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Selenium and tellurium enrichment in palaeo-oil reservoirs

John Parnell [a,*], David Bellis [b], Joerg Feldmann [b], Timothy Bata [a]

[a] School of Geosciences, University of Aberdeen, UK
[b] School of Natural and Computing Sciences, University of Aberdeen, UK

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ABSTRACT

The exploration for selenium (Se) and tellurium (Te) will become intensified as the technological demand for these elements grows. It is known that they are enriched in organic-rich sedimentary rocks over crustal mean values. LA-ICP-MS measurement of pyrite in two biodegraded palaeo-oil reservoirs in central England shows that Se and Te are enriched in them, but not in other sulfide samples from the region and elsewhere. The Carboniferous source rock shales in the region are Se-rich, implying that this enrichment was conferred to the oil generated from them. The Se and Te are located in pyrite precipitated in the palaeo-reservoirs by microbial activity. Exhumed oil reservoirs merit further investigation for concentrations of these elements.

1. Introduction

Selenium (Se) and tellurium (Te) are rare elements, whose resources are regarded as of critical importance for their use in future technologies (DEFRA, 2012; Moss et al., 2011). However, because of their rarity their behaviour and occurrence are incompletely understood. Except for scarce occurrences of selenide and telluride minerals in hydrothermal systems, they normally occur as trace elements in other minerals, especially sulfides. Hence, data on their distribution in sedimentary rocks are available from laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) analyses of pyrite, especially in black shales (Large et al., 2011) and coals (Diehl et al., 2012). These data show that Se and Te are enriched in organic-rich sediments, relative to the crustal mean compositions of 0.05 ppm and 0.001 ppm respectively. However, there is negligible data on the degree to which Se and Te are coupled, and the greater mobility of Se in oxidizing conditions (Schirmer et al., 2014; Xiong, 2003) could cause a fractionation of the two elements. The affinity to organic matter reflects similarities in their chemistry to that of sulfur (they are all in periodic table group 16/6A), and the formation of organic-selenium bonds (Ralston et al., 2008) similar to organic-sulfur bonds. Here we examine whether Se and Te are also enriched in palaeo-oil reservoirs, in which the organic matter is a solid oil residue. There is some evidence that Se in source rocks is conferred to the hydrocarbons released from them (Ellrich et al., 1985), and consequently selenium has to be removed in oil refineries (Lawson and Macy, 1995). Reservoir rocks represent a different type of organic-rich sediment, where the organic component is allochthonous rather than autochthonous. Data for this type of material may give us new insights into the behaviour of Se and Te in organic-rich environments. As in black shales and coals, measurements can be made in pyrite, which forms in oil reservoirs where microbial populations exploit sulfur in the oil as well as in associated water and reduce it to sulfide (Amrani et al., 2005).

2. Geological setting

Samples were examined from two fossil oil traps containing diagenetic sulfides in Carboniferous rocks in England (Figs. 1,2). Oil-bearing sandstone was sampled from Row Brook, Pitchford Bridge, Shropshire, where it has been exhumed from beneath a shale cover. The oil is degraded to solid bitumen, patchily mineralized with pyrite (Parnell, 1983). The deposit is of historical importance, as it was worked opencast as a source of oil in the seventeenth century, and an ancient oil-bearing well is close nearby (Plot, 1684). The second deposit, in a karstic brecciated limestone trap sealed by shale at Windy Knoll, Derbyshire (Moser et al., 1992; Pering, 1973), contains highly viscous oil within which crystals of pyrite are suspended. Both oils are heavily altered and yield biomarkers indicating biodegradation (Ewbank et al., 1993; Parnell et al., 1991; Pering, 1973).

3. Methodology

Samples of the Row Brook pyrite-bearing sandstone, and pyrite crystals recovered from the Windy Knoll oil by solvent extraction of the oil, were polished and then analysed by LA-ICP-MS. Four other sulfide samples from southern-central Britain (1 pyrite, 3 copper sulfides) were also analysed for comparison (Table 1). Analysis was performed using a UP213 laser ablation (LA) system (New Wave, Freemont, CA) coupled

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* Corresponding author at: School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, UK. Tel.: +44 1224 273464.
E-mail address: J.Parnell@abdn.ac.uk (J. Parnell).

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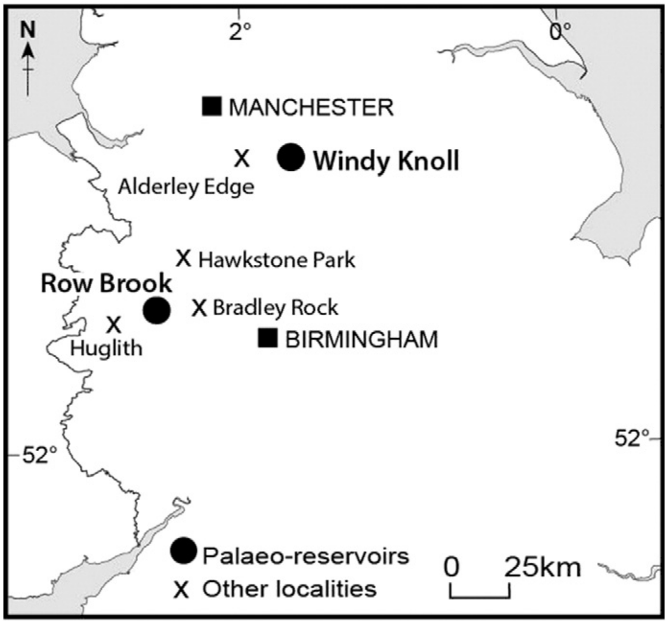

Fig. 1. Location map for sample sites, central England.

to an Agilent (Wokingham, UK) 7500ce inductively coupled plasma mass spectrometer (ICP-MS). LA-ICP-MS was tuned for maximum sensitivity and stability using standard SRM 612 for trace elements in glass (NIST, Gaithersburg MD), optimising the energy fluence to about 2 J/cm^2. A semi-quantitative calibration was provided using MASS-1 Synthetic Polymetal Sulfide (USGS, Reston, VA). Samples and the standard were analysed using a 100 μm diameter round spot moving in a straight line at 50 μm s^{-1}. A 15 s laser warm-up preceded 30 s of ablation (1.5 mm) and 15 s delay. ^{82}Se and ^{125}Te were monitored for 0.1 s each. Three lines were analysed for each sample or standard. The average count signal over 20 s of the ablation was calculated for each element and subtracted by the average signal over 10 s for the initial gas blank. The standard was used to calculate the concentration (μg g^{-1})/counts ratio, which was multiplied by the sample counts to estimate concentration. The sulfur isotopic composition of the Row Brook and Windy Knoll pyrite was measured using the method of Robinson and Kusakabe (1975).

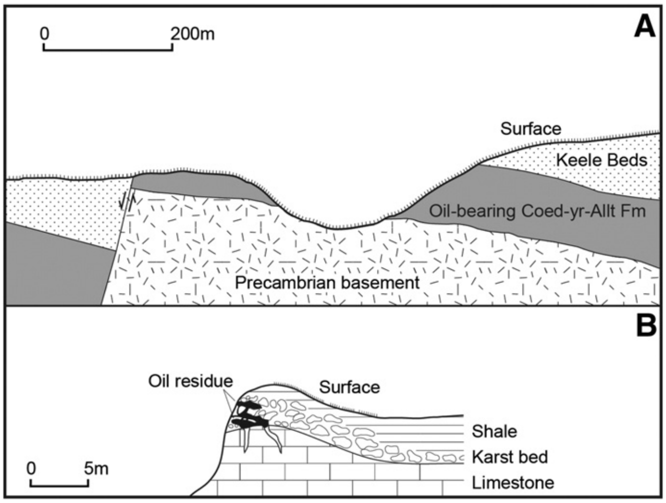

Fig. 2. Geometry of fossil oil traps. A, Fault-bounded oil-bearing sandstone, Coed-yr-Allt Formation, below seal of Keele Beds. Surface exposures of Coed-yr-Allt Formation were worked opencast and processed to extract oil. Interpreted from maps of Geological Survey of Great Britain (Pocock et al., 1938). B, Oil trapped in fold structure in karst limestone, below shale seal, Windy Knoll (after Pering, 1973).

Table 1
LA-ICP-MS data for sulfide minerals.

Locality (grid reference)	Mineral	Se (ppm)	Te (ppm)
Row Brook (SJ532046)	Pyrite	54	0.31
		60	0.34
		23	0.26
Windy Knoll (SK125830)	Pyrite	42	0.12
		23	0.05
		39	0.10
Bradley Rock (SJ633018)	Pyrite	<2	<0.03
Alderley Edge (SJ8677)	Chalcopyrite	<2	<0.03
Huglith (SJ405016)	Chalcocite	<2	<0.03
Hawkstone Park (SJ5729)	Cu sulfides	<2	<0.03

New biomarker data was collected from the Row Brook material sampled for pyrite. The sandstone was solvent extracted using 93:7 v: v dichloromethane and methanol. The extracted oil was then separated using thin layer chromatography. The saturate fraction was analysed by gas chromatography–mass spectrometry (GC–MS), using an Agilent 6890N GC fitted with a J&W DB-5 phase 50 m length column (0.25 mm id, 0.25 μm thickness) connected to a 5975 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 to 10 °C min^{-1} for 8 min and then 3 °C min^{-1} and finally holding the maximum temperature for 10 min. Compounds were identified by comparing retention times to well-characterised materials that served as reference samples.

4. Results

The LA-ICP-MS data indicate a marked difference between the pyrite samples from the two palaeo-reservoirs and the other samples. The Row Brook and Windy Knoll pyrites have Se and Te contents consistently above the detection limits of 2 ppm and 0.03 ppm respectively, while the other sulfides have contents below the detection limits. The Se values for both Row Brook and Windy Knoll, and the Te values for Row Brook are an order of magnitude greater than in the non-reservoir samples. Measurements in the carbonaceous oil residue at Row Brook did not record any Se or Te, i.e. it is concentrated in the pyrite. A range of other sulfide samples measured at the same time also did not exceed the detection limit.

Sulfur isotopic compositions were determined for pyrite from Windy Knoll (−5.1, −7.2, −7.7‰) and Row Brook (−13.6, −19.1‰). Polished sections of the Row Brook sandstone show that the pyrite in it occurs as framboids within solidified bitumen (Fig. 3). The bitumen exhibits variable intensity in backscattered images, due to variable sulfur content.

The pyrite-bearing Row Brook sample yielded a total ion chromatogram dominated by an unresolved complex mixture (Fig. 4). 25-Norhopanes are identified on the m/z 177 chromatogram, where they are detected at a lower retention time compared to the homohopanes on the m/z 191 chromatogram (López, 2014).

5. Discussion

5.1. Microbial origin of sulfides

The light sulfur isotope compositions strongly indicate microbial sulfate reduction (Machel, 2001). A biogenic origin for the pyrite is comparable with occurrences in other oil reservoirs also attributed to microbial activity (Sassen et al., 1988; Wolicka et al., 2010), and is consistent with previous biomarker data for Windy Knoll and Row Brook indicating biodegradation (Ewbank et al., 1993; Parnell et al., 1991). The new gas chromatography data is dominated by an unresolved complex