



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



John Parnell ^{a,*}, Connor Broolly ^a, Sam Spinks ^{a,b}, Stephen Bowden ^a

^a School of Geosciences, University of Aberdeen, Aberdeen AB24 3UE, United Kingdom

^b CSIRO Mineral Resources Flagship, Australian Resources Research Centre, Perth, Australia

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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.

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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,

* Corresponding author.

E-mail address: J.Parnell@abdn.ac.uk (J. Parnell).

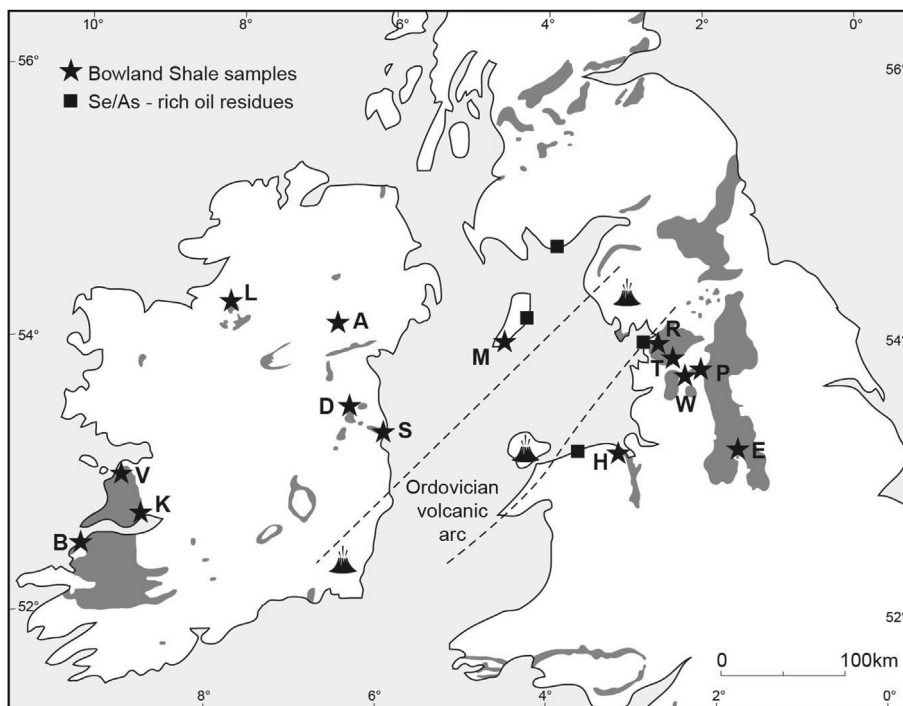


Fig. 1. Map of central British Isles, showing outcrop of Namurian rocks, region of Ordovician volcanic basement, sampled localities in Bowland Shale Formation, and localities for Se/As-rich oil residues. A, Altмыш; B = Ballybunion; D, Dunshaughlin; E = Edale; H = Holywell; K = Killadysert; L, Co. Leitrim (Glenfarne, Thur Mountain); M = Poyllvaish, 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 $\mu\text{g}/\text{l}$ (Fontenot et al., 2013). All 10 values were at or exceeded the more demanding European Union maximum permitted level of 10 $\mu\text{g}/\text{l}$, and there are arguments that the European Union level be lowered further to just 1 $\mu\text{g}/\text{l}$ (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

Table 1
Summary geochemical data for Bowland Shale samples.

Full data set	Strat range	n	Se (ppm)	As (ppm)	Mo (ppm)
P1-E2 samples					
Mean	P1-E2	37	21.1	22.8	42.0
Standard Deviation			9.9	10.3	32.5
Q1			15.5	16.6	23.2
Q2 (Median)			18.2	20.2	31.0
Q3			28.8	28.5	61.3
Minimum			2.9	9.0	3.4
Maximum			42.0	51.8	154.5
H-R samples					
Mean	H-R	5	4.6	16.9	25.9
Standard Deviation			3.3	14.5	10.7
Q1			3.3	1.2	22.5
Q2 (median)			3.9	26.4	29.3
Q3			4.1	26.5	30.6
Minimum			1.3	0.8	9.2
Maximum			10.2	29.4	37.7
Regions (localities)					
		Se range	As range	Mo range	
NE Lancs (P,W)	P1-E1	9	3–33	11–52	9–39
NW Lancs (R,T)	P2-E1	6	13–34	16–46	3–68
Derbyshire (E)	E1-E2	3	15–21	21–38	23–50
Isle of Man (M)	P1-P2	3	18–27	11–21	8–41
Cos. Meath/Dublin (A, D,S)	P2-E1	10	8–36	9–41	8–65
Co. Kerry (B)	P1-E1	4	16–42	17–29	68–155
Co. Leitrim (L)	P1-E1	2	12–17	10–20	17–35
North Wales (H)	H-R	2	4–10	26–29	22–31
Co. Clare (K,V)	H-R	3	1–4	1–27	29–38

Black Sea and the Cariaco Basin, Venezuela (Algeo and Lyons, 2006; Rowe et al., 2008), and is also consistently higher in the Bowland Shale than the Barnett Shale (Fig. 2).

There are no published data for S in the Barnett Shale, but the Se contents of two Barnett Shale samples measured in this study are 8 ppm and 9 ppm. The Mo contents of these samples are typical of a much larger database of Barnett Shale samples (Rowe et al., 2008), implying that the Se contents are also typical. The Se contents of the Bowland Shale clearly range to much higher values than the Barnett Shale samples, with maximum values of 34 ppm 36 ppm and 42 ppm in the Trough of Bowland, Co. Meath and Co. Kerry, Ireland (Fig. 2). A cross-plot of Se and sulphur for the Bowland Shale samples indicates that there is a positive correlation between Se and S (Fig. 3), and that Se substitutes within sulphide minerals, as commonly found in other marine shales (Large et al., 2014). This relationship also indicates that the higher Se contents in the Bowland Shale reflect higher sulphide contents. The two lowest Se values (2.9 ppm, 5.6 ppm) determined in the main Bowland Shale data set are from samples with negligible S contents. The Se values are also much higher than values determined for other black shales (Fig. 2), including the Cambrian Alum Shale, Devonian New Albany Shale and Jurassic Posidonia Shale, which range up to 3.3 ppm, 1.1 ppm and 3.9 ppm respectively (Mitchell et al., 2012). The As content of the Bowland Shale samples range up to 52 ppm (two highest values from Lancashire), and almost all values exceed Barnett Shale values of 8 and 9 ppm. The As values are strongly related to the S content (Fig. 3).

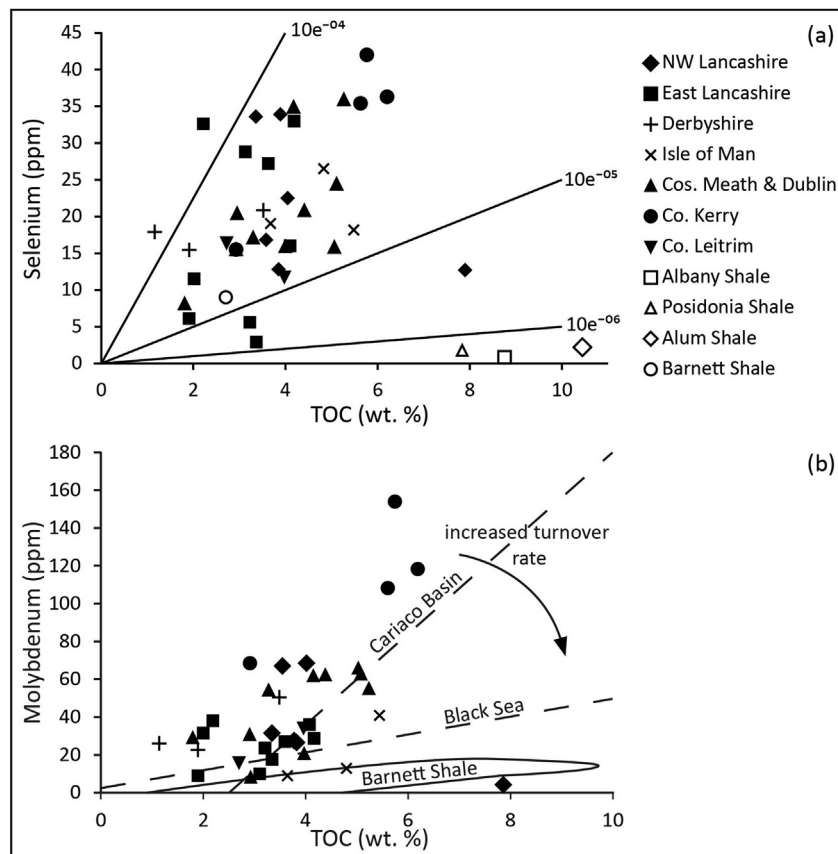


Fig. 2. Cross-plots for (A) Se against TOC. Se/TOC ratios for Bowland Shale are higher than for mean values for other black shales (data from Mitchell et al., 2012, except Barnett Shale mean value based on 2 measurements in this study). (B) Mo against TOC. Mo/TOC plot shows Mo and Mo/TOC values for Bowland Shale are consistently higher than in Barnett Shale. Mo/TOC correlation lines for Black Sea and Cariaco Basin show data for Bowland Shale is also high relative to some modern anoxic environments. (Mo data for Barnett Shale and modern environments from Rowe et al., 2008).

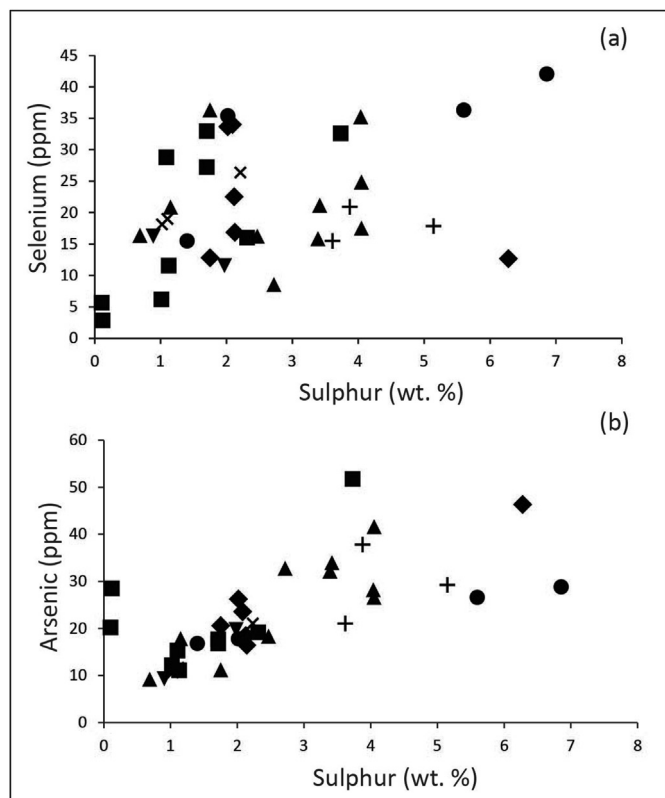


Fig. 3. Cross-plots for (A) Se against S, and (B) As against S. Broad trends of increasing Se and As with S are consistent with residence of Se and As within pyrite. Key as in Fig. 2.

In summary, both the high sulphur content and rapid turnover of water contributed to the high metal content of the Bowland Shale.

4. Discussion

4.1. Anomalous selenium availability

Much of the Se in black shales is associated with organic matter, but Se/TOC ratios vary according to Se availability (Mitchell et al., 2012). The Se/TOC ratios for the Bowland Shale markedly exceed values for other black shales (Fig. 2), implying anomalous availability. The high Se content of the British and Irish Carboniferous shales may reflect an anomalous source in the watershed. The region is bisected by an Ordovician volcanic arc, from the English Lake District through Anglesey and SE Ireland (Fig. 1), including the volcanic massive sulphide deposits at Parys Mountain, Anglesey, and Avoca, Ireland. In each of these areas, the Ordovician is unconformably overlain by the Carboniferous, and would have been supplying runoff waters into the Carboniferous sea. Stream sediments draining the Ordovician volcanic centres in North Wales today are Se-rich (Fordyce, 2013), so the Ordovician represents a potential source of Se-rich water to the Carboniferous. Contemporaneous tuffs in the late Dinantian-early Namurian of the British Isles indicate that there was also a direct input of volcanic ash into the local Carboniferous sea. Tuff deposition occurred in the Bowland Shale and its time equivalents in central England (Spears et al., 1999), southern Scotland (Monaghan and Pringle, 2004) and Ireland (Legg et al., 1998). The Se content of tuffaceous volcanic rocks can be relatively high (Fordyce, 2013), and the aerosols associated with volcanic activity can be 1 to 3 orders of magnitude

richer in Se than associated ash, and add anomalous selenium to the surface environment (Witham et al., 2005; Floor and Román-Ross, 2012). Interbedded tuffs have been interpreted to indicate a volcanic source of high Se levels in black shales elsewhere (Kulp and Pratt, 2004), and it is very possible that this was also the case in the Bowland Shale. The high As levels in the Bowland Shale may have a similar origin, as volcanic rocks contribute to high As levels in groundwater (e.g. Welch et al., 2000), and the Ordovician volcanogenic sulphide deposits in the palaeo-watershed of the Carboniferous shales are known to release anomalous arsenic into the surface environment today (Mayes et al., 2010).

Clues to the chemistry of waters derived from these sulphur-rich shales can be provided by natural springs. The Clare Shales host spa waters at Lisdoonvarna, Co. Clare; the Fingal Group hosts spa waters at Lucan, Co. Dublin; and two of the biggest spas in England at Harrogate and Buxton are supplied by waters that have passed through the Bowland Shale (Bottrell et al., 1996; Gunn et al., 2006). Together this represents a notable set of mineralized springs derived from the shales. All four spas are strongly sulphur-rich, and implicate leaching of the pyrite in the shales. More generally, Carboniferous rocks in northern England host numerous 'sulphur springs' (Murphy et al., 2014). As the pyrite is the main residence of Se and As, this implies liberation of Se and As into the groundwaters. The flow of sulphur-rich water through these springs over at least a historical record of hundreds of years implies a long-term alteration of the pyritic sources and long-term liberation of Se.

Selenium and arsenic may also be associated with hydrocarbons generated from black, organic-rich shales, as evidenced from Se/As-rich by-products in oil refineries (Lawson and Macy, 1995), shale oil processing (Sikonia, 1985) and coal gasification (Liu et al., 2006). The Bowland Shale is a major hydrocarbon source rock in the Irish Sea (Armstrong et al., 1997). Bituminous oil residues around the margins of the Irish Sea in North Wales, Lancashire and southern Scotland (Fig. 1) all contain traces of selenide mineralization (Parnell, 1988 and unpublished data), and selenium enrichments occur in Carboniferous palaeo-oil reservoirs in the south of the region (Parnell et al., 2015). For example, hydrocarbon residues in Carboniferous sandstones at Heysham, Lancashire (Harrison, 1970) are Se-rich. Oil residues in the Isle of Man additionally contain arsenide mineralization (Parnell, 1988). This implies that the fluids expelled from the Irish Sea Basin are Se- and As-rich, and likely related to hydrocarbon expulsion from the Bowland Shale. The highest Se values in the Carboniferous shales are recorded from Co. Kerry, western Ireland, which is the most thermally mature region in the gas window (Clayton et al., 1989), showing that hydrocarbon generation has not mobilized all of the Se. Notably, base metal sulphide mineralization in the Trough of Bowland and other parts of northern England is also attributed to the release of metals from the Carboniferous shales (Jones et al., 1994). The Clare Shales in Ireland have interacted with groundwater to yield secondary Se mineralization (Francis and Ryback, 1987). Overall, we have a picture of the Bowland Shale as a black shale anomalously rich in trace elements, especially Se and As, and with the potential to release those elements into subsurface fluids.

4.2. Implications

Black shales confer high levels of Se to groundwaters through subsurface leaching (e.g. U.S. Department of Energy, (2011)), leaching of rock waste (e.g. Stillings and Amacher, 2010) and via overlying soils (e.g. Park et al., 2010; Tuttle et al., 2014). In most cases where groundwaters contain more than the maximum level of selenium permitted for drinking water after interaction with black shales, the parent black shale contains much less Se than the mean determined here for the Bowland Shale (Mayland et al., 1989;

U.S. Department of Energy, 2011; Fontenot et al., 2013). For example, high levels of dissolved Se occur in water from wells drilled into Cretaceous black shales in Montana with up to 10 ppm Se (Mayland et al., 1989). This maximum value in Montana is exceeded by most of the Bowland Shale analyses. An average of 1 ppm Se for Cretaceous black shales responsible for soil contamination in the southwestern United States (Tuttle et al., 2014) is over an order of magnitude less than in the Bowland Shale. Concern about high Se levels in drinking water have recently spread to western Europe, and some wells in France where the water has been exposed to black shale have had to be abandoned (Bassil et al., 2014). As noted above, the As levels in the Bowland Shale consistently exceed those in the Barnett Shale, whose exploitation has led to groundwater values above the U.S. limit for drinking water. There is a direct implication that the Se and As levels of groundwaters that have interacted with the Bowland Shale require monitoring.

So, should there be concern over these high metal contents in the Bowland Shale, if it is exploited for shale gas? There is awareness of the need to consider such issues in the UK (Stuart, 2012; Cai and Offerdinger, 2014), but fortunately a very robust oil and gas regulatory system, covering licence application, planning permission, well construction and environmental permits, makes it very unlikely that the UK would experience the environmental problems encountered in the USA (The Royal Society, 2012).

The concentration of Se, and possibly other trace elements, in extraction waters could also be regarded as an opportunity. Selenium is a rare element for which demand is likely to increase (Moss et al., 2011), but the current supply as a by-product of copper production is in jeopardy as production methods change. Alternative methods of extraction that do not include high temperature (high energy) or toxic chemicals are desirable. Waters produced from Se-rich shales offer new possibilities. An understanding of how to do this can build on methodology being developed to deal with Se-rich waters associated with the storage of coal waste. Some coals, like some black shales, contain anomalous concentrations of Se, leading to environmental problems in several parts of the world, including the Elk River Valley, British Columbia (Lussier et al., 2003). Approaches to sequester Se at low temperature include precipitation onto iron oxides (Wei et al., 2012), precipitation onto activated carbon (Wasewar et al., 2009) and microbial selenate reduction (Tucker et al., 1998). These are all low-energy approaches which could contribute to securing new Se resources, and in the process add incentive to ensuring that extraction waters are processed in an environmentally sensitive manner.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.apgeochem.2015.12.008>.

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