Enrichment of germanium and associated arsenic and tungsten in coal and roll-front uranium deposits

Barbara Etschmann[a], Weihua Liu[b], Kan Li[c], Shifeng Dai[d], Frank Reith[e,h], Donna Falconer[f], Gemma Kerr[f], David Paterson[g], Daryl Howard[g], Peter Kappen[g], Jeremy Wykes[g], Joël Brugger[a,*]

[a] School of Earth, Atmosphere and the Environment, Monash University, Clayton, 3800, Victoria, Australia
[b] CSIRO Mineral Resources, Clayton, Victoria 3168, Australia
[c] Mineralogy, South Australian Museum, Adelaide 5000, South Australia, Australia
[d] State Key Laboratory of Coal Resources and Safe Mining, China University of Mining and Technology, Beijing 100083, China
[e] School of Biological Sciences, The Sprigg Geobiology Centre, The University of Adelaide, South Australia 5005, Australia
[f] Geology Department, University of Otago, Dunedin, New Zealand
[g] Australian Synchrotron, Clayton, Vic. 3168, Australia
[h] CSIRO Land and Water, PMB2, Glen Osmond, South Australia 5064, Australia

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ABSTRACT

Most of the World's germanium (Ge) is mined from Ge-rich lignite, where it is commonly associated with elevated arsenic (As), tungsten (W) and beryllium (Be) contents. Over the past decade, new evidence showing that World-class Ge deposits result from the interaction of hydrothermal fluids with organic matter in coal seams has emerged. Yet, the chemical state of Ge and associated metals in lignite remains poorly understood. We used Mega-pixel Synchrotron X-ray Fluorescence (MSXRF), X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) to characterize the oxidation states and chemical bonding environment of Ge, As, and W in two world-class Mesozoic Ge-in-lignite deposits (Lincang, Yunnan, south-western China; Wulantuga, Inner Mongolia, northeastern China); in lignite-bearing uranium (U) ores from the Beverley deposit (South Australia) hosted in Eocene sandstones; and in lignite and preserved wood in late Oligocene-Miocene fluviatile sediments (Gore, Southland, New Zealand). The aim was to improve our understanding of the enrichment mechanism of Ge in lignite and better evaluate the environmental mobility of Ge and some of the associated metals (specifically As and W) in lignite ores.

In all samples, chemical maps show that Ge is distributed homogeneously (down to 2 μm) within the organic matter. XANES and EXAFS data show that Ge exists in the tetravalent oxidation state and in a distorted octahedral coordination with O, consistent with complexing of Ge by organic ligands. In some pyrite-bearing samples, a minor fraction of Ge is also present as Ge(IV) in association with pyrite. In contrast, As displays a more complex speciation pattern, sometimes even in a single sample, including As(III), As(V), and As($-$I/$+$II) in solid solution in sulfides. Arsenic in sulfides occurs in anionic and cationic forms, i.e., it shows both the common substitution for S_2^{2-} and the substitution for Fe recently discovered in some hydrothermal pyrites. Tungsten was present as W(VI) in distorted octahedral (3 + 3) coordination. The EXAFS data confirm the absence or minor contribution of individual W-rich minerals such as scheelite or ferberite to W mass balance in the studied samples.

These data show that Ge, W, and probably some As are scavenged via formation of insoluble, oxygen-bridged metal organic complexes in lignite. Destruction of the organic ligands responsible for fixing Ge and W (As) in these lignites is required for liberating the metals, e.g. from waste materials. Geochemical modelling suggests that Ge, W, Be and As all can be extracted from granitic rocks by dilute, low temperature hydrothermal fluids. Germanium is transported mainly as the tetrahedral Ge(OH)$_4$(aq) complex, but fixed as an octahedral oxy-bridged organic complex. The same situation is valid for W, which is transported at the tetrahedral tungstate ion, but most likely scavenged via formation of a 6-coordinated metal-organic species. The Ge-Be-W ± As association in Ge-rich coals reflects the source of the metals as well as related scavenging mechanisms.

1. Introduction

Rare metals, such as Ge, gallium (Ga), selenium (Se), lithium (Li) as well as rare earth elements play a key role in emerging energy-efficient and alternative power technologies. As the demand for these commodities as well as their strategic value is rapidly increasing, a push to expand existing resources and develop new sustainable recovery methods for extracting these metals from complex ores is the result. Increased rates of use of these metals also create new environmental issues via increased anthropogenic outputs associated with their mining and extraction.

Germanium-rich coal is the most important economic source of this metal. Germanium is commonly associated with As and W in these ores. Yet, the geochemical form (oxidation state and chemical bonding environment) of Ge in coal remains poorly constrained. By characterizing the distribution and chemical state of Ge, As and W in a range of lignite samples and contrasting the geochemistry of Ge, As and W in these samples, we aim to improve our understanding of the enrichment mechanism of metals and semi-metals in coal, better evaluate the environmental mobility of Ge, As and W in the lignite ores, and provide the fundamental geochemical information to support the development of more efficient exploration and extraction methods.

1.1. The World's supply of germanium

Germanium as well as other rare metals (Ga, Se, Li, REE) can be enriched in some coals, at levels comparable to or even higher than in conventional economic deposits (Dai et al., 2016; Seredin et al., 2013; Seredin and Finkelman, 2008). Historically, the coal and metal production industries have rarely associated with each other, except for two examples that resulted in profitable metal recovery (Seredin, 2012). The first is the production of U from coal seams, which initially helped to establish a nuclear industry in the USA and the former USSR following World War II. The second example is the extraction of Ge. Germanium extraction from coal began in the late 1950s and has continued successfully to the present time. Today, coal is the main source of Ge, providing more than half of the World's production of this rare metal. Germanium is used in many high-tech applications, e.g., semiconductors, fiber-optic cables, solar cells as well as for some specific high-tech usages such as IR sensor or X-ray detectors (Cook et al., 2015; Frenzel et al., 2014; Guberman, 2013; Höll et al., 2007; Seredin, 2012).

China is by far the World's largest Ge producer: in 2014 it produced 110 of the 155 tons produced world-wide. (https://minerals.usgs.gov/minerals/pubs/commodity/germanium/mcs-2016-germa.pdf). Yet, only recently have geological studies assessed the mechanisms responsible for the formation of the Ge-rich coals in China (Dai et al., 2015a; Qi et al., 2011; Seredin, 2012). At both Lincang (Yunnan, southwestern China) and Wulantuga (Inner Mongolia, China), Ge enrichment of up to 2176 ppm (1590 ppm and 273 ppm on average in the Lincang and Wulantuga ores, respectively) is attributed to hydrothermal fluids leaching the adjacent granitoids (Dai et al., 2015a; Seredin, 2012).

1.2. Germanium geochemistry

Germanium is an intriguing element, which can behave as a chalcophile, lithophile, organophile or siderophile, depending on the environment (Bernstein, 1985). The crustal abundance of Ge is approximately 1.4–1.6 ppm (Frenzel et al., 2014; Taylor and McLennan, 1985; Wedepohl, 1995). This concentration is similar to that of Mo and W (Wedepohl, 1995), yet while there are many Mo and W deposits with grades of > 0.1 wt% and metal contents > 10,000 t, there are no comparable Ge deposit (Frenzel et al., 2014).

Most crustal Ge is distributed throughout silicate minerals on the order of a few ppm, in the form of $[Ge(IV)O_4]^{4-}$ substituting for $[SiO_4]^{4-}$ moieties. The highest Ge concentrations occur in Zn and Cu sulfide deposits, where sphalerite for example can contain up to 1000's of ppm Ge, and a number of sulfide minerals have Ge as an essential component (Belissont et al., 2016; Cook et al., 2015); and in coal and lignitized wood (Bernstein, 1985; Frenzel et al., 2014; Seredin and Finkelman, 2008; Yudovich, 2003). V.M. Goldschmidt first reported the presence of substantial amounts of Ge in coal in the 1930s (see Goldschmidt, 1935).

Germanium can exist in the 4 + and 2 + oxidation states (see review in Brugger et al., 2016), although the Ge^{2+} aqua ion and Ge^{2+} halide complexes are metastable at room temperature (Babich et al., 2000). All known Ge minerals contain Ge(IV), and Ge in substitution for Zn in sphalerite is also in the 4 + state (Belissont et al., 2016; Cook et al., 2015). Pokrovski and Schott (1998b) showed that in hydrothermal solutions, Ge(IV) is transported mainly as tetrahedral hydroxide complexes, with $Ge(OH)_4(aq)$ being the main species at acidic to mildly basic conditions, bonded to four oxygen atoms at an average distance of 1.75(2) Å. At ambient conditions, Ge(IV) forms stable complexes with a variety of organic ligands (Pokrovski et al., 2000; Pokrovski and Schott, 1998a). The carboxylic acid (oxalic, citric) and catechol (1,2-dihydroxybenzene) ligands used by Pokrovski et al. (2000) contain the same functional groups as humic and fulvic acids. Germanium(IV) generally occurs in tetrahedral coordination (Bernstein, 1985), but in carboxylic acid (acidic pH) and in catechol solutions (pH > 4), Ge(IV) is coordinated to six oxygen atoms at a distance of 1.85 to 1.94 Å (Pokrovski et al., 2000). The formation of such six-coordinated (distorted octahedral) complexes suggests a bidentate covalent (chelate–type) bond (Pokrovski and Schott, 1998a), an observation that is supported by the absence of Ge complexed to mono-functional carboxylic acid such as acetic acid. Pokrovski et al. (2000) suggested that Ge(IV) bonds to the organic ligands via oxygen atoms, based on a comparison with other metal-organic complexes listed by Martell and Hancock (1996). The ability of Ge(IV) to increase its coordination number from four to six explains the high stability of Ge-organic complexes. Note that silicon (Si), a smaller atom, encounters a larger steric hindrance to octahedral coordination, so it exists predominantly in four-coordinated form; yet, some of the few octahedral Si complexes at ambient pressure are with catechol and carboxylic ligands, emphasizing the strong effect of the ligand and polydentate bond on the geometry of the complex (Brugger et al., 2016; Logemann et al., 2011; Pokrovski and Schott, 1998a).

1.3. The germanium-arsenic-tungsten association

Germanium-rich coal is commonly enriched in As, W and Be (Fig. 1). For example, the average Chinese coal contains 3.79 ppm of As (Dai et al., 2012a), whereas Ge-rich Chinese coal often contains > 100 ppm of As (Fig. 1b). In the case of W, a number of coal deposits contain between 0.1 and 5 wt% of W (Seredin and Finkelman, 2008). Among the studied samples, the Lincang coals contain up to > 900 ppm, and there is a distinct positive correlation between Ge and W in the Ge-rich coals from Wulantuga (Fig. 1c). The Ge-As-W association provides an opportunity to contrast the geochemistry of these elements in coal.

All three elements can occur in different oxidation states in Nature. The oxidation state and speciation of an element affect its mobility, extraction, and environmental impact and toxicity (e.g. Brugger et al., 2016; Huggins et al., 2009), in addition to providing some insight into the mechanisms that led to its enrichment to ore-grade. The oxidation state and speciation of Ge in the ores has yet to be directly determined. The occurrence of Ge(II) in Nature has yet to be demonstrated beyond doubt (Belissont et al., 2016; Cempirek and Groat, 2013; Cook et al., 2015), and coal offers a likely environment for the occurrence of highly reduced Ge. Tungsten exists mostly in the W(VI) form in nature, although W(IV) is present in the mineral tungstenite, WS_2 (Brugger et al., 2016); similarly to Ge, there is no detailed study of W speciation in coal. In contrast, a large amount of data is available on As speciation in coal, reflecting the environmental significance of this information.