Downloaded from http://pygs.lyellcollection.org/ at University of Aberdeen on February 7, 2020

Research article

Published online February 22, 2019

Proceedings of the Yorkshire Geological Society

https://doi.org/10.1144/pygs2018-008 | Vol. 62 | 2019 | pp. 229-237

Emplacement of oil in the Devonian Weardale Granite of northern England

M. Baba^{1*}, J. Parnell¹, S. Bowden¹, J. Armstrong¹, M. Perez² & X. Wang²

¹ Department of Geology and Petroleum Geology, University of Aberdeen, Aberdeen AB24 3UE, UK

D M.B., 0000-0002-6713-3006; J.A., 0000-0002-1342-3710; X.W., 0000-0001-7071-6555

*Correspondence: babamasud@gmail.com

Abstract: Oil residues occur as solid bitumen in mineralized zones within the Devonian Weardale Granite of the northern Pennines, northern England. Comparable residues are present in the overlying Mississippian rocks and were probably derived from a Carboniferous source, i.e. during later mineralization of the granite. The bitumen was already solidified during fluorite mineralization, which does not contain oil inclusions. The residues do not show the high thermal maturity of organic matter in the region altered by the earliest Permian Whin Sill. Like the sulphide-fluorite mineralization, oil emplacement post-dated intrusion of the sill. Pyrite associated with the oil residues is enriched in trace elements including lead, silver, gold, selenium and tellurium, which suggests that mineralizing fluids at least shared pathways with migrating hydrocarbons and possibly also suggests undiscovered valuable metal resources.

Received 21 June 2018; revised 6 November 2018; accepted 5 December 2018

The North Pennine orefield contains base metal sulphide (lead-zinc) ore deposits, regarded as belonging to a fluoriterich class of Mississippi Valley-type deposits (Dunham 1983, 1990), focussed around the buried Weardale Granite of Early Devonian (Emsian) age (399 Ma; Kimbell *et al.* 2010). The mineralization occurs primarily within unconformably overlying Mississippian rocks, particularly in the limestones of the Great Scar Limestone and Yoredale groups. The region underlain by the granite is a prominent structural high, the Alston Block (Fig. 1).

Oil and oil residues occur in granites and other crystalline basement in many parts of the world. These occurrences are now an accepted feature of oil migration rather than a possible indicator of abiogenic hydrocarbons (Gold 1999), and in some areas are on a large enough scale to allow commercial exploitation (P'An 1982; Petford & McCaffrey 2003). In most cases, the granite pre-dates oil formation and even oil source rock deposition. However, the granites become oil reservoirs because they form structural highs and so are updip from younger basins, and are also susceptible to the development of fracture porosity. Granites may also be a source of long-term high heat flow, which drives the convection of metalliferous fluids that mineralize the granite and surrounding rocks. Consequently, some granites could be hosts to charges by both ore fluids and hydrocarbons. The Weardale Granite is an example of this dual role, and offers an opportunity to assess how the two relate to each other.

A widely accepted model for the mineralization involves circulation of brines from Carboniferous–Permian basins adjacent to the orefield, focussed by the granite (Solomon *et al.* 1971; Dunham 1990; Cann & Banks 2001; Bouch *et al.* 2008). The Weardale Granite was proved by the Rookhope Borehole [National Grid Reference NY 938 428] at a depth of 1281 feet (390 m), directly below Mississippian rocks

(Dunham et al. 1961, Dunham 1988). The borehole was sited near the surface position of the hanging wall of the Red Vein (Fig. 1), a mineralized lineament that has yielded extensive fluorite and galena. The borehole intersected several examples of metalliferous mineralization, mostly in the Mississippian rocks. However two mineralized veins were intersected in the granite, one of which was accompanied by extensive alteration of the granite from 1585 to 1656 feet (483 to 505 m) and may represent the Boltsburn Vein, which meets the Red Vein at Rookhope (Dunham 1990). Subsequently, a second borehole at Eastgate [NY 9389 3820], c. 5 km south of Rookhope, also penetrated the granite, and similarly encountered granite-hosted mineralization (Manning et al. 2007). The granite clearly focussed hot fluids during at least one period of enhanced heat flow, which would have reactivated old (Caledonian) hydrothermal fractures within the granite, through which fluids from surrounding younger Carboniferous basins passed.

Solid oil residues (bitumen) were recorded in several samples of mineralized Weardale Granite in the Rookhope Borehole (Parnell 1988). This account presents organic biomarker, fluid inclusion and laser ablation data determined to investigate the occurrence of bitumen. In particular, new data are used to determine:

- (i) The degree of preservation of biomarkers.
- (ii) The thermal maturity of the oil, and how that relates to the temperature of mineralization.
- (iii) Whether the oil was fresh or biodegraded.
- (iv) If associated pyrite is enriched in trace elements, which may reflect the passage of mineralizing fluids.

Oil residues with no obvious relationship to the Weardale Granite also occur at several localities in the Northumberland Basin, as recorded by Creaney *et al.* (1980), and one such



PYGS

² Trace Element Speciation Laboratory (TESLA), Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, UK

230

M. Baba et al.



Fig. 1. Map of the Alston Block, northern Pennines, showing the limit of the buried Weardale Granite, the region of fluorite mineralization in the overlying limestone, and sample localities (after Bott & Masson Smith 1957).

occurrence at Moot Law [NZ 011 760], 35 km to the north, was sampled for comparison.

Methodology

Samples of bitumen-bearing veinrock were taken for organic geochemistry and microthermometry at depths of 1645 feet (501 m), 1650 feet (503 m) and 1686 feet (514 m) in the Rookhope Borehole. Comparative samples were collected from Moot Law (see Creaney *et al.* 1980) and from Mississippian argillaceous rocks cropping out close to the borehole site at Rookhope [NY 938 428].

Samples (single wafers) for microthermometric analysis were extracted at depths 1647 feet (502 m) (quartz) and 1645 feet (501 m) (fluorite). For comparison, fluorite mineralization within the Mississippian rocks above the buried granite was sampled at the Grove Rake Mine [NY 897 442], on the Red Vein (Fig. 1). All samples were examined using a Linkam THM 600 heating-freezing stage. Homogenization temperatures have not been pressure-corrected.

Rock samples were prepared by rinsing with distilled water two times, and again with dichloromethane (DCM). The dry rocks were crushed and extracted using a soxhlet apparatus for 48 h. All glassware was thoroughly cleaned with a 93:7 mixture of DCM/methanol (MeOH). Crushed samples were weighed, recorded and transferred into pre-extracted thimbles. The extracts were then dried down using a rotary evaporator, separated into aliphatic, aromatic and polar fractions via a silica column chromatography using hexane, hexane/DCM in the ratio 3:1 and DCM/MeOH, respectively. Prior to gas chromatography-mass spectrometry (GC-MS) analysis, an internal standard (5 β -Cholane, Agilent

Technologies) was added to the saturate fraction before injection into the GC-MS machine and subsequent biomarker identification. This was done using an Agilent 6890N gas chromatograph fitted with a J&W DB-5 phase 50 m MSD and a quadruple mass spectrometer operating in SIM mode (dwell time 0.1 s per ion and ionisation energy 70 eV). Samples were injected manually using a split/splitless injector operating in splitless mode (purge 40 ml min⁻¹ for 2 min). The temperature programme for the GC oven was 80-295°C, holding at 80°C for 2 min, rising by 10°C min⁻¹ for 8 min and then by 3°C min⁻¹, and finally holding at the maximum temperature of 295°C for 10 min. Quantitative biomarker data were obtained for isoprenoids, hopanes, steranes and diasteranes by measuring responses of these compounds on m/z 85, 125, 191, 217, and 218 mass chromatograms and comparing them to the response of the internal standard. Biodegradation was assessed using the ratio of phytane to the C_{18} *n*-alkane (Ph/nC₁₈), which increases with degradation as n-alkanes are altered more rapidly (Peters & Moldowan 1993). Biodegradation also causes the breakdown of steranes at a faster rate than diasteranes, including in the shallow subsurface in aerobic conditions, so the diasterane/sterane ratio (D/S) can be elevated due to shallow biodegradation (Seifert & Moldowan 1979), but is also controlled by thermal maturity and source rock lithology (Burton et al. 2018). Thermal maturity was estimated from the 20S/20S + 20R ratio for C₂₉ steranes, based on the increasing proportion of the S isomer with maturation (Peters & Moldowan 1993).

As oil residues are co-located with mineralization in the Weardale Granite, and may be involved in mineralization elsewhere, this possibility was assessed by study of pyrite



Fig. 2. Segment of Rookhope Borehole core, depth 1647 feet (502 m), consisting of Weardale Granite cut by bitumen-bearing quartz vein (dark) mineralized by pyrite. The quartz-bitumen vein is cut by a thin fluorite-bearing vein.

directly related to the oil residues. Pyrite was analysed using laser ablation-inductively coupled plasma-mass spectrometry (LA-CP-MS). Quantitative measurements were made of Pb, Cu, As, Ag, Au, Se and Te contents. The methodology is given by Parnell *et al.* (2015).

Results

Mineral paragenesis

In a mineralized zone at 1647 feet (502 m) where bitumen was encountered, the granite is veined by quartz (Fig. 2). The quartz consists of interlocking subhedral crystals of submillimetre-size. Remaining porosity after quartz precipitation was infilled by bitumen (Fig. 3). The bitumen-quartz mixture is also mineralized by pyrite (Fig. 2). Later calcite and dolomite occur as a replacement of the quartz and the granite host rock, and infill shrinkage cracks in the bitumen. Fluorite (purple, also clear and brown) followed the carbonates and occurs in and beyond the quartz veinrock, which was post-dated by the fluorite. The bitumen does not occur in the cavities filled with fluorite, which implies that it had already precipitated and solidified at the time of fluorite mineralization (Fig. 2). The samples examined did not include the green fluorite that is widely found in mineralization in the North Pennines.

Organic biomarkers

Each of the bitumen-bearing samples from the Rookhope Borehole yielded biomarkers that can be identified and quantified (Table 1). Mass chromatograms for m/z 85 and



Fig. 3. Thin section photomicrograph of bitumen (black) interstitial to quartz in the Weardale Granite, depth 1686 feet (514 m) in the Rookhope Borehole.

217 are shown for the granite-hosted bitumen and the bitumen at Moot Law (Figs 4 and 5).

The m/z 85 chromatograms (Fig. 4) show very limited unresolved complex mixtures (humps). The Ph/nC_{18} ratio in the three granite-hosted samples is in the range 0.46–0.85, and the D/S ratio is in the range 0.08–0.90 (Table 1).

The distribution of C_{27} , C_{28} and C_{29} steranes shows that all of the samples have similar composition, dominated by C_{27} and C_{29} (Fig. 6). The sterane C_{29} S/S + R thermal maturity parameter is in the range 0.27–0.36 for the three granite-hosted samples, and by contrast is 0.55 for the Moot Law bitumen and 0.54 for the shale sample (Table 1).

Fluid inclusions

The quartz and fluorite within the granite yield different thermometric data (Fig. 7). Homogenization temperatures for quartz and fluorite overlap significantly at the cooler end of the fluorite field. The granite-hosted phases yield final ice melting temperatures characteristic of moderate salinities.

The limestone-hosted fluorite yielded a lower range of temperatures than the granite-hosted fluorite (Fig. 7), which may reflect a cooling as the fluids rose to shallower levels. The large spread of data from the granite-hosted fluorite suggests that there may be a mixture from primary and secondary inclusions. The two sets of fluorite data are characterized by different final ice melting temperatures. The limestone-hosted fluorite yielded lower final melting temperatures (Fig. 7), reflecting greater salinities and a calcic component to the mineralizing brines. Detailed fluid inclusion studies from Grove Rake Mine (Greenwood & Smith 1977) show that temperatures vary with depth, but

Table 1. Biomarker data for samples from Weardale Granite, Moot Law and Rookhope shale

	D/S	C ₂₉ 20S/S + R	Pr/Ph	Pr/nC_{17}	Ph/nC_{18}	C ₂₇ (%)	C ₂₈ (%)	C ₂₉ (%)
Weardale 1645	0.90	0.36	0.76	0.85	0.85	40	31	29
Weardale 1650	0.08	0.29	1.20	0.52	0.53	32	32	36
Weardale 1686	0.50	0.27	1.13	0.34	0.46	36	30	34
Moot Law	0.45	0.55	2.02	1.98	0.98	33	16	51
Rookhope shale	0.38	0.54	0.99	1.25	3.58	37	29	34

Key: C₂₉ βαR diasterane/C₂₉ αββR sterane; Pr/Ph: Pristane/Phytane

M. Baba et al.



Fig. 4. Mass fragmentograms for m/z 85 for bitumen samples from the Weardale Granite (Rookhope Borehole) and Carboniferous limestone (Moot Law).

they are broadly comparable with those shown in Figure 7. All inclusions observed are aqueous. None of the fluorite contains oil inclusions.

Previous fluid inclusion data for the orefield (Sawkins 1966; Smith & Philips 1975; Greenwood & Smith 1977; Atkinson *et al.* 1982; Bouch *et al.* 2006) show the existence of anomalously hot regions within the fluorite zone, including the Great Sulphur Vein (Fig. 1) with temperatures

up to 220°C, around which temperatures decrease with distance. The range of salinities is wide, from 7 to 27 wt. % equiv. NaCl (Sawkins 1966).

LA-ICP-MS

Mapping of the pyrite directly associated with the oil residues shows that it contains a range of trace elements (Fig. 8).



Fig. 5. Mass fragmentograms for m/z 217 for bitumen samples from the Weardale Granite (Rookhope Borehole) and Carboniferous limestone (Moot Law). Emplacement of oil in the Weardale Granite



Fig. 6. Composition of C_{27} , C_{28} and C_{29} steranes ($\alpha\beta\beta$ S + R) in samples from the Weardale Granite, from Moot Law, and from shale at the surface at Rookhope. Data determined from m/z 218 chromatograms. Compositions cluster between C_{27} and C_{29} predominance.

Integration of the data gives a measurement of 8450 ppm Pb, 2718 ppm Cu, 8846 ppm As, 252 ppm Ag, 0.83 ppm Au, 24 ppm Se and 32 ppm Te in the mapped pyrite, and spot measurements of different pyrite crystals show that all are enriched in Au. Extensive experience in this laboratory suggests that these trace element contents are over an order of magnitude greater than is typical for authigenic pyrite in Phanerozoic sedimentary rocks. Measurements from pyrite at Allenheads, 8 km to the NW, show much lower levels of trace elements (Fig. 9).

Discussion

Biomarker compositions

The biomarkers in samples from the Rookhope Borehole are typical of oil residues. The sterane compositions (Figs 5 and 6) are typical of marine organic matter as they are deficient in the C_{28} sterane, which is more prominent in continental organic matter. The similarity in compositions between the samples is consistent with derivation of the oil residues from the marine Carboniferous shales. The sterane data indicate a thermal maturity equivalent to about 0.6% vitrinite reflectance (Peters *et al.* 2007) in the granite-hosted samples. The data for the Moot Law bitumen and the shale are both at the upper limit for this parameter, and so are equivalent to reflectance values of any level above 0.8% (Peters *et al.* 2007).

The very limited complex mixtures in the m/z 85 chromatograms and the values of Ph/nC18 below unity suggest that the oil was not heavily biodegraded, although it has solidified. The D/S values below unity are consistent with lack of biodegradation. Solidification of the oil could alternatively have been a consequence of interaction with water (Peters et al. 2007). The data alone do not constrain when solidification occurred, but the lack of oil inclusions within the younger fluorite suggests that the oil had been already solidified by that time. Regardless of the timing, the occurrence of the oil residues in borehole samples indicates that the solidification occurred at a depth below the surface of at least the present core depth of 500 m. Given the assumed thickness of the post-granite succession of 1.5 km (see below) at the time of oil generation and mineralization (Bouch et al. 2006; Manning et al. 2007), the depth of burial of the residues in the granite may have been up to 2 km.

The lack of evidence for biodegradation contrasts with other instances of oil emplacement in basement rocks. This difference may reflect the geometry of oil emplacement into the basement. Studies of biodegraded oil residues in the Proterozoic rocks of Ross-shire (Parnell *et al.* 2017*a*) and Shropshire (Parnell *et al.* 2017*b*) concluded that the ingress of oil was by up-dip migration from sedimentary basins into basement structural highs. In contrast, the model for mineralization through the Weardale Granite involves the convection of fluids from depth upwards through the pluton (Solomon *et al.* 1971; Bouch *et al.* 2008). The convection



Fig. 7. Cross-plot of homogenization temperature (Th) against final ice melting temperature (Tm) for granite-hosted phases and fluorite in limestone.

M. Baba et al.



Fig. 8. LA-ICP-MS element maps for a pyrite crystal in a bitumen-bearing quartz vein (Fig. 2) in the Weardale Granite. Note pyrite is enriched in trace elements including Au, Ag, Se and Te.

geometry (Bott & Smith 2018) may not have allowed the opportunity for interaction with microbes that seems to have been possible in the other cases.

Anomalous heating on the Alston Block

A high thermal maturity for organic matter on the Alston Block is expected, based on multiple lines of evidence. Measurements of conodont alteration indices in Mississippian rocks in the Rookhope Borehole, i.e. from a shallower level than the bitumen-bearing granite section, indicate high thermal maturity and possibly also a high geothermal gradient (Burnett 1987). Vitrinite reflectance measurements in the Carboniferous section of the borehole are similarly high (Manning *et al.* 2007). The extensive mineralization of the North Pennines Orefield involved fluids at temperatures above 200°C (Dunham 1990; Cann & Banks 2001; Bouch *et al.* 2006). More specifically, Creaney (1980) showed that coals on the Alston Block are at anthracite rank. The region of coal devolatilization coincides with the high-temperature region of fluorite mineralization and both coincide with the area of underlying Weardale Granite (Dunham 1988), implying that the granite remained a focus of anomalous heat long after emplacement. Methane anomalies in limestones SE of Rookhope (Ferguson 1984) have been related to the mineralization, either through chemical reactions involving organic matter and sulphate ions, or by the action of prolonged high heat flow on organic matter. However, at the margins of the Alston Block, vitrinite reflectance measurements are below 1% (Creaney 1980; Burnett 1987), and the ambient temperature beyond mineral veins was probably below 100°C (Dunham 1990), at 'oil window' temperatures typical of many sedimentary basins.

The timing of oil migration through the granite is constrained by indirect evidence. Creaney (1980) showed that coals on the Alston Block were at a high stage of thermal maturity and anthracite rank prior to the intrusion of the Whin Sill, which is dated as earliest Permian (e.g. Stone et al. 2010). Solid bitumen (oil residues) in limestone on the Alston Block is similarly contact metamorphosed by the Whin Sill (Creaney et al. 1980), so oil had been generated by the time of intrusion. The Carboniferous succession on the Alston Block was 1.5 km thick at the most at that time (Chadwick et al. 1995; Manning et al. 2007; Bott & Smith 2018, figs 4 and 7), so the high maturity must represent very high heat flow, which could include fluid flow through the granite. Creaney (1980) suggested that this heating was related to a hot Weardale Granite and that it generated hydrocarbons from the Carboniferous rocks on the Alston Block (Creaney et al. 1980, p. 78). The subsequent discovery of bitumen in the granite (Parnell 1988) provided direct evidence for the involvement of hydrocarbons in granitehosted mineralizing activity, although it does not constrain the timing of oil generation and emplacement.

The varying evidence from different sources implies different dates for thermal reactivation of the granite. The data from metamorphosed organic matter (Creaney 1980; Creaney *et al.* 1980) imply a late Carboniferous age, Brown *et al.* (1987) suggested an early Permian date, the most recent treatments of the North Pennine Orefield attribute it to late Permian or Triassic (Halliday *et al.* 1990; Cann & Banks 2001; Bouch *et al.* 2008), and the region still has relatively high heat flow today (Bott *et al.* 1972; England *et al.* 1980; Downing & Gray 1986; Manning *et al.* 2007). Bott & Smith (2018) have most recently ascribed the increased heat flow to underplating of the granite by quartz-tholeiitic magma during the late Carboniferous.

Mineralizing and oil-bearing fluids

The quartz veins in which the oil residues occur are the predominant form of mineralization in the granite (Dunham 1990; Manning et al. 2007). Some, but not most, of the quartz veins are also mineralized by fluorite and sulphides (Manning et al. 2007). In our limited sample set from the Rookhope Borehole, the quartz predates fluorite mineralization (Fig. 2), and the quartz-sulphide assemblage is observed to be the earliest in nearby fluorite mines in the Carboniferous rocks (Dunham 1988). However, the fluid inclusion data suggest that the quartz and fluorite were both products of a high-salinity, high-temperature brine, as similarly concluded for data sets recorded by previous workers (Cann & Banks 2001; Bouch et al. 2006). The thermal maturity data for the oil residues in the granite, lower than those from the vicinity of the Whin Sill, suggest that the hydrocarbons were not generated by the magmatic underplating associated with the Whin Sill. While the magmatic underplating caused hydrothermal convection and heating of coal (Creaney 1980), the Carboniferous section was



Fig. 9. Cross-plot of Au and Se in pyrite from the Weardale Granite in the Rookhope Borehole and from mining waste from Allenheads, measured from LA-ICP-MS. Pyrite from the Weardale Granite consistently shows higher Au and Se contents.

mineralized by post-sill penetration of hot fluids (Bott & Smith 2018).

The presence of calcic brines in the limestone-hosted fluorite, as opposed to sodium chloride brines in the granitehosted phases, suggests that the mineralizing fluids interacted with the host rocks. Studies of the brine chemistry of fluid inclusions in the fluorite (Rankin & Graham 1988), the strontium isotope composition of fluorite and barite (Cann & Banks 2001; Bau *et al.* 2003) from the Alston Block, and the composition of modern spring water in Weardale (Manning & Strutt 1990) all similarly suggest that mineralizing fluids interacted with the Weardale Granite.

Although the mineral veins record temperatures up to 220°C, such temperatures were spatially and temporally limited, and do not represent the long-term conditions required for hydrocarbon generation. The lower temperatures experienced by the rocks away from the veins are recorded in stratabound mineralization in the region, in which quartz and fluorite have yielded fluid inclusion homogenization temperatures of 90-130°C, but in which monophase inclusions also indicate temperatures of 60°C or cooler (Bouch et al. 2006, 2008). These lower temperatures are typical of oilgenerating sedimentary basins. The relatively low thermal maturity of the granite-hosted oil residues constrains their origin. The low reflectance equivalent values contrast with the higher values obtained from the Carboniferous section in the borehole and from the shale at the surface. The Carboniferous rocks were thermally metamorphosed by post-emplacement heat from the granite, but the oil residues in the granite do not appear to have been metamorphosed in this way. Instead, the oil residues have a maturity comparable to sediment samples from regions towards the margins of the Alston Block. These data are consistent with derivation of the oil from Carboniferous sedimentary rocks that were not metamorphosed. Emplacement of the oil must have happened after intrusion of the Whin Sill as the large extent of the sill would have metamorphosed any pre-existing oil residues, as at localities documented by Creaney et al. (1980). Beyond the influence of the sill, heating was

inadequate for hydrocarbon generation until after sill emplacement.

It had been anticipated that oil inclusions might be found in the fluorite, given the presence of bitumen in the mineralizing system and the occurrence of oil inclusions in fluorite further south in the Pennines (Moser *et al.* 1992). The lack of oil inclusions may be explained by the relative timing of bitumen and fluorite, in which the bitumen had entered as oil and solidified before fluorite mineralization.

The relatively early timing of the oil, before fluorite mineralization, invites the possibility that the oil might be derived from Lower Palaeozoic rocks penetrated by the granite and the hydrothermal convection system. Where Lower Palaeozoic sedimentary rocks are exposed west of the Pennines, their thermal maturity is low (Bergström 1980), so they were capable of yielding oil. However, in our experience the chromatograms are more similar to those known to be from Carboniferous-sourced oils than those derived from the Lower Palaeozoic.

The pyrite in the bitumen-bearing quartz veins is strongly enriched in trace elements. The high level of Pb could indicate that the pyrite records the mineralizing fluid that precipitated base metal sulphides, especially Pb and Zn veins, widely over the Alston Block, but further analysis is required to explore this possibility.

The high levels of Ag and Au suggest a potential for precious metal mineralization. Silver minerals have been recorded on the Alston Block (Ixer 1986; Ixer & Stanley 1987), and several of the Pb deposits produced Ag as a by-product (Nall 1904; Dunham 1990; Dunham *et al.* 2001). Gold is unknown in the ore deposits on the Alston Block, and the occurrence requires further investigation.

The enrichment of Au associated with the oil residues in the Weardale Granite is consistent with other cases where Au mineralization occurs in oil migration pathways and reservoirs (Drennan & Robb 2006; Gu *et al.* 2012). Similarly, the enrichments in Se and Te in the pyrite are significant because both elements may be concentrated by oil residues (Parnell *et al.* 2015) and may be pathfinders for gold mineralization (Boyle 1987). The Te/Se ratio above unity (i.e. 1.33) for the sample at 1647 feet (502 m) is very unusual; Te is much rarer than Se, and in our experience is usually associated with gold mineralization.

Conclusions

The organic geochemical, fluid inclusion and laser ablation studies of granite-hosted mineralization suggest that:

- (1) The bitumen in the Weardale Granite is an oil residue derived from the Carboniferous sedimentary rocks around the granite in the surrounding deep Carboniferous basins.
- (2) The oil was degraded to a solid within the granite, but was not biodegraded.
- (3) Solidification predated fluorite, in which no oil inclusions occur.
- (4) The oil residues have a thermal maturity typical of the oil window, and do not show evidence of alteration by the Whin Sill or by pre-Whin Sill heating during the thermal event prior to sill emplacement.

(5) Mineralizing fluids accompanied or followed hydrocarbon migration, transporting base metals and precious metals.

Acknowledgements MB is in receipt of a PhD studentship from PTDF (Nigeria). K.C. Dunham kindly provided samples from the Rookhope Borehole. P. Eakin collected bitumen at Moot Law. We are most grateful to very careful reviews by F. Smith and D. Holliday, which greatly improved presentation of the work.

Funding The research was partly supported by NERC grant NE/M010953/1.

Scientific editing by Douglas Holliday and Stewart Molyneux

References

- Atkinson, P., Moore, J.M.M. & Evans, A.M. 1982. The Pennine orefields of England with special reference to recent fluid inclusion investigations. *Bulletin* du Bureau de Recherches Géologiques et Minières, Section II, 2, 149–156.
- Bau, M., Romer, R.L., Lüders, V. & Dulski, P. 2003. Tracing element sources of hydrothermal mineral deposits: REE and Y distribution and Sr-Nd-Pb isotopes in fluorite from MVT deposits in the Pennine Orefield, England. *Mineralium Deposita*, **38**, 992–1008, https://doi.org/10.1007/s00126-003-0376-x
- Bergström, S.M. 1980. Conodonts as paleotemperature tools in Ordovician rocks of the Caledonides and adjacent areas in Scandinavia and the British Isles. *Geologiska Föreningen i Stockholm Förhandlingar*, **102**, 377–392, https:// doi.org/10.1080/11035898009454495
- Bott, M.H.P. & Masson Smith, D. 1957. The geological interpretation of a gravity survey of the Alston Block and the Durham Coalfield. *Quarterly Journal of* the Geological Society of London, 113, 93–117, https://doi.org/10.1144/GSL. JGS.1957.113.01-04.05
- Bott, M.H.P. & Smith, F.W. 2018. The role of the Devonian Weardale Granite in the emplacement of the North Pennine mineralization. *Proceedings of the Yorkshire Geological Society*, 62, 1–15, https://doi.org/10.1144/pygs2017-391
- Bott, M.H.P., Johnson, G.A.L., Mansfield, J. & Wheildon, J. 1972. Terrestrial heat flow in north-east England. *Geophysical Journal of the Royal Astronomical Society*, 27, 277–288, https://doi.org/10.1111/j.1365-246X.1972.tb06093.x
- 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). *Mineralium Deposita*, **41**, 821–835, https://doi.org/10. 1007/s00126-006-0093-3
- Bouch, J.E., Naden, J., Shepherd, T.J., Young, B., Benham, A.J., McKervey, J.A. & Sloane, H.J. 2008. Stratabound Pb-Zn-Ba-F mineralisation in the Alston Block of the North Pennine Orefield (England) – origins and emplacement. British Geological Survey Research Report, RR/08/06.
- Boyle, R.W. 1987. Gold. History and Genesis of Deposits. Springer, New York.
- Brown, G.C., Ixer, R.A., Plant, J.A. & Webb, P.C. 1987. Geochemistry of granites beneath the north Pennines and their role in orefield mineralization. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied Earth Science)*, 96, 65–76.
- Burnett, R.D. 1987. Regional maturation patterns for late Visean (Carboniferous, Dinantian) rocks of northern England based on mapping of conodont colour. *Irish Journal of Earth Sciences*, 8, 165–185.
- Burton, Z., Moldowan, J.M., Sykes, R. & Graham, S. 2018. Unraveling petroleum degradation, maturity, and mixing and addressing impact on petroleum prospectivity; Insights from frontier exploration regions in New Zealand. *Energy & Fuels*, https://doi.org/10.1021/acs.energyfuels.7b03261
- Cann, J.R. & Banks, D.A. 2001. Constraints on the genesis of the mineralization of the Alston Block, Northern Pennine Orefield, northern England. *Proceedings of the Yorkshire Geological Society*, **53**, 187–196, https://doi. org/10.1144/pygs.53.3.187
- Chadwick, R.A., Holliday, D.W., Holloway, S. & Hulbert, A.G. 1995. The structure and evolution of the Northumberland-Solway Basin and adjacent areas. Subsurface Memoir of the British Geological Survey. HMSO, London.
- Creaney, S. 1980. Petrographic texture and vitrinite reflectance variation on the Alston Block, NE England. *Proceedings of the Yorkshire Geological Society*, 42, 553–580, https://doi.org/10.1144/pygs.42.4.553
- Creaney, S., Jones, J.M., Holliday, D.W. & Robson, P. 1980. The occurrence of bitumen in the Great Limestone around Matfen, Northumberland - its characterisation and possible genesis. *Proceedings of the Yorkshire Geological Society*, 43, 69–79, https://doi.org/10.1144/pygs.43.1.69
- Downing, R.A. & Gray, D.A. 1986. Geothermal Energy the Potential in the United Kingdom. HMSO, London.
- Drennan, G.R. & Robb, L.J. 2006. The nature of hydrocarbons and related fluids in the Witwatersrand Basin, South Africa: Their role in metal redistribution. *Geological Society of America Special Paper*, 405, 353–385.
- Dunham, K. 1983. Ore genesis in the English Pennines: a fluorite subtype. In: International Conference on Mississippi Valley type lead-zinc deposits. University of Missouri, Rolla, 86–112.
- Dunham, K.C. 1988. Pennine mineralization in depth. Proceedings of the Yorkshire Geological Society, 47, 1–12, https://doi.org/10.1144/pygs.47.1.1

236

Emplacement of oil in the Weardale Granite

- Dunham, K.C. 1990. Geology of the North Pennine Orefield, Volume 1, Tyne to Stainmore, 2nd edn. Economic Memoir of the British Geological Survey. HMSO, London.
- Dunham, K.C., Bott, M.H.P., Johnson, G.A.L. & Hodge, B.L. 1961. Granite beneath the Northern Pennines. *Nature*, **190**, 899–900, https://doi.org/10. 1038/190899a0
- Dunham, K.C., Young, B., Johnson, G.A.L., Colman, T.B. & Fossett, R. 2001. Rich silver-bearing lead ores in the Northern Pennines? *Proceedings of the Yorkshire Geological Society*, **53**, 207–212, https://doi.org/10.1144/pygs.53. 3.207
- England, P.C., Oxburgh, E.R. & Richardson, J.W. 1980. Heat refraction and heat production in and around granite plutons in north-east England. *Geophysical Journal of the Royal Astronomical Society*, **62**, 439–455, https://doi.org/10. 1111/j.1365-246X.1980.tb04866.x
- Ferguson, J. 1984. The methane content of some Carboniferous limestones from the northern Pennines and its relationship to mineralisation. *Proceedings of the Yorkshire Geological Society*, **45**, 67–69, https://doi.org/10.1144/pygs.45.1-2.67 Gold, T. 1999. *The Deep Hot Biosphere*. Copernicus, Berlin.
- Greenwood, D.A. & Smith, F.W. 1977. Fluorspar mining in the northern Pennines. Transactions of the Institution of Mining and Metallurgy (Section B: Applied Earth Science), 86, 181–190.
- Gu, X.X., Zhang, Y.M., Li, B.H., Dong, S.Y., Xue, C.J. & Fu, S.H. 2012. Hydrocarbon- and ore-bearing basinal fluids: a possible link between gold mineralization and hydrocarbon accumulation in the Youjiang basin, South China. *Mineralium Deposita*, 47, 663–682, https://doi.org/10.1007/s00126-011-0388-x
- Halliday, A.N., Shepherd, T.J., Dickin, A.P. & Chesley, J.T. 1990. Sm-Nd evidence for the age and origin of a Mississippi Valley-type ore deposit. *Nature*, 344, 54–56, https://doi.org/10.1038/344054a0
- Ixer, R.A. 1986. The ore mineralogy and paragenesis of the lead-zinc-fluoritebaryte orefields of the English Pennines and Mendip Hills. *In*: Craig, J.R. (ed.) *Mineral Parageneses*. Theophrastus, Athens, 179–211.
- Ixer, R.A. & Stanley, C.J. 1987. A silver-nickel-cobalt mineral association from Tynebotom Mine, Garrigill, near Alston, Cumbria. *Proceedings of the Yorkshire Geological Society*, 46, 133–139, https://doi.org/10.1144/pygs.46.2.133
- Kimbell, G.S., Young, B., Millward, D. & Crowley, Q. 2010. The North Pennine batholith (Weardale Granite) of northern England: new data on its age and form. *Proceedings of the Yorkshire Geological Society*, 58, 107–128, https:// doi.org/10.1144/pygs.58.1.273
- Manning, D.A.C. & Strutt, D.W. 1990. Metallogenetic significance of a North Pennine springwater. *Mineralogical Magazine*, 54, 629–636, https://doi.org/ 10.1180/minmag.1990.054.377.16
- Manning, D.A.C., Younger, P.L., Smith, F.W., Jones, J.M., Dufton, D.J. & Diskin, S. 2007. A deep geothermal exploration well at Eastgate, Weardale, UK: a novel exploration concept for low-enthalpy resources. *Journal of the Geological Society, London*, 164, 371–382, https://doi.org/10.1144/0016-76492006-015
- Moser, M.R., Rankin, A.H. & Milledge, H.J. 1992. Hydrocarbon-bearing fluid inclusions in fluorite associated with the Windy Knoll bitumen deposit, UK.

Geochimica et Cosmochimica Acta, 56, 155–168, https://doi.org/10.1016/0016-7037(92)90123-Z

- Nall, W. 1904. The Alston mines. Transactions of the Institution of Mining Engineers, 24, 392–412.
- P'An, C.H. 1982. Petroleum in basement rocks. American Association of Petroleum Geologists Bulletin, 66, 1597–1643.
- Parnell, J. 1988. Migration of biogenic hydrocarbons into granites: a review of hydrocarbons in British plutons. *Marine and Petroleum Geology*, 5, 385–396, https://doi.org/10.1016/0264-8172(88)90032-3
- Parnell, J., Bellis, D., Feldmann, J. & Bata, T. 2015. Selenium and tellurium enrichment in palaeo-oil reservoirs. *Journal of Geochemical Exploration*, 148, 169–173, https://doi.org/10.1016/j.gexplo.2014.09.006
- Parnell, J., Baba, M. & Bowden, S. 2017a. Emplacement and biodegradation of oil in fractured basement: the 'coal' deposit in Moinian gneiss at Castle Leod, Ross-shire. *Earth and Environmental Science Transactions* of the Royal Society of Edinburgh, **107**, 23–32, https://doi.org/10.1017/ S1755691017000056
- Parnell, J., Baba, M., Bowden, S. & Muirhead, D. 2017b. Subsurface biodegradation of crude oil in a fractured basement reservoir, Shropshire, UK. Journal of the Geological Society, London, 174, 655–666, https://doi.org/ 10.1144/jgs2016-129
- Peters, K.E. & Moldowan, J.M. 1993. The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Prentice Hall, Englewood Cliffs, NJ.
- Peters, K.E., Walters, C.C. & Moldowan, J.M. 2007. The Biomarker Guide: Volume 1, Biomarkers and Isotopes in the Environment and Human History. Cambridge University Press, Cambridge.
- Petford, N. & McCaffrey, K. 2003. Hydrocarbons in Crystalline Rocks. Geological Society, London, Special Publications, 214.
- Rankin, A.H. & Graham, M.J. 1988. Na, K and Li contents of mineralizing fluids in the Northern Pennine Orefield, England, and their genetic significance. *Transactions of the Institution of Mining and Metallurgy (Section B: Applied Earth Science)*, 97, 99–107.
- Sawkins, F.J. 1966. Ore genesis in the North Pennine Orefield in the light of fluid inclusion studies. *Economic Geology*, **61**, 385–401, https://doi.org/10.2113/ gsecongeo.61.2.385
- Seifert, W.K. & Moldowan, J.M. 1979. The effect of biodegradation on steranes and terpanes in crude oils. *Geochimica et Cosmochimica Acta*, 43, 111–126, https://doi.org/10.1016/0016-7037(79)90051-6
- Smith, F.W. & Philips, R. 1975. Temperature gradients and ore deposition in the North Pennine orefield. *Fortschritte der Mineralogie*, **52**, 491–494.Solomon, M., Rafter, T.A. & Dunham, K.C. 1971. Sulphur and oxygen isotope
- Solomon, M., Rafter, 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, 259–275.
- Stone, P., Millward, D., Young, B., Merritt, J.W., Clarke, S.M., McCormac, M. & Lawrence, D.J.D. 2010. British Regional Geology: Northern England, 5th edn. British Geological Survey, Keyworth.