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High selenium in the Carboniferous Coal Measures of Northumberland, North East England

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ABSTRACT

The Carboniferous Lower and Middle Coal Measures coals of the Northumberland Coalfield are anomalously rich in selenium (Se) content (up to 62 ppm) compared to the averages for the common UK and worldwide coals. As well as posing an environmental toxicity threat, Se is now regarded as an important resource for alloys, photovoltaic products and nanotechnologies, and high Se coals in North East England offer an opportunity to assess the Se means of occurrence, origins, transport mechanisms and enrichment in coals. At least two generations of pyrite host high Se in the sampled coal seams: microbial-formed disseminated pyrite (both cubic and framboidal in habit) and later cleat-filling pyrite, identified by petrographic observations, laser ablation methods and sulphur isotope compositions. There is a notable Se enrichment of up to 250 ppm in later formed cleat-filling pyrite. Trace element enrichment may have been sourced and influenced by seawater distribution during diagenesis, and localised dykes and deformation may have acted as an enrichment mechanism for sampled seams in the region. The high Se coals in Northumberland may provide a potential E tech element source and should be considered and carefully managed as coal mining and production are reduced in the area. The study also highlights the nature of Se enrichment in pyritic coals affected by cleat formation and multiple episodes of mineralisation, important as critical element demand continues to increase worldwide.

1. Introduction

Improved understanding of the concentration and spatial distribution of critical elements such as selenium (Se) in coals is economically important, particularly as the worldwide demand for viable sources of Se continues to grow. The Carboniferous-aged coals in the Northumberland Coalfield (North East England) have been previously shown to contain high pyrite (of multiple generations) and sulphur (S), important for resource development and utilisation (Turner and Richardson, 2004). High-S coals may contain high Se (Coleman et al., 1993), as Se and S share chemical affinities and substitute readily in pyrite (Emsbo et al., 2003; Pals et al., 2003; Yudovich and Ketris, 2006; Tanner et al., 2016; Keith et al., 2017). Multiple generations of pyrite formation in coals may also enrich Se content of coals (e.g. Ayrshire coals; Bullock et al., 2018b).

Sedimentary settings where Se enrichment is typically evident include organic and pyritic coals and black shales (Clark et al., 1980; Mao et al., 1988; Dreher and Finkelman, 1992; Zheng et al., 1992; Coleman et al., 1993; He et al., 2002; Lemly, 2004; Liu et al., 2006; Yudovich and Ketris, 2006; Li and Zhao, 2007; Ketris and Yudovich, 2009; Dai et al., 2015a, 2015b, 2017; Diehl et al., 2012; Lei, 2012; Zhu et al., 2012; Pazand, 2015; Parnell et al., 2016, 2018a; Armstrong et al., 2018; Bullock et al., 2018a, 2018b), red bed sediments (Hofmann, 1991; Parnell et al., 2016, 2018b; Spinks et al., 2014, 2016) or sandstone-hosted roll-type uranium deposits (Harshman, 1966; Howard, 1977; Granger and Warren, 1978; Reynolds and Goldhaber, 1983; Min et al., 2005; Abzalov, 2012; Dai et al., 2015a; Bullock and Parnell, 2017). Selenium is mobilised under oxidising conditions (Howard, 1977; Northrop and Goldhaber, 1990; Simon et al., 1997; Xiong, 2003; Min et al., 2005; Spinks et al., 2014, 2016), and may be precipitated and immobilised in the presence of a reducing agent (e.g. carbonaceous materials, sulphides, biogenic H_2S, ferromagnesian minerals; Spinks et al., 2014, 2016). In continental sandstone settings, Se may be co-precipitated with iron oxides and adsorbed from solution (Parnell et al., 2018b). Selenium is often accompanied by high V, Cr, Mo, U and Te (Yudovich and Ketris, 2006; Dai et al., 2015a; Bullock and Parnell,

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2017).

The average Se content for UK and worldwide coals are 1.8 and 1.3 ppm respectively (Spears and Zheng, 1999; Ketris and Yudovich, 2009; Yudovich and Ketris, 2015). Selenium is considered a coalphile element, with a strong affinity to organic and inorganic (e.g. sulphides) coal matter, similar to elements such as Ge and S (Yudovich and Ketris, 2006). Inorganically associated Se in coal typically occurs in association with pyrite and may also occur in association with rare clausthalite (PbSe), ferroselite ($FeSe_2$), galena (PbS), and clays (Finkelman et al., 1979; Finkelman, 1980; Swaine, 1990; Goodarzi and Swaine, 1993; Hower and Robertson, 2003; Dai et al., 2006, 2008; Li and Zhao, 2007). Metalliferous enrichment in coal may occur during peat accumulation, during diagenesis, or by epigenesis (Seredin and Finkelman, 2008; Dai et al., 2015b; Bullock et al., 2018b). In reducing coal-forming environments, Se concentrates in syngenetic or epigenetic sulphide phases, while in oxidising environments, Se is enriched in bed oxidation zones (closely associated with precipitation of U, Fe, Mo, V and Pb; Yudovich and Ketris, 2006). Elevated Se (and other associated trace elements) in coals may also be attributed to input from sediment source regions and percolating solutions (e.g. the Yili coals of Xinjiang, northwestern China; Dai et al., 2015a).

Over recent years, Se has become an increasingly important 'E tech' element, used in alloys, photovoltaic products and nanotechnologies (Jin et al., 2016; Wei et al., 2016), and coal has been specifically identified as a promising source for future resources (Seredin and Finkelman, 2008; UKERC, 2012; Seredin et al., 2013; Dai and Finkelman, 2018; Yang et al., 2018). Pyrite has also been noted as a potential economic source of Se (Keith et al., 2017). As well as economic benefits, trace elements such as Se have the potential for release into the environment from coal utilisation and combustion (Lakin and Davidson, 1973; Swaine, 1990). High Se coals may pose an environmental threat to air quality (coal combustion), and to local soils, surface and groundwater systems (Agnihotri et al., 1998; McDonald and Strosher, 1998; Lemly, 2004; Dai et al., 2012; Hendry et al., 2015). Therefore, sites of potentially high pyritic and S content with ongoing coal mining operations, such as in areas of Northumberland, northeast England (Fig. 1), warrant attention for their Se in coal potential. Identification of high Se in pyritic coals is essential for future advances and decisions in E tech development, coal processing and site management. While coals are not currently considered a viable source of Se compared to more conventional extractable deposits (e.g. by-product recovery of Cu processing; Brown, 2000; Plant et al., 2013), its presence in high abundances may prove an important by-product in regions where coal processing is winding down (such as historically extensive coal-producing areas of the UK), and as methods of critical element extraction continue to improve globally. This is particularly significant as demand for Se increases, while worldwide conventional Se-hosting deposits are exhausted. Coals with potential economic significance for critical elements, with concentrations in coal at least 10-times higher than the respective averages for world coals (Seredin and Finkelman, 2008), have been termed 'coal-hosted rare-metal deposits' (Dai and Finkelman, 2018) or 'metalliferous coals' (Seredin and Finkelman, 2008). As demand increases for critical elements such as Se, it is important to identify regions of metalliferous coals.

Existing Se data from Northumberland coals are limited, with concentrations of 16 bituminous coals available in the world coal database of Bragg et al. (1998). This Northumberland sample set gives an average of 3.4 ppm, higher than the averages for the common UK and world coals. These 16 coals were all sampled at the Ellington coal mine, near Lynemouth (Fig. 1). The sample set includes an anomalous Se value of 15 ppm, taken from the Brass Thill coal bed, which contains pyrite and ankerite (Bragg et al., 1998). This suggests that pyritic Northumberland coals may contain anomalously high Se, meriting further investigation. This paper aims to describe Se concentrations in six seams from the Northumberland Coalfield to determine the means of mineralogical occurrence, the source of abundant Se in the sampled coals, the economic viability of the region and to compare Northumberland coals to other recorded Se-bearing coals, both locally and worldwide. The origin of pyrite, Se occurrence, source and transport mechanisms will also be assessed, and the future importance of this resource will be discussed. The Shotton Surface Mine (Cramlington) was chosen as the main sample site due to the ongoing coal mining and processing operations, and the exposure of multiple seams, including pyritic coals. Three other localities were sampled and measured for a local comparison, and studies of worldwide Se-bearing coals were included for a global comparison. Results have important implications for Se-bearing coals as a potential semi-metal resource, particularly as means of extraction continue to improve. Though high Se in selected seam samples do not apply to the full extent of the Northumberland Coalfield, the identification of particularly enriched seams and strata in the region allows us to pinpoint Se targets and potential means of enrichment that could affect other seams locally, regionally or indeed worldwide.

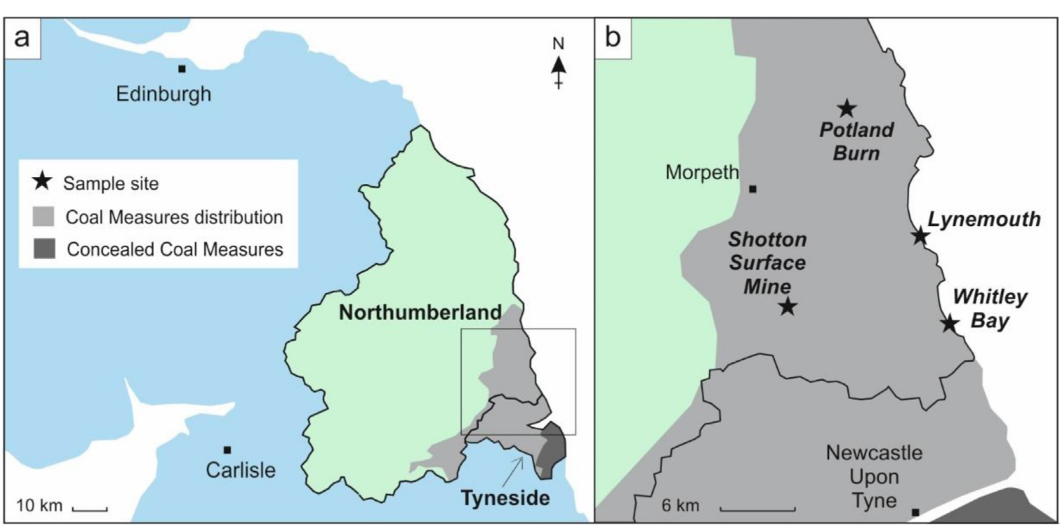

Fig. 1. The county of Northumberland (with the conurbation of Tyneside to the south) in North East England (a) and study sample sites in South East Northumberland (b). Coal Measures distribution and concealed Coal Measures also shown for Northumberland and Tyneside (after Bloodworth et al., 2000).