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Selenium enrichment in Carboniferous Shales, Britain and Ireland: Problem or opportunity for shale gas extraction?

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ABSTRACT

The Carboniferous Bowland Shale in England, and its correlatives in Ireland, contain anomalously high concentrations of trace elements, including selenium (Se), molybdenum (Mo) and arsenic (As). High levels of these elements reflect high sulphur contents as these elements occur as trace constituents of pyrite. Anomalous Se in particular may have a volcanic provenance, from contemporary volcanic activity and/or drainage from Ordovician volcanogenic sulphide deposits. Following concern over the release of Se and As into groundwater during shale gas extraction in the US, the potential fate of Se and As during any future shale gas extraction from the Bowland Shale merits attention. It is at least an environmental issue that must be managed, but at best it could be an opportunity for extraction of Se in an environmentally sensitive manner.

1. Introduction

The Carboniferous Bowland Shale, and its correlatives in Ireland, is receiving much attention for their potential resources of shale gas (Smith et al., 2010; Jones, 2012; Andrews, 2013; Taylor et al., 2013). Trace element data help to evaluate the environmental impacts of hydraulic fracturing during shale gas extraction (Chermak and Schreiber, 2014). However, although organic geochemical data is available for the Bowland Shale (Armstrong et al., 1997; Andrews, 2013), and an assessment of radionuclide flux from shale gas exploitation has been made (Almond et al., 2014), there is no modern published database on trace element geochemistry. This is surprising, given concern over the possible contamination of ground waters by fracking (Myers, 2012; Vidic et al., 2013; Vengosh et al., 2014; Shonkoff et al., 2014). In particular there is concern over the environmental implications of metals released from shales during gas extraction (Haluszczak et al., 2013; Chermak and Schreiber, 2014). The need to be at least aware of the trace element chemistry of these particular Carboniferous black shales is evident from long-known selenium toxicity in farm animals from some Irish soils (Fleming and Walsh, 1957; Rogers et al., 1990), which can be traced to Se enrichments in the underlying black shales (Keily and Fleming, 1969; McGrath and Fleming, 2007; Fellowes et al., 2013). Livestock health problems have also arisen due to high molybdenum contents in the Irish black shales (Alloway, 2012). Selenium availability is important to plants and animals, but in excess can become toxic, which in the case of human consumption is above 400 μg/day (MacFarquhar et al., 2010), with possible consequences including neurotoxicity, cancer and diabetes (Vinceti et al., 2014; Sun et al., 2014). Care is therefore often taken to avoid the delivery of elevated concentrations of selenium to the environment, for example through the processing of fossil fuels, including coal storage (Lussier et al., 2003), coal burning (Zeng et al., 2001), and oil refining (Lawson and Macy, 1995). Recently, concern has been expressed over the release of Se to ground waters through shale gas exploration in the USA (Fontenot et al., 2013, reiterated in numerous open access publications, e.g. Hildenbrand et al., 2013, Meyer, 2013, Schug et al., 2013).

We report here trace element data for a set of 42 samples of the Bowland Shale and its correlatives, from 17 localities across an outcrop width of 600 km (7 England, 1 Wales, 1 Isle of Man, 8 Ireland; Fig. 1; Supplementary Table S1), focusing on selenium (Se), arsenic (As) and molybdenum (Mo). Selenium and As are of strong environmental concern, and Mo is a key indicator of redox conditions as it is enriched in reducing sediments (Algeo and Lyons,

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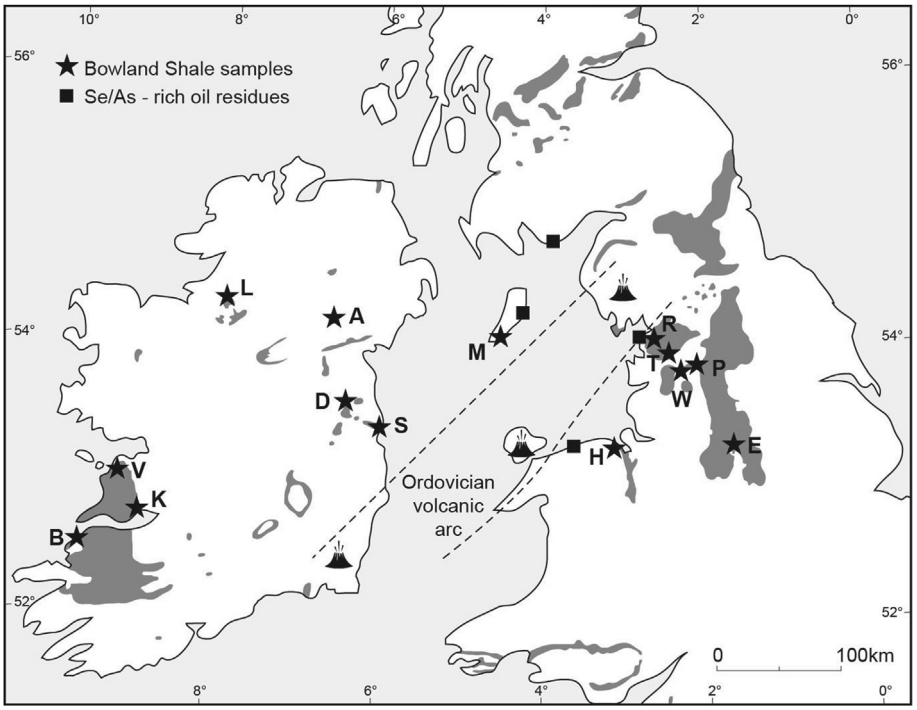

Fig. 1. Map of central British Isles, showing outcrop of Namurian rocks, region of Ordovician volcanic basement, sampled localities in Bowland Shale Formation, and localities for Se/As-rich oil residues. A, Altmush; B = Ballybunion; D, Dunshaughlin; E = Edale; H = Holywell; K = Killadysert; L, Co. Leitrim (Glenfarne, Thur Mountain); M = Poyllvaaish, Isle of Man; P = Pendle Hill and Earby; R = Walmsley Bridge; S = Loughshinny; T = Trough of Bowland; V = Lisdoonvarna; W, Whalley and Wiswell.

2006). Selenium and Mo are closely related in both the Carboniferous black shales and their soils (Webb et al., 1966; McGrath and Fleming, 2007). Data from the Barnett Shale, Texas, of comparable age to the Bowland Shale, indicate the release of Se into groundwaters within 2 km of shale gas drilling, at a mean (n = 10) concentration an order of magnitude greater than historical levels, and including individual values greater than the U.S. maximum level permitted in drinking water of 50 μg/l (Fontenot et al., 2013). All 10 values were at or exceeded the more demanding European Union maximum permitted level of 10 μg/l, and there are arguments that the European Union level be lowered further to just 1 μg/l (Vinceti et al., 2013). The same data set showed that the mean As level in 90 water wells in active extraction areas exceeded the maximum permitted level for drinking water (Fontenot et al., 2013). Following environmental concern about exploration in the Barnett Shale, we compare the Bowland Shale and Barnett Shale data.

2. Methods

The targeted shales span the Dinantian-Namurian boundary. Carboniferous black shales represent one of the best prospects for shale gas resources in the British Isles (Smith et al., 2010). The Upper Bowland Shale (lowest Namurian, especially the Pendleian and Arnsbergian stages E1-E2) is most widespread and correlates with the Edale Shale, Derbyshire, the Ardagh Shale (Ardagh Formation), eastern Ireland, and the Clare Shales (Clare Shale Formation), Cos. Kerry and Clare, western Ireland. The Lower Bowland Shale (uppermost Dinantian, especially the Brigantian stage P1–P2) correlates with the black shales of the Fingal Group, Cos. Dublin and Meath, eastern Ireland, black shales in Co. Leitrim, Northwest Ireland, and in the Isle of Man. In addition, the uppermost stratigraphic sections of the Bowland Shale were deposited in the Chokierian to Marsdenian stages (H-R). Sections of this age include the Holywell Shale, North Wales, and much of the Clare Shales. Detailed stratigraphies are summarized by Waters et al. (2011).

Trace element contents were measured in shale samples using inductively coupled plasma-mass spectrometry (ICP-MS). Samples of ~30 g rock were milled and homogenised, and 0.25 g digested with perchloric, nitric, hydrofluoric and hydrochloric acids to near dryness. The residue was topped up with dilute hydrochloric acid, and analysed using a Varian 725 instrument. Samples with high concentrations were diluted with hydrochloric acid to make a solution of 12.5 mL, homogenized, then analysed by ICP-MS. Results were corrected for spectral inter-element interferences. The limits of resolution are 0.05 and 10,000 ppm.

3. Results

The data for Mo, Se and As in the Bowland Shale are shown in Table 1, and Figs. 2 and 3. The mean values for Mo, Se and As in the Bowland Shale samples of P1-E2 age are 44.1 ppm, 21.5 ppm and 20.5 ppm respectively. These values are much higher than global mean shale values of 2.6 ppm, 0.6 ppm and 13.0 ppm respectively (Turekian and Wedepohl, 1961). The younger Bowland Shale samples of H-R age have lower Se contents, but comparable Mo and As contents, to the samples of P1-E2 age.

The Mo values for the Bowland Shale range up to 155 ppm. The highest values are recorded from Ballybunion, Co. Kerry, but most of the samples are in the range 20–70 ppm. Mo is characteristically correlated with the organic carbon content in shales (Algeo and Lyons, 2006). This relationship holds for both the Bowland Shale (Fig. 2) and Barnett Shale (Rowe et al., 2008). However, Mo values for the Bowland Shale are much higher than those of the Barnett Shale (Fig. 2). The Mo/TOC ratio varies with deep water renewal time, increasing with turnover rate as shown by data sets for the