Liberation of selenium from alteration of the Bowland Shale Formation: evidence from the Mam Tor landslide

John Parnell1*, Liam Bullock1, Joseph Armstrong1 & Magali Perez2

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

© 2018 The Author(s). This is an Open Access article distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0/). Published by The Geological Society of London. Publishing disclaimer: www.geolsoc.org.uk/pub_ethics

Abstract: The Bowland Shale Formation is anomalously rich in selenium (Se) at levels an order of magnitude greater than other black shales. The Mam Tor landslide, Derbyshire, England, offers an opportunity to measure whether the Se anomaly is confined to the alteration products formed by oxidative water flow through the shale. Selenium in the shale is concentrated in diagenetic pyrite. Alteration of the shale causes decomposition of the pyrite to iron oxyhydroxide, which is carried in colloidal form (ochre) by springs draining the landslide. The iron oxyhydroxide contains anomalously high Se, and anomalously high Se was measured in water ponded where the ochre precipitated, although not in flowing groundwater. Other trace elements including cadmium and thallium also occur at concentrations higher than in other ochres. Given the widespread nature of the Se anomaly in the Bowland Shale Formation and equivalents across Britain and Ireland, any alteration products derived from workings through the shale should be disposed of with care.

Received 9 February 2018; revised 15 June 2018; accepted 15 June 2018

The Upper Carboniferous (early Namurian) Bowland Shale Formation consists of hemipelagic–pelagic shale deposited across central Britain and Ireland (Andrews 2013; Newport et al. 2018). To the north it passes into successions dominated by shallow water limestone and coal. The shale is dark grey to black, reflecting the geology of Mam Tor (Hope Valley, Derbyshire, UK, National Grid Reference SJ 133834) consists of turbidite sandstones (Mam Tor Sandstone) above black pyritic hemipelagic shales (Bowland Shale Formation: Allen 1960; Banks et al. 1996; Banks 1997). Over 3000 years ago a landslide was initiated, which is still active (Vear & Curtis 1981; Skempton et al. 1989). The landslide forced the closure of the A625 between Sheffield and Manchester across Mam Tor in 1979. Near-surface groundwater drains down through the landslide, oxidizing the pyrite and emerging as acidic, ochre-precipitating springs (Vear & Curtis 1981; Steward & Cripps 1983; Banks et al. 1996; Adams et al. 2007). There have been several studies on the water chemistry, whole-rock geochemistry and mineralogy of the shales, the acidic and ferruginous water runoff, and the associated ochre and gypsum precipitates (Allen 1960; Smith et al. 1967; Spears & Amin 1981; Banks et al. 1996; Banks 1997; Adams et al. 2007). Fe concentrations show a
where it is visibly altered to varying degrees, and from beyond the landside, where it is unaltered, including from an undisturbed section at Edale village (Stevenson et al. 1971). Bulk analyses of the ochre and shale samples (Table 1) were made after multi-acid digestion (perchloric, nitric, hydrofluoric and hydrochloric acids) by inductively coupled plasma mass spectrometry (ICP-MS). In addition to Se, measurements were also made of arsenic (As), cadmium (Cd) and thallium (Tl) in the ochres, as these elements have an affinity for iron oxide but can be a cause of environmental pollution. Pyrite in the fresh shale from Edale village was analysed by laser ablation (LA)-ICP-MS. Details of the ICP-MS and LA-ICP-MS techniques have been given by Parnell et al. (2017). Water was sampled from three sites in the spring and stream system (Fig. 1).

**Results**

Ochres at Mam Tor are predominantly orange–red in colour, with lesser quantities of white ochre. The ochres analysed were orange–yellow powders, sieved to exclude coarse particles (above 125 μm) before milling, consisting particularly of quartz, goethite, hematite and gypsum. Variations in colour reflect the different abundances of gypsum compared with hematite (red) and goethite (orange–yellow), with white ochres containing more gypsum.

The shales are black mudrocks with a bedding-parallel fabric along which they split. None of the samples was conspicuously fossiliferous. They consist predominantly of quartz, illitic clay and organic matter. Eight samples of shale contain 4.1–40.5 ppm Se, and a mean concentration of 18.4 ppm Se (Table 1). Excluding two samples that are conspicuously weathered to a rusty appearance, and likely to be leached, the mean concentration is 23.1 ppm Se.

Measurement of 11 samples of ochre gave a range of 1.0–7.2 ppm Se, and a mean concentration of 5.0 ppm Se. Low Se concentrations (1.0–2.0 ppm) occur in the ochre samples from the upper part of the landside, in the region of slipped blocks. Higher concentrations (5.5–7.2 ppm) occur in the lower, debris-flow, region. Concentrations of As, Cd (Fig. 2) and Tl follow this general pattern. Measurement of three samples of spring water gave a single concentration above the detection limit of 0.2 mg kg⁻¹ Se, at 1.72 mg kg⁻¹ Se, measured where the water is ponding between the slipped blocks and the debris field, in the same area as the most Se-rich ochres.

LA-ICP-MS mapping showed that Se residence is strongly concentrated in crystals of pyrite (Fig. 3). Measurements of the pyrite yielded a mean composition of 31 ppm Se and 130 ppm As, and local concentrations up to 80 ppm Se and 250 ppm As.

**Discussion**

**Anomalous Se in Mam Tor alteration products**

The Se content of the ochres is greater than in most other measured ochres. Most ochres in drainage systems from coal mines, derived from the oxidation of pyrite in coal and mudrock, in the UK contain <0.5 ppm Se (Fig. 4; Coal Authority, unpublished data). Published analyses of ochres usually record Se at below the detection limit (Sapsford et al. 2015; Hedin 2016). Natural ochres of non-specific origin, used as pigments and studied by the archaeological community, similarly have Se contents of about 1 ppm or lower (Green & Watling 2007; Iriarte et al. 2009). The Mam Tor ochres are, therefore, anomalous for their high Se concentrations relative to all measured ochre deposits. This reflects the high Se concentrations in the Bowland Shale Formation protolith.

The mean concentrations of As, Cd and Tl in Mam Tor ochres are 16.7 ppm, 13.9 ppm and 3.5 ppm respectively. The concentrations of trace elements in the ochres are consistently higher in the lower part of the landside (Fig. 2), where the water becomes ponded.
Concentrations of Se in the ochres are about one-third of the concentrations in the parent rock, but are still high because the concentrations in the shale are so much greater than in most other rocks. The mean As concentrations of ochre is similarly about one-third of that in the shales (mean 47.4 ppm). In contrast, the concentrations of Cd in the ochres are much higher than in the parent shale (mean 1.5 ppm), although Cd concentrations an order of magnitude greater have been measured in the Bowland Shale Formation further north (Lepp 1981; Mislin & Ravera 1986). The natural enrichment of Cd is comparable with experimental data, which show Cd to be the most enriched metal in ochre in a multi-element study (Abed et al. 2017).

The ready adsorption of As, Cd and Tl has led to the application of ochres and iron oxides to sequester these elements out of groundwaters (Doi et al. 2005; Abed et al. 2017; Li et al. 2017). The As concentration in the Mam Tor ochre is higher than concentrations in some ochres from UK coal mines (Dobbie et al. 2005; Olimah et al. 2015), but not in others (Sapsford et al. 2015) or in ochres elsewhere (e.g. Bowell & Bruce 1995; Cravotta 2008; Valente et al. 2011), but is nonetheless above the crustal mean concentration of 5.7 ppm. Soluble forms of both Se and As are adsorbed strongly onto iron oxides in acid conditions (Manning et al. 1998; Su & Suarez 2000), as pertain in waters draining through pyritic shales. The mean Cd concentration in the ochres is above concentrations previously reported in ochres (Fuge et al. 1994; Hammarstrom et al. 2003; Doibie et al. 2005; Iriarte et al. 2009; Sapsford et al. 2015). The mean Tl concentration of the ochre is also higher than the few concentrations recorded previously for ochres (Iriarte et al. 2009; Sapsford et al. 2015). Notably, As and Cd concentrations are also well above soil guideline value (SGV) levels (Environment Agency 2009a, b). The anomalous concentrations are of interest as even small volumes of ochre, if dried out, can become a

| Table 1. Mineral, whole-rock, ochre precipitate and water compositions for Mam Tor samples |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Sample type                  | Map ID | Fe (%) | S (%) | Se (ppm) | As (ppm) | Cd (ppm) | Tl (ppm) |
| Edale pyrite                  |        | 23.1   | –     | 30.7     | 130.5    | –        | –        |
| Shale 1                      | 1      | 4.8    | 5.6   | 4.1      | 71.1     | 0.6      | 0.4      |
| Shale 2                      | 2      | 0.5    | 0.1   | 4.3      | 6.9      | 0.1      | 0.1      |
| Shale 3                      | 3      | 1.6    | 2.0   | 4.6      | 40.0     | 0.3      | 0.1      |
| Shale 4                      | 4      | 3.9    | 4.3   | 20.9     | 38.0     | 2.5      | 0.7      |
| Shale 5                      | 5      | 6.9    | 0.2   | 40.5     | 86.5     | 0.8      | 0.8      |
| Shale 6                      | 6      | 6.7    | 0.2   | 39.6     | 85.7     | 0.7      | 0.8      |
| Shale 7                      | 7      | 4.5    | 3.6   | 15.5     | 21.4     | 3.4      | 0.4      |
| Shale 8                      | 8      | 6.1    | 5.1   | 17.9     | 29.3     | 3.4      | 0.7      |
| Mean shale                   |        | 4.4    | 2.6   | 18.4     | 47.4     | 1.5      | 0.5      |
| Median shale                 |        | 4.7    | 2.8   | 16.7     | 39.0     | 0.8      | 0.5      |
| Ochre sediment 9             | 9      | 39.0   | 3.5   | 1.0      | 7.6      | 0.03     | 0.2      |
| Ochre sediment 10            | 10     | 40.7   | 2.4   | 2.0      | 7.6      | 0.05     | 0.2      |
| Ochre sediment 11            | 11     | 40.4   | 2.4   | 1.9      | 8.3      | 0.04     | 0.1      |
| Ochre sediment 12            | 12     | 2.3    | 4.3   | 5.5      | 8.1      | 2.5      | 0.2      |
| Ochre sediment 13            | 13     | 9.5    | 0.3   | 6.3      | 25.5     | 12.9     | 0.5      |
| Ochre sediment 14            | 14     | 17.2   | 0.5   | 7.2      | 28.4     | 21.1     | 0.7      |
| Ochre sediment 15            | 15     | 2.1    | 0.9   | 6.4      | 14.6     | 6.5      | 0.4      |
| Ochre sediment 16            | 16     | 11.2   | 1.6   | 5.6      | 37.8     | 3.5      | 0.6      |
| Ochre sediment 17            | 17     | 15.6   | 1.0   | 6.4      | 17.9     | 44.7     | 15.1     |
| Ochre sediment 18            | 18     | 15.5   | 1.0   | 6.3      | 17.6     | 43.9     | 15.1     |
| Ochre sediment 19            | 19     | 15.2   | 1.3   | 6.6      | 10.7     | 18.0     | 5.1      |
| Mean ochre sediment          |        | 19.0   | 1.7   | 5.0      | 16.7     | 13.9     | 3.5      |
| Median ochre sediment        |        | 15.5   | 1.3   | 6.3      | 14.6     | 6.5      | 0.5      |
| Ochre water 20               | 20     | <LOD   | <LOD  | <LOD     | 5.24     |          |          |
| Ochre water 21               | 21     | <LOD   | <LOD  | 1.53     |          |          |          |
| Ochre water 22               | 22     | 1.72   | 1.1   | 2.05     |          |          |          |

Water LOD (level of detection): As, 0.97 ppb; Cd, 1.99 ppb; Se, 1.59 ppb.

Concentrations of Se in the ochres are about one-third of the concentrations in the parent rock, but are still high because the concentrations in the shale are so much greater than in most other rocks. The mean As concentrations of ochre is similarly about one-third of that in the shales (mean 47.4 ppm). In contrast, the concentrations of Cd in the ochres are much higher than in the parent shale (mean 1.5 ppm), although Cd concentrations an order of magnitude greater have been measured in the Bowland Shale Formation further north (Lepp 1981; Mislin & Ravera 1986). The natural enrichment of Cd is comparable with experimental data, which show Cd to be the most enriched metal in ochre in a multi-element study (Abed et al. 2017).

The ready adsorption of As, Cd and Tl has led to the application of ochres and iron oxides to sequester these elements out of groundwaters (Doi et al. 2005; Abed et al. 2017; Li et al. 2017). The As concentration in the Mam Tor ochre is higher than concentrations in some ochres from UK coal mines (Dobbie et al. 2005; Olimah et al. 2015), but not in others (Sapsford et al. 2015) or in ochres elsewhere (e.g. Bowell & Bruce 1995; Cravotta 2008; Valente et al. 2011), but is nonetheless above the crustal mean concentration of 5.7 ppm. Soluble forms of both Se and As are adsorbed strongly onto iron oxides in acid conditions (Manning et al. 1998; Su & Suarez 2000), as pertain in waters draining through pyritic shales. The mean Cd concentration in the ochres is above concentrations previously reported in ochres (Fuge et al. 1994; Hammarstrom et al. 2003; Doibie et al. 2005; Iriarte et al. 2009; Sapsford et al. 2015). The mean Tl concentration of the ochre is also higher than the few concentrations recorded previously for ochres (Iriarte et al. 2009; Sapsford et al. 2015). Notably, As and Cd concentrations are also well above soil guideline value (SGV) levels (Environment Agency 2009a, b). The anomalous concentrations are of interest as even small volumes of ochre, if dried out, can become a

Fig. 2. Cross-plots of (a) Se and As, (b) Se and Cd for samples of Bowland Shale Formation and ochres at Mam Tor. Altered samples of shale show depletion of elements. Ochres are enriched in Cd relative to parent shales. All data are anomalous relative to global mean shale concentrations (from Rudnick & Gao 2003; Hu & Gao 2008; Stüeken et al. 2015).
source of wind-blown contamination, as occurred in a residential region of Anglesey near a former copper mining site (Isle of Anglesey County Council 2010).

The concentration of 1.72 mg kg\(^{-1}\) Se in the ponded water is also anomalously high. For comparison, this is above a mean concentration of 0.4 mg kg\(^{-1}\) Se in 32 water samples in groundwaters in Manchester and East Cheshire, immediately to the west of the study area (Griffiths et al. 2003), and above all concentrations measured in groundwaters measured in the East Midlands to the east (Smedley & Edmunds 2002). However, two other samples of spring water contained less than 0.2 mg kg\(^{-1}\), indicating that there is no evidence of a Se anomaly in flowing groundwater.

Selenium residence

The residence of Se in the pyrite within the shale indicates that the Se is likely to be mobile once the shale becomes weathered and the pyrite is oxidized. Whereas sulphur liberated from altered pyrite is highly mobile as sulphuric acid, some Se may occur in elemental form or as selenide ions. These Se species can be adsorbed onto iron oxide (Balistrieri & Chao 1990; Rovira et al. 2008), so there is potential for retention of Se on the ochres resulting from pyrite oxidation. A combination of fine particles, high surface area and the affinity of iron oxides for Se and other trace elements makes ochres a natural trap for groundwater solutes. Ochre has even been deployed to extract Se from waters draining through coal waste (Donovan & Ziemkiewicz 2013). The situation at Mam Tor is very similar, where ochres are precipitated from, but also extracting Se from, the waters draining through the landslipped shale.

Potential pollution at high Se concentrations

The anomalously high nature of the ochre Se concentrations can be put into context by comparison with the Se concentrations of rocks...
that are regarded as problematic because of their Se (Fig. 4), and that have experienced comparable burial histories to depths of a few kilometres. The mean concentrations of coal in West Virginia, and Elk Valley, British Columbia, both of which are held responsible for environmental contamination by Se, are 3.6 ppm Se (Vesper et al. 2008) and 2.6 ppm Se (Kennedy et al. 2015) respectively. The mean concentration of shale held responsible for Se contamination of water supply in the Paris Basin, and consequent closure of water wells (Cary et al., 2014), is 2.3 ppm Se (Bassil et al. 2016). The mean Se concentration of the Cretaceous Mancos Shale, a cause of widespread environmental concern for agriculture, water supply and endangered aquatic species in southwestern USA, is cited as 1.1 ppm Se (Tuttle et al. 2014), is 2.0 ppm Se (US Department of Energy 2011). The mean concentration of Se in the Mam Tor ochres exceeds all of these concentrations from other regions where they give rise to environmental problems.

Although the Se concentration of the shale is an order of magnitude above that in typical shales, it is in the lower half of the range of concentrations measured in the Bowland Shale Formation equivalents across Britain and Ireland (Parnell et al. 2016). The highest concentration that we have measured is 80 ppm Se in County Cork, Ireland, about four times that of the mean concentration of the shale tested from Mam Tor. These data imply that alteration of the Bowland Shale Formation elsewhere could yield alteration products that are more loaded with Se than at Mam Tor, and potentially more hazardous.

Conclusions

Analysis of the ochres (iron oxyhydroxide deposits) from the Mam Tor landslide shows that they contain elevated concentrations of Se, relative to crustal mean concentrations and ochres elsewhere. The high concentrations of Se and other toxic elements including As, Cd and TI in the ochre are attributed to the elevated concentrations recorded in the Bowland Shale Formation, which would have released iron oxide and trace elements upon oxidation of the pyrite content. The mean Se concentration of the ochres is greater than that in rocks that have caused environmental problems elsewhere. The ochres at Mam Tor are volumetrically very limited, and the waters draining Mam Tor are not used for public supply, so do not constitute a hazard, but the data indicate the need for caution in any large-scale working of the Bowland Shale Formation in Britain and Ireland.

Acknowledgements

We are grateful to the UK Coal Authority for provision of analytical data for ochres. The paper was much improved by anonymous review and editing.

Funding

This work was funded by the Natural Environment Research Council (NE/M010953/1).

Scientific editing by Cherith Moses; David Entwisle

References


