcoats; W, Winscale; Z, Frizington Parks. Cross-section from Powell et al. (2010). Displacements of the Dinantian-Namurian section across faults are large enough to cause isolation of aquifers.

3.2. Sulphur isotope analysis

Sulphur isotope analysis was performed on samples of barite (BaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and pyrite (FeS_2) to assess the sulphur source variations between deposits. Sulphur-bearing minerals were extracted from samples using a high precision rotary drill and powdered using a quartz-agate pestle and mortar. Isotopic analysis was performed at SUERC, East Kilbride, following standard extraction methods (Coleman and Moore, 1978) and analysed using a VG Isotech SIRA II mass spectrometer. All sulphur from each sample was volatilised to SO_2 by heating at 1100°C with an excess of cooper(I) oxide (Cu_2O) within a vacuum-sealed line. Extraneous gaseous phases were removed by the use of multiple freezing stages using liquid nitrogen and pentane traps. Pure samples of extracted SO_2 gas were then analysed with the mass

spectrometer. Standard corrections were applied to raw data and the results are reported in standard notation ($\delta^{34}\text{S}$) as per mil (‰) variation relative to Vienna Cañon Diablo Troilite (V-CDT). Analytical uncertainty (1σ) based on repeat analysis of internal and international standards (NBS 127, IAEA-S-3 and NBS 123) was better than $\pm 0.3\text{‰}$ for $\delta^{34}\text{S}$.

3.3. Fluid inclusion analysis

Transparent crystals of barite from four principal haematite mines in Cumbria (Mowbray, Pallafiat, Florence and Ullcoats) were examined for fluid inclusions using a Linkam TH-600 heating-freezing stage. These samples were chosen as they adequately represent deposits from across the Cumbrian ore field, demonstrating any variability in

Table 1
Composition of sulphur isotopes ($\delta^{34}\text{S}$) in barite, gypsum and coal pyrite, Cumbria and other localities.

Lab no.	Locality	Sample Source	Grid Reference	Setting	Mineral	$\delta^{34}\text{S}_{\text{VCDT}}$ (‰)
<i>Cumbria haematite</i>						
564	Pallaflat Mine	Mine Spoil	NX 997 126	Haematite Mine	Barite	+9.8
565	Bigrigg Mine	Mine Spoil	NY 003 128	Haematite Mine	Barite	+11.3
598	Ullcoats Mine	Mine Spoil	NY 024 105	Haematite Mine	Barite	+13.8
567	Dalmellington Mine	Uni of Aberdeen Museum	NY 035 161	Haematite Mine	Barite	+20.6
562	Florence Mine	Mine Spoil	NY 017 101	Haematite Mine	Barite	+11.2
562	Florence Mine	Mine Spoil	NY 017 101	Haematite Mine	Barite	+10.3
566	Frizington Parks Mine	Mine Spoil	NY 037 159	Haematite Mine	Barite	+20.3
613	Goose Green Mine	Mine Spoil	NY 037 159	Haematite Mine	Barite	+23.6
573	Gutterby Pit Mine	Mine Spoil	NY 005 134	Haematite Mine	Barite	+7.9
573	Gutterby Pit Mine	Mine Spoil	NY 005 134	Haematite Mine	Barite	+6.0
563	Haile Moor Mine	Kendall Museum	NY 041 087	Haematite Mine	Barite	+17.6
563	Haile Moor Mine	Kendall Museum	NY 041 087	Haematite Mine	Barite	+17.5
569	Mowbray Mine	Kendall Museum	NY 037 164	Haematite Mine	Barite	+22.4
568	Parkside Mine	Kendall Museum	NY 033 155	Haematite Mine	Barite	+20.9
570	Winscales Mine	Mine Spoil	NY 025 094	Haematite Mine	Barite	+8.2
570	Winscales Mine	Mine Spoil	NY 025 094	Haematite Mine	Barite	+9.0
700	Southam Mine	Mine Spoil	NX 996 122	Haematite Mine	Barite	+10.9
<i>Other haematite</i>						
550	Auchenleck Quarry A	Mine Spoil	NX 772 525	Haematite Mine	Barite	+7.8
550	Auchenleck Quarry B	Mine Spoil	NX 772 525	Haematite Mine	Barite	+7.7
574	Taffs Well A, South Wales	Quarry Spoil	ST 119 821	Haematite Mine	Barite	+16.7
575	Taffs Well B, South Wales	Quarry Spoil	ST 119 821	Haematite Mine	Barite	+17.6
577	Machen Quarry, South Wales	Quarry Spoil	ST 222 886	Iron mining district	Barite	+17.8
653B	Winford Ochre Pit, Somerset	Mine Spoil	ST 535 637	Haematite Mine	Barite	+10.9
654A	Providence Mine, Somerset	Mine Spoil	ST 535 709	Haematite Mine	Barite	+11.2
648A	Sharkham Mine, Devon	Mine Spoil	SX 936 547	Haematite Mine	Barite	+6.7
<i>Cumbria coal</i>						
542	Haig Colliery Coal A	Mine Spoil	NX 965 176	Coal Mine	Pyrite	+2.5
542	Haig Colliery Coal A (Rep)	Mine Spoil	NX 965 176	Coal Mine	Pyrite	+2.7
542	Haig Colliery Coal B	Mine Spoil	NX 965 176	Coal Mine	Pyrite	+2.4
542	Haig Colliery Coal B (Rep)	Mine Spoil	NX 965 176	Coal Mine	Pyrite	+1.8
544	Parton Bay A	Mine Spoil	NX 979 210	Coal Outcrop	Pyrite	+9.0
544	Parton Bay A	Mine Spoil	NX 979 210	Coal Outcrop	Pyrite	+9.1
544	Parton Bay B	Mine Spoil	NX 978 212	Coal Outcrop	Pyrite	+25.6
544	Parton Bay B	Mine Spoil	NX 978 212	Coal Outcrop	Pyrite	+24.9
539	Pica Lake Coal A	Mine Spoil	NY 032 215	Coal Mine	Pyrite	+8.9
539	Pica Lake Coal A	Mine Spoil	NY 032 215	Coal Mine	Pyrite	+15.6
539	Pica Lake Coal B	Mine Spoil	NY 032 215	Coal Mine	Pyrite	+16.1
547	Providence Bay A	Coal Seam	NX 978 217	Coal Outcrop	Pyrite	+4.9
547	Providence Bay B	Coal Seam	NX 978 217	Coal Outcrop	Pyrite	+5.4
<i>Cumbria gypsum</i>						
571	Barrowmouth Mine	Mine Spoil	NX 957 156	Permian Gypsum	Gypsum	+8.8
571	Barrowmouth Mine	Mine Spoil	NX 957 156	Permian Gypsum	Gypsum	+9.6
614	Kirkby Thore Mine	Mine Spoil	NY 645 268	Permian Gypsum	Gypsum	+7.6
572	Kirkby Thore Mine	Mine Spoil	NY 645 268	Permian Gypsum	Gypsum	+10.4
615	Kirkby Thore Mine	Mine Spoil	NY 645 268	Permian Gypsum	Gypsum	+7.5

mineralization temperatures between fault blocks across the region (Fig. 3).

4. Results

4.1. Sulphur isotope analysis

Sulphur isotope compositions ($\delta^{34}\text{S}_{\text{VCDT}}$) for extracted barite from the 13 Cumbrian mine samples range from +7.9 to +23.6‰ (Table 1), i.e. a range of 15.7‰ (Fig. 4). There is a marked contrast between the 5 mines in the north, which have compositions in the range +20.3‰ to +23.6‰ and those in the south which have lower values (Fig. 3). Two ‘intermediate’ values of +13.8‰ and +17.5‰ were measured from mines in fault-bound blocks northeast of the blocks yielding the lowest values.

Five samples of Permian gypsum, from Barrowmouth Mine (West Cumbria) and Kirkby Thore Mine (East Cumbria) have a mean composition of +8.8‰. Samples of Cumbrian coal pyrite have a wide range of $\delta^{34}\text{S}$ values, +1.8 to +25.6‰, with variations of up to 16.6‰ from the same locality. Barite from haematite mines in other parts of Britain

yield values of about +17‰ (South Wales), +11‰ (Bristol), +7‰ (Devon) and +8‰ (Southwest Scotland) (Fig. 4).

4.2. Fluid inclusion analysis

Multiple crystals of barite examined from Mowbray, Pallaflat, Florence and Ullcoats haematite mines all contained only monophasic aqueous inclusions (Fig. 5). Inclusions consistently occur in clustered bands, concordant with mineralization, with individual inclusions 2–10 μm in size, identified as primary in nature.

5. Discussion

5.1. Evidence for fluid compartmentalization

The variable S-isotope compositions of barite in Cumbrian haematite deposits provides information on the provenance of mineralizing fluid sources. Proposed sources of sulphate in the vicinity include Permian or Lower Carboniferous evaporites in West Cumbria (Llewellyn et al., 1968; Arthurton and Hemingway, 1973) and barite cements in

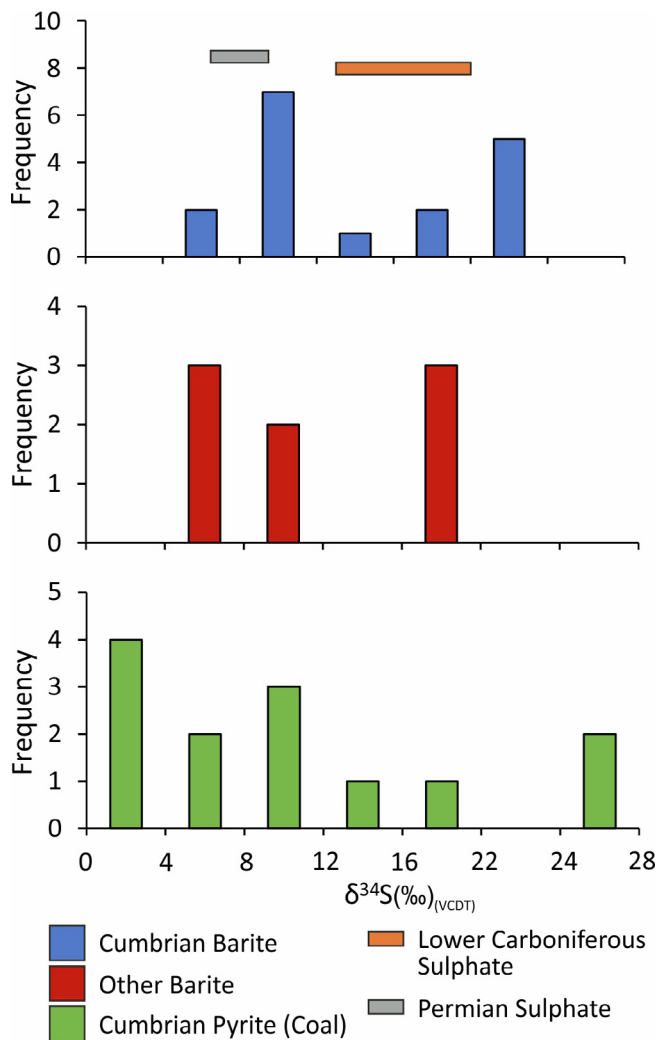


Fig. 4. Distribution of sulphur isotope compositions for barite in haematite deposits and pyrite in coal deposits, Cumbria, and barite from other haematite deposits in Britain compared with compositions of regional sulphate evaporites.

Permo-Triassic sandstones around Sellafield (Milodowski et al., 1998). Alternatively, oxidative weathering of sulphides (pyrite) from the Upper Carboniferous Coal Measures in the region could have provided a sulphur source for the barite mineralization (Akhurst et al., 1997). Barium is made available by the diagenetic alteration of associated sandstones, through the breakdown of feldspars and cements from Upper Carboniferous sandstones or Permian red beds (Plant et al., 2000). Dissolution of sulphate and barium ions by low temperature (< 60 °C) groundwater brines is proposed as the principle method of fluid transport and barite mineralization, as indicated by the uniform presence of primary, monophasic aqueous fluid inclusions (Bouch et al., 2006).

Existing sulphur isotope data for the region are available from studies of mineralization in the North Pennines (Solomon et al., 1971; Crowley et al., 1997), mineralization in the Lower Palaeozoic rocks of the Lake District (Patrick and Russell, 1989; Lowry et al., 1991), diagenetic minerals in rocks proposed for nuclear waste disposal at Sellafield (Milodowski et al., 1998), and hydrocarbon exploration in the Solway Basin (Crowley et al., 1997). The previous sulphur data have been interpreted by comparison with values from known sulphate evaporite horizons of Lower Carboniferous and Permian age in the region, which are in the ranges +15 to +22‰ and +8.5 to +11.5‰ respectively (Crowley et al., 1997; Milodowski et al., 1998). Barite deposits in the North Pennines, Lower Palaeozoic basement, and the

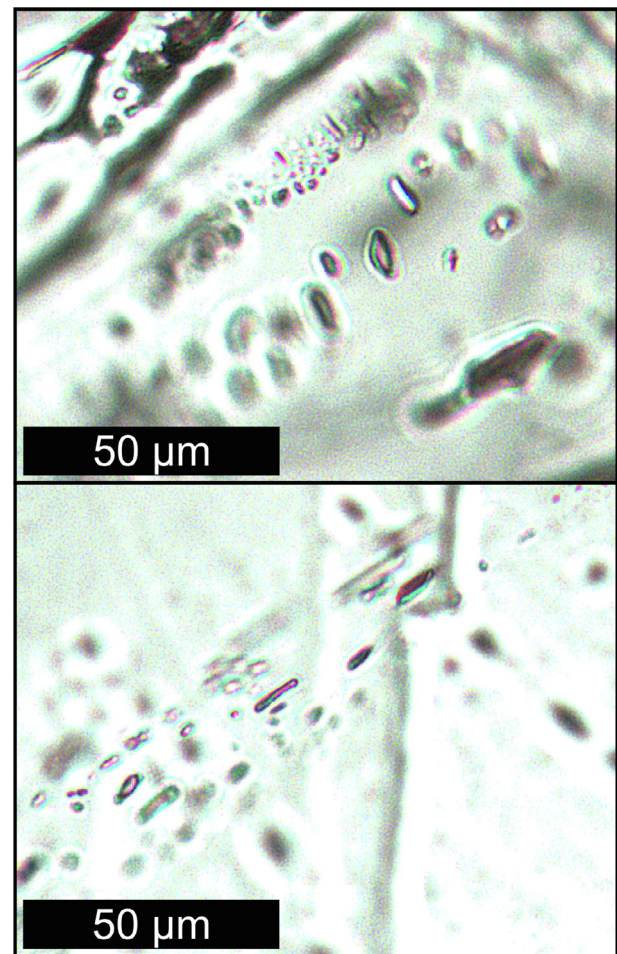


Fig. 5. Images of clustered, primary fluid inclusions in barite, Mowbray Mine.

margins of the Solway Basin, all have compositions similar to that of Lower Carboniferous evaporites, and are assumed to be derived from that source of sulphate (Patrick and Russell, 1989; Lowry et al., 1991; Crowley et al., 1997). Barite cements in Permo-Triassic sandstones at Sellafield, which are in the vicinity of the Cumbrian Ore Field, have a lighter composition in the range +3.9 to +8.1‰ (Milodowski et al., 1998). These data do not match either Lower Carboniferous or Permian evaporite compositions and are more comparable with data presented here from pyrite in the Upper Carboniferous Coal Measures, which range +1.8 to +25.6‰, with the majority of pyrite values < +9.1‰ (Table 1; Fig. 4). The presence of three isotopically distinct sulphur sources in the region, with examples of barite derived from both Lower Carboniferous evaporites and Upper Carboniferous pyrite suggests that local variations in fluid flow regime and geology may have impacted the source(s) of mineralizing fluids in the Cumbrian ore field.

The new data (Table 1; Fig. 4) indicate that there was more than one source of sulphate for the haematite deposits in the Cumbrian ore field, and the spatial distribution relative to faults indicates that the sources were separated into distinct compartments (Fig. 3). Many ore fields globally are cross-cut by arrays of sub-parallel faults, conferring a marked heterogeneity to fluid flow in the fields (e.g. Achziger-Zupančič et al., 2017; Fridovsky, 2018; Wang et al., 2019). The ubiquitous occurrence of primary, monophasic aqueous fluid inclusions across the Cumbrian ore field (Fig. 5) indicate that barite mineralization occurred through convection attributed crystallisation temperatures of < 60 °C (Bouche et al., 2006), in agreement with previous studies (Akhurst et al., 1997; Young, 2012). Based on the contemporaneous formation of haematite and barite, the consistent variations in barite S-isotope compositions are indicative of localised

compartmentalization of fluids during Fe-ore mineralization also. The 15.7‰ range of sulphur isotope values (+6.0 to +23.6‰) from the 13 iron ore mines in West Cumbria overlaps previous values for the Lower Carboniferous evaporites in the adjacent Solway Basin (+15 to +22‰) (Crowley et al., 1997), as well as new data for Permian evaporites (+7.5 to +10.4‰) and for Upper Carboniferous coal pyrite (+1.8 to +25.6‰). Distinctly higher S-isotope values occur to the NE of the region (+20.3 to +23.6‰), comparable to Carboniferous sulphate and some sulphides, with values becoming progressively lower in faulted blocks to the south and west (+6.0 to +11.3‰), more comparable to Permian sulphate compositions. Fault isolated deposits at Ullcoats and Haile Moor to the SW have intermediate values of +13.8 and +17.5‰ respectively, indicating a mixed sulphur source.

This distinction in barite composition across the ore field implies compartmentalization of fluids by impermeable faults. A cross-section across the field (Fig. 3) shows that displacement across faults are large enough to act as discontinuities, which would cause isolation of aquifers, and compartmentalization of fluids. The presence of overlying Namurian or Permian mudstones restricted mineralizing fluid flow, with ore bodies less common below these low permeability units (Dunham, 1983; Akhurst et al., 1997). These same mudstones could have contributed to fault sealing by introducing low permeability fault smears. The compartmentalization would be reinforced as minerals started to precipitate in fractures and thereby reduced porosity and permeability to become self-sealing. Further evidence of fault-controlled fluid flow is apparent by the discontinuous nature of the haematite deposits across the Cumbrian ore field, with ore deposits concentrated around regions of major faulting, with a reduction in ore bodies distally (Fig. 3).

Locally, Permian evaporites occur at Barrowmouth gypsum mine along fault-strike from the barite localities with lower $\delta^{34}\text{S}$ compositions (+7.9 to +11.3‰), which are broadly within the range of Permian evaporite compositions (+7.5 to +10.4‰). Lower Carboniferous rocks occur at depth over a wide area, so there is the possibility of access to this evaporite source across the entire region. However, the Lower Carboniferous strata generally reach shallower levels in the north of the region than in the south (Fig. 3), which likely caused shallow groundwater fluids to become dominated by Lower Carboniferous sulphate in the northern fault-bound compartments. This is supported by the significantly higher $\delta^{34}\text{S}$ ratios present in the northwest barite samples (+20.3 to +23.6‰), which closely align to the Lower Carboniferous evaporite values of +15 to +22‰ from the Easton-1 borehole in the adjacent Solway Basin (Crowley et al., 1997). A mixed Lower Carboniferous and Permian evaporite source in the central area to the southeast is indicated by intermediate values of 13.8‰ and 17.5‰, further supporting this argument. A locally identifiable source of Lower Carboniferous sulphate (anhydrite) is also present in the Cumbrian ore field, adjacent to Florence mine (Fig. 3), however isotopic data was not obtained for these deposits. The isotopic range of +15 to +22‰ is therefore assumed from the adjacent Solway Basin data given that they are time-equivalent to those at Florence, though exact values may differ.

The data from pyrite in local coal indicate a broad range of sulphur isotope compositions from +1.8 to +25.6‰, and large variations were recorded from a single locality. The values span the entire range determined from the barite samples and it is therefore conceivable that this pyrite may have acted as a sulphur source for some, or all of the barite deposits analysed. However, there is not a systematic variation in the pyrite data from north to south that would explain the barite data. A wide range of S-isotope values is common in coal pyrite, even from the same locality. Pyrite formation through both microbial sulphate reduction and remobilisation of sulphur from nearby sources during diagenesis can result in numerous phases of cross-cutting pyrite in the same sample, with different isotopic compositions (Bullock et al., 2018). Therefore it is not possible to make a definitive conclusion about the possible role of pyrite as a source of sulphate to the barite. Pyrite is

unlikely to have acted as the sole or dominant sulphur source for barite mineralization in these haematite deposits given the distinct isotopic signatures in the northeast and southwest, which are consistent with Carboniferous and Permian evaporite signatures respectively. However, the relatively low values yielded by several pyrite samples indicate that this source could explain the lower barite values determined at Sellafield, which are believed to have been deposited during the same mineralizing event as the Cumbrian barite (Milodowski et al., 1998).

Oxygen isotope measurements of the proposed Permian and Lower Carboniferous evaporite sources in the Cumbrian ore field could be used in future studies to better distinguish variations in the sulphur sources for barite mineralization, coupled with the S-isotope data presented here. Strontium isotope analysis could additionally be used to identify fluid-rock interaction and the potential dissolution of Upper Carboniferous pyritic sequences.

5.2. Other geological evidence for sulphide sources

The age of the sulphur source could be constrained by the timing of the mineralization. Multiple studies have attempted to date the haematite ores using palaeomagnetism (DuBois, 1962; Evans and El-Nikhely, 1982; Rowe et al., 1998; Crowley et al., 2014), but have reached differing conclusions ranging from late Carboniferous-Permian (Rowe et al., 1998) to Triassic (Crowley et al., 2014). The integration of paragenetic sequences for regional mineralization and diagenesis in Permo-Triassic sandstones equates haematite mineralization with deep burial diagenesis during the Triassic (Akhurst et al., 1997; Milodowski et al., 1998), and the occurrence of iron ore in faults cutting the sandstones also implies a Triassic or younger age (Shepherd and Goldring, 1993). Palaeomagnetic analysis of the sandstones confirms that haematite authigenesis occurred during deep burial, in Triassic or younger time (Turner et al., 1995). Thus, although some palaeomagnetic studies have concluded a Carboniferous-Permian age for the ores, there is strong evidence for a younger age, and a source of sulphur in Permo-Triassic evaporites is therefore possible.

The Upper Carboniferous was very substantially weathered below the sub-Permian unconformity. In the region of several haematite deposits in west Cumbria, the entire Upper Carboniferous succession was stripped off and the Permian lies unconformably upon Lower Carboniferous limestones or even Lower Palaeozoic metamorphosed basement. Huge volumes of Upper Carboniferous coal and shale, both pyritic, were altered and eroded. Where the Coal Measures are preserved, along the west coast of Cumbria, they exhibit pronounced reddening (Trotter, 1953). The coals and associated sediments are pyritic at several levels (Taylor, 1961; Akhurst et al., 1997), however the pyrite is altered to haematite and gypsum below the unconformity (Akhurst et al., 1997). Whole coal seams have been destroyed by sub-Permian oxidation (Young and Armstrong, 1989), so sulphate was available from the weathering of pyrite.

5.3. British haematite deposits

It is important to discuss the widespread occurrence of other haematite (+barite) deposits across the UK for comparison to those found in Cumbria, all of which are hosted close to the sub-Permian unconformity, within Lower Carboniferous limestone. The occurrence of haematite ores in a similar stratigraphic context in other parts of Britain, including South Wales and the Forest of Dean, the Mendips (Somerset), and North Wales, constrains their origin, if we assume that they share a common genesis. It suggests that regionally limited rocks, such as the granite in Cumbria, were not involved, but rather more uniform aspects of stratigraphic evolution were responsible. These deposits are not necessarily of the same age, as the Lower Carboniferous is the only period of pre-Jurassic stratigraphy with widely distributed carbonate deposits which control mineralization. A model for the haematite ores of South Wales has been developed independently of

those of Cumbria, but similarly invokes brine leaching of iron from red beds in the Triassic (Bevins and Mason, 2010). In contrast, a model for haematite ores and associated minerals in the Mendips attributes the metals to the alteration of pyrite-bearing Carboniferous rocks (Bridges et al., 2012). Notably, the speleological community attribute the origin of haematite-bearing palaeokarst in Carboniferous limestone to acidic fluids derived from weathering of Carboniferous pyrite (Bowen, 2010; Farrant and Harrison, 2017). The models for haematite mineralization elsewhere in Britain thus reflect the possibilities to explain haematite mineralization in Cumbria, although they were not necessarily contemporaneous. Ore mineralization within carbonate sequences is common across many deposit types globally, due to the alteration of fluid pH caused by dissolution of limestones and the accommodation space produced during karstification by acidic fluids (Bouch et al, 2006; Paradis and Lavoie, 1996; Zhang et al, 2015). As the principal carbonate sequence of the British Palaeozoic, the Lower Carboniferous limestones present the most effective host rock for ore-fluid mineralization in the region, regardless of source or timing.

Haematite deposits below the sub-Permian unconformity in several other parts of Britain also contain barite, from Scotland to Devon. These occurrences indicate that the mineralizing fluids were commonly sulphur-bearing. In the oxidizing conditions that characterize haematite deposition the sulphur was precipitated as barite. However, the inference of multiple sources for the sulphur does not extend to the iron in the haematite. The widespread nature of the sub-Permian haematite (Fig. 1) suggests a process that was ubiquitous at the time, though the timing and source(s) of haematizing fluids across the UK have few constraints and remain ambiguous. The association of quartz and calcite with these haematite deposits suggests a period of higher temperature mineralization in the Cumbrian ore field (Shepherd and Goldring, 1993; Young, 2012), followed by barite crystallisation during a period of waning (< 60 °C). This indicates a fluctuation of hydrothermal flow regimes between higher temperature, advective flow and lower temperature, gravity-driven flow, which was likely hypersaline. This model is in agreement with previous hypotheses for mineralization in the Cumbrian ore field which primarily utilised field observations (Dunham, 1983). The timing of mineralizing events in other British deposits may have differed substantially between ore fields.

The barite from haematite deposits in other parts of Britain have $\delta^{34}\text{S}$ values comparable with the lighter group in Cumbria, in Somerset and Southwest Scotland, and closer to the heavier group in Cumbria, in South Wales. This emphasizes that sulphur from more than one source contributed to the mineralization that precipitated haematite. It further suggests that the mineralization was a widespread process that did not depend upon only a single source horizon for the sulphur.

Sulphur isotope data for barite in base metal ore deposits in northern Britain are similarly divided into compositions that suggest a Permian sulphate source (central Scotland; Jassim et al., 1983) and those that are attributed a Carboniferous sulphate source (northern England; Crowley et al., 1997).

The haematite and barite precipitation overlap within the mineral paragenesis in Cumbria (Shepherd and Goldring, 1993), so constraining the origin of the barite should help to understand the origin of the haematite. The fluid inclusion observations show that the barite was deposited at low-temperature, which is consistent with derivation of the sulphur from dissolution of shallow evaporites. While these results do not exclude a deeper sulphur source, there is no evidence of an alternative source in the surrounding area. These results also support a shallow (diagenetic) origin for the haematizing fluids, such as from the Permo-Triassic red beds, as suggested in previous studies (Dunham, 1983). Although the barite mineralization may represent the waning phase of hydrothermal mineralization, the low formation temperature inferred from fluid inclusions across the ore field suggests that gravity driven flow of dense, hypersaline fluids may have become increasingly influential in the formation of these ore deposits. A shallow source for the mineralizing fluids is further supported by the reduction of ore

bodies where overlying Permian and Namurian mudstones occur (Akhurst et al., 1997), which would have limited shallow fluid flow, but not deep sourced fluids.

5.4. Global implication for deposits

The data presented here has implications for fault-bound fluid flow in mineralizing systems globally. The kilometre-scale compartmentalization observed in the Cumbrian ore field and resultant heterogeneity of mineralizing sources across the deposit is a feature of many other fault-controlled mineralizing systems, including examples in Germany (Achtziger-Zupančič et al, 2017), Russia (Fridovsky, 2018) and China (Wang et al, 2019). Similar compartmentalization of ore-fluids has likely occurred in numerous other deposits. At this scale, any variation in fluid sources may not be apparent without detailed sampling and analysis of the deposit, which could result in significant under-, or over-estimation of resources.

6. Conclusions

Measurement of the sulphur isotope composition of barite from 13 haematite mines in the West Cumbria iron ore field indicates kilometre-scale compartmentalization of fluids. In particular:

- (i) Within a relatively small 5 km wide ore field, barite accompanying haematite ore ranges widely in composition over 14‰.
- (ii) The spatial variations in $\delta^{34}\text{S}$ composition indicate a relatively heavy source in the north, and a relatively light source to the south.
- (iii) The higher and lower $\delta^{34}\text{S}$ compositions are comparable with those of Lower Carboniferous and Permian sulphate evaporites respectively, which occur in the region.
- (iv) All 13 compositions are higher than that of barite in the Permo-Triassic rocks at Sellafield, believed to belong to the same episode of barite deposition, immediately south of the ore field.

These data combine to show that sulphate-mineralizing fluids were strongly compartmentalized on a kilometre-scale. Dominantly shallow, gravity driven brines, formed during low temperature hydrothermal activity were the primary mineralizing fluid. The NNW-SSE faults cutting the ore field would have facilitated the separation of fluid flow pathways. The variations in composition in Cumbria suggest that haematite mineralization in the Carboniferous elsewhere in Britain may similarly have had a range of sources and has implications for compartmentalization of fluids in deposits globally.

The case study in Cumbria emphasizes the need for spatially extensive sampling for isotopic studies in ore fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Achtziger-Zupančič, P., Loew, S., Hiller, A., 2017. Factors controlling the permeability distribution in fault vein zones surrounding granitic intrusions (Ore Mountains/Germany). *J. Geophys. Res. Solid Earth* 122, 1876–1899.
- Akhurst, M.C., Chadwick, R.A., Holliday, D.W., McCormac, M., McMillan, A.A., Millward, D., Young, B.R., Ambrose, K., Auton, C.A., Barclay, W.J., Barnes, R.P., Glover, B.W., Hawkins, M.P., James, J.W.C., Johnson, H., Jones, N.S., Kimbell, G.S., MacPherson, K.A.T., Merritt, J.W., Milodowski, A.E., Riley, N.J., Robins, N.S., Stone, P., Wingfield, R.T.R., Beddoe-Stephens, B.W. 1997. Geology of the West Cumbria District. Memoir of the Geological Survey of England and Wales.
- Arthurton, R.S., Hemingway, J.E., 1973. The St. Bees Evaporites – a carbonate-evaporite formation of Upper Permian age in West Cumberland, England. *Proc. Yorkshire Geol. Soc.* 38, 565–592.
- Bevins, R.E., Mason, J.S., 2010. Wales. In: Bevins, R.E., Young, B., Mason, J.S., Manning, D.A.C., Symes, R.F. (Eds.), *Mineralization of England and Wales. Geological Conservation Review Series No. 36. Joint Nature Conservation Committee, Peterborough*, pp. 199–381.
- Bouch, J.E., Naden, J., Shepherd, T.J., McKervey, J.A., Young, B., Benham, A.J., Sloane, H.J., 2006. Direct evidence of fluid mixing in the formation of stratabound Pb–Zn–Ba–F mineralization in the Alston Block, North Pennine Orefield (England). *Miner. Deposita* 41, 821–835.
- Bowen, C., 2010. An interim report on Wigpool Cave: a syncline-guided, palaeo drainage cave in the Forest of Dean limestone basin, UK. *Cave Karst Sci.* 36, 59–62.
- Boyce, A.J., Fletcher, T.J., Fallick, A.E., Ashton, J.H., Russell, M.J., 1993. Petrographic and $\delta^{34}\text{S}$ study of the Lower Palaeozoic under the Navan Zn + Pb deposit: A source of hydrothermal sulphur. In: Fenoll Hach-Ali, P., Torres-Ruiz, J., Gervilla, F. (Eds.), *Current Research in Geology Applied to Ore Deposits, Proc. of the 2nd Biennial SGA Meeting. Publ. Univ. of Granada, Spain*, pp. 53–56.
- Bridges, T.F., Turner, R., Rumsey, M.S., 2012. A geochemical study of the lead oxychloride mineral assemblage of the Mendip Hills, Somerset, UK using a stability field model. *J. Russell Soc.* 15, 18–28.
- Bullock, L.A., Parnell, J., Perez, M., Boyce, A., Feldmann, J., Armstrong, G.T., 2018. Multi-stage pyrite genesis and epigenetic selenium enrichment of Greenburn coal (East Ayrshire). *Scottish J. Geol.* 54, 37–49.
- Coleman, M.L., Moore, M.P., 1978. Direct reduction of sulfates to sulfur dioxide for isotopic analysis. *Anal. Chem.* 50, 1594–1595.
- Crowley, S.F., Bottrell, S.H., McCarthy, M.D.B., Ward, J., Young, B., 1997. $\delta^{34}\text{S}$ of Lower Carboniferous anhydrite, Cumbria and its implications for barite mineralization in the northern Pennines. *J. Geol. Soc., London* 154, 597–600.
- Crowley, S.F., Piper, J.D.A., Bamarouf, T., Roberts, A.P., 2014. Palaeomagnetic evidence for the age of the Cumbrian and Manx hematite ore deposits: implications for the origin of hematite mineralization at the margins of the East Irish Sea Basin, UK. *J. Geol. Soc., London* 171, 49–64.
- DuBois, R.L., 1962. Magnetic characteristics of a massive hematitic body. *J. Geophys. Res.* 97, 2887–2893.
- Dunham, K.C., 1983. Genesis of the Cumbrian haematite deposits. *Proc. Yorkshire Geol. Soc.* 45, 130.
- Dunham, K., 1984. Classification, age and origin of the Cumbrian hematite. *Proceedings of the Cumberland Geological Society* 4, 259–266.
- Evans, A.M., El-Nikhely, A., 1982. Some Palaeomagnetic dates from the west Cumbrian hematite deposits, England. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)* 91, 41–43.
- Fallick, A.E., Ashton, J.H., Boyce, A.J., Ellam, R.M., Russell, M.J., 2001. Bacteria were responsible for the magnitude of the world-class hydrothermal base metal sulfide orebody at Navan Ireland. *Econ. Geol.* 96, 885–890.
- Farrant, A.R., Harrison, T., 2017. Hypogenic caves in the UK. In: Klimchouk, A. (Ed.), *Hypogene Karst Regions and Caves of the World*. Springer, Berlin, pp. 43–60.
- Fraser Harris, A.P., McDermott, C.I., Kolditz, O., Haszeldine, R.S., 2015. Modelling groundwater flow changes due to thermal effects of radioactive waste disposal at a hypothetical repository site near Sellafield, UK. *Environ. Earth Sci.* 74, 1589–1602.
- Fridovsky, V.Y., 2018. Structural control of orogenic gold deposits of the Verkhoyansk-Kolyma folded region, northeast Russia. *Ore Geol. Rev.* 103, 38–55.
- Goldring, D.C., Greenwood, D.A., 1990. Fluorite mineralization at Beckermert iron ore mine, Cumbria. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)* 99, 113–119.
- Gutmanis, J.C., Lanyon, G.W., Wynn, T.J., Watson, C.R., 1998. Fluid flow in faults: a study of fault hydrogeology in Triassic sandstone and Ordovician volcanoclastic rocks at Sellafield, north-west England. *Proc. Yorkshire Geol. Soc.* 52, 159–175.
- Hughes, R.A. 2003. Permian and Triassic rocks of the Appleby district (part of Sheet 30, England and Wales). *British Geological Survey Research Report RR/02/01*. <http://nora.nerc.ac.uk/id/eprint/3674/1/RR02001.pdf>.
- Jassim, R.Z., Patrick, R.A.D., Russell, M.J., 1983. On the origin of the silver + copper + cobalt + barite mineralization of Ochil Hills, Scotland: a sulphur isotope study. *Transactions of the Institution of Mining and Metallurgy. (Section B: Applied Earth Science)* 92, B213–B216.
- Llewellyn, P.G., Mahmoud, S.A., Stabins, R., 1968. Nodular anhydrite in Carboniferous Limestone, west Cumberland. *Transactions of the Institution Mining & Metallurgy (Section B Applied Earth Science)* 77, B18–B25.
- Lowry, D., Boyce, A.J., Patrick, R.A.D., Fallick, A.E., Stanley, C.J., 1991. A sulphur isotopic investigation of the potential sulphur sources for lower Palaeozoic-hosted vein mineralization in the English Lake District. *J. Geol. Soc., London* 148, 993–1004.
- Milodowski, A.E., Gillespie, M.R., Naden, J., Fortey, N.J., Shepherd, T.J., Pearce, J.M., Metcalfe, R., 1998. The petrology and paragenesis of fracture mineralization in the Sellafield area, west Cumbria. *Proc. Yorkshire Geol. Soc.* 52, 215–241.
- Paradis, S., Lavoie, D., 1996. *Sed. Geol.* 107, 121–139.
- Patrick, R.A.D., Russell, M.J., 1989. Sulphur isotopic investigation of Lower Carboniferous vein deposits of the British Isles. *Miner. Deposita* 24, 148–153.
- Plant, J.A., Jones, D.G., Haslam, H.W., 2000. The Cheshire Basin – Basin Evolution, Fluid Movement and Mineral Resources in a Permo-Triassic Rift Setting. *British Geological Survey, Keyworth*.
- Powell, J.H., Waters, C.N., Millward, D., Robins, N.S., 2010. Managing radioactive waste safely: Initial geological unsuitability screening of West Cumbria. *British Geological Survey Research Report CR/10/072*.
- Rankin, A.H., Criddle, A.J., 1985. Mineralizing fluids and metastable low-temperature inclusion brines at Llanharry iron deposit, South Wales. *Trans. Inst. Min. Metall. (Sect. B: Appl. Earth Sci.)* 94, 126–132.
- Rose, W.C.C., Dunham, K.C., 1977. *Geology and Haematite Deposits of South Cumbria. Economic Memoir of the Geological Survey of Great Britain*, HMSO, London.
- Rowe, J., Turner, P., Burley, S., 1997. Palaeomagnetic dating of the west Cumbrian hematite deposits and implications for their mode of formation. *Proc. Yorkshire Geol. Soc.* 52, 59–71.
- Rye, R.O., Ohmoto, H., 1974. Sulfur and carbon isotopes and ore genesis: A review. *Econ. Geol.* 69, 826–842.
- Shanks, W.C.P., 2014. *Stable Isotope Geochemistry of Mineral Deposits*. In: *Treatise on Geochemistry (2nd edition)*. Elsevier, Amsterdam, pp. 59–85.
- Shepherd, T.J., Goldring, D.C., 1993. Cumbrian hematite deposits, Northwest England. In: Patrick, R.A.D., Polya, D. (Eds.), *Mineralization in the British Isles*. Chapman & Hall, London, pp. 419–445.
- Solomon, M., Rafer, T.A., Dunham, K.C., 1971. Sulphur and oxygen isotope studies in the northern Pennines in relation to ore genesis. *Transactions of the Institution of Mining and Metallurgy (section. B: Applied Earth Science)* 80, B259–B275.
- Taylor, B.J., 1961. The stratigraphy of exploratory boreholes in the West Cumberland Coalfield. *Bull. Geol. Surv. Great Br.* 17, 1–74.
- Trotter, F.M., 1945. The origin of the West Cumbrian haematites. *Geol. Mag.* 82, 67–80.
- Trotter, F.M., 1953. Reddened beds of Carboniferous age in north-west England and their origin. *Proc. Yorkshire Geol. Soc.* 29, 1–20.
- Turner, P., Burley, S.D., Rey, D., Prosser, J., 1995. Burial history of the Penrith Sandstone (Lower Permian) deduced from the combined study of fluid inclusion and Palaeomagnetic data. In: Turner, P., Turner, A. (Eds.), *Palaeomagnetic Applications in Hydrocarbon Exploration and Production*, pp. 43–78 *Geological Society Special Publication*, 98.
- Wang, S.R., Yang, L.Q., Wang, J.G., Wang, E.J., Xu, Y.L., 2019. Geostatistical determination of ore shoot plunge and structural control of the Sihuang world-class epizonal orogenic gold deposit, Jiaodong Peninsula, China. *Minerals* 9. <https://doi.org/10.3390/min9040214>.
- Young, B. & Armstrong, M. 1989. *The Applied Geological Mapping of the Dearham and Gilcrux area, Cumbria*. British Geological Survey Technical Report WA/89/70.
- Young, 2012. *Geology and Mineralization at Florence Mine, Egremont, Cumbria*. *J. Russell Soc.* 15, 3–18.
- Zhang, C., Wu, Y., Hou, L., Mao, J., 2015. *J. Asian Earth Sci.* 103, 103–114.