



# Tellurium and selenium in Mesoproterozoic red beds

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## ABSTRACT

Samples of red bed sediments in several Mesoproterozoic successions contain enrichments of tellurium (Te), including discrete telluride minerals. The tellurides were neofomed during redox-controlled diagenesis, rather than representing mechanical concentrations of heavy minerals. Tellurium is enriched relative to selenium, which may reflect erosion of Archean and Palaeoproterozoic rocks with high Te contents. High continentality during the Mesoproterozoic would have limited the delivery of Te and other trace elements to the oceans, so accumulated Te on the continents.

## 1. Introduction

A key consequence of the oxygenation of the atmosphere after the Great Oxidation Event was the enhanced weathering of the continents. It has been reasoned that this weathering released redox-sensitive metals, sulphur and other elements, which then progressively changed the chemistry of the oceans (Anbar and Knoll, 2002; Scott et al., 2008; Parnell et al., 2012). The build-up of trace elements, such as molybdenum, copper, zinc and selenium in the oceans, is regarded as critical to the development of multicellular life, which are required for a range of metabolic functions (Zerkle et al., 2005; Williams, 2006; Lobanov et al., 2007; Dupont et al., 2010). The evidence for trace element release is indirect, through a progressive change in the trace element contents of marine anoxic black shales (Anbar and Knoll, 2002; Lyons et al., 2014) and the appearance of extensive gypsum deposits (Kah et al., 2001) that imply weathering of bedrock sulphides to soluble sulphates. Both lines of evidence date the availability of trace elements to the Mesoproterozoic, which matches the timing of expansion of the eukaryotes (Knoll et al., 2006). Here we report direct evidence for the availability of redox-sensitive elements in Mesoproterozoic continental sandstones, which were a reservoir for delivery to the oceans.

In continental sandstones, the predominant residence of trace elements is in iron oxide grain coatings. A wide variety of redox-sensitive and other metals are deposited from groundwaters in the coatings during shallow burial (Zielinski et al., 1983; Cave and Harmon, 1997). The trace elements may be co-precipitated with the iron oxides, but at least in the case of selenium they may be adsorbed from solution, and both natural and artificial iron oxides are used to remove Se from groundwaters for environmental clean-up (Balistrieri and Chao, 1990;

Ziemkiewicz et al., 2011). Tellurium and gold are similarly adsorbed from water by iron oxides (Ran et al., 2002; Qin et al., 2017). Consequently, the trace element chemistry of the coatings can aid the exploration for regional metal anomalies (Schmidt Mumm et al., 2013), and the leaching of the coatings is hypothesized to be a critical stage in the generation of metalliferous ore fluids in sandstones (Rose and Bianchi-Mosquera, 1993; Metcalfe et al., 1994). In the context of trace element fluxes, the coatings provide a measure of the elements that are available in continental environments. In most cases, the contents of trace elements in the grain coatings are too low to be detectable. However, red sandstones commonly contain reduction spheroids, in which the trace elements leached from the grain coatings in a reduced spherical volume can become concentrated in a central mineralized core during burial diagenesis (Harrison, 1975; Hofmann, 1991, Fig. 1). The spheroids, which occur in red beds back to the Mesoproterozoic, are attributed to microbial activity (Hofmann, 1990, 2011; Parnell et al., 2016a). This is based on widespread reduction in modern soils by Fe(III) reducing bacteria which strip off the iron oxide grain coatings (Lovley, 1997), and which can mobilize and concentrate a range of trace elements (Coates et al., 1996). The mineralized cores provide a detectable signature of the trace elements in the grain coatings. More generally, the cores are evidence that trace elements were available in mobile form to the environment. Thus, they have potential value in recording the availability of trace elements in continental environments in deep geological time.

The trace elements that are concentrated within reduction spheroids are particularly those that are redox-sensitive, and are mobile in oxidizing conditions but become precipitated in authigenic minerals in reducing conditions. They therefore ‘fix’ the elements that are being

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Fig. 1. Reduction spheroids with dark cores rich in metals and semi-metals. A, Belt Supergroup, Montana, USA; B, Sibley Group, Ontario, Canada.

transported through the continental environment during their passage from weathering to the oceans or lakes. In Phanerozoic rocks, the metals most commonly concentrated in the spheroids are vanadium, copper and uranium (Harrison, 1975; Hofmann, 1991), whose mobility is highly redox-sensitive. However, the concentrations of other scarcer elements can be informative. Reduction spheroids have been found variably enriched in gold, silver, platinoids and rare earth elements. Many spheroids contain selenides (Hofmann, 1991; Spinks et al., 2014), and enrichments in Te also occur (Parnell et al., 2016b). Both Se and Te are redox-sensitive and both can be concentrated in iron oxides (Harada and Takahashi, 2009) so may be enriched in red beds. However, Se dissolves in water more readily than Te over a wide range of redox conditions, as Se(VI) has a relatively high solubility. This reflects greater affinity of Te(IV) and Te(VI) to Fe(III) hydroxides than Se(VI), due to the formation of inner-sphere complexes of Te(IV), Te(VI) and Se(IV) to Fe(III) hydroxides while Se(VI) forms outer-sphere complexes (Harada and Takahashi, 2009; Qin et al., 2017). It has been suggested that the ratio of the two elements reflects redox conditions (Schirmer et al., 2014), whereby Te/Se increases with more oxidizing conditions, although this model awaits support through laboratory experiments.

A critical aspect of the late Palaeoproterozoic-Mesoproterozoic sedimentary record is the marked abundance of red beds (Turner, 1980; Goodwin, 1996). The widespread distribution of continental red beds bears comparison with younger episodes in the Devonian (Old Red Sandstone) and Permo-Triassic (New Red Sandstone). In each case the red beds are predominantly the products of sedimentation in arid and semi-arid climates, where redox conditions favour the precipitation of iron (III) oxides during early diagenesis. The aridity reflects continentality (e.g. Morón et al., 2014), as in the case of Permian red beds

developed on the Pangea continent (Gibbs et al., 2002). The palaeogeography of the Palaeoproterozoic-Mesoproterozoic has been elucidated by palaeomagnetic and zircon provenance studies (Pisarevsky et al., 2014). There is a consensus for an increase in continentality through the Proterozoic, and supercontinent development especially over the period 1.9–1.2 Ga (Ernst, 2009; Condie and Aster, 2010; Piper, 2013). Red beds may also have occupied a broader range of climatic zones in the Precambrian, before the development of land plants and soils rich in organic matter (Chukhrov, 1973).

Despite their age, reduction spheroids and other reduction phenomena have been recognized in many Mesoproterozoic successions, including the Belt Supergroup, Montana, USA (Hargrave and Lonn, 2011), Sibley Group, Ontario, Canada (Rogala et al., 2007), Apache Group, Arizona, USA (Spencer and Richard, 1995), Keweenaw Supergroup, Michigan, USA (Mitchell and Sheldon, 2010), Thule Group, northern Greenland (Dawes, 1997) and Canada (Jackson, 1986), Eriksfjord Formation, southern Greenland (Tirsgaard and Øxnevad, 1998), Satakunta Sandstone, Finland (Kohonen et al., 1993), Collier Group, Western Australia (Martin and Thorne, 2004), and the Stoer Group, Scotland (Spinks et al., 2010). We expect that they occur elsewhere but are unrecognised or unrecorded. It is evident that in some of these occurrences, the spheroids are markedly abundant (e.g. Tirsgaard and Øxnevad, 1998).

This study reports analysis of reduction spheroids in several Mesoproterozoic successions, to determine if Se and Te could be detected, and if so whether they occur at high levels of enrichment. The behaviour of Te in sedimentary rocks is not well documented, so data for the distribution of Te-bearing diagenetic phases is valuable.

## 2. Methodology

Samples of Mesoproterozoic massive, horizontally bedded red siltstone, and one late Palaeoproterozoic red sandstone, containing reduction spheroids (Fig. 1) were collected from four regions:

- (i) Samples of Mesoproterozoic Belt Supergroup, USA, collected at two distinct localities in the Spokane Formation, at Flesher Pass and Sieben Ranch (about 25 km apart), Lewis and Clark County, Montana.
- (ii) Samples of Mesoproterozoic Sibley Group, Ontario, Canada, drilled through winter ice on Lake Superior in Nipigon Bay about 120 km east of Thunder Bay (UTMs E 4,25,430 and N 54,10,540).
- (iii) Samples of Mesoproterozoic Stoer Group, Scotland, UK, collected at Culkein (National Grid Reference NC 043329).
- (iv) Samples of late Palaeoproterozoic Tawallah Group, McArthur Basin, Northern Australia collected from diamond drill cores DD91-RC18 and 14MCDDH002, archived at the Northern Territory Geological Survey drill core library facility in Darwin, NT, Australia.

Samples were examined using electron microscopy and laser ablation-inductively coupled plasma mass spectrometry (LA-ICP-MS).

High-resolution element mapping and semi-quantitative mineralogy of Tawallah Group reduction spheroids were determined using a Zeiss Ultra Plus field emission gun Scanning Electron Microscope (FEG-SEM), fitted with a Bruker XFlash 6 energy-dispersive spectrometer at the CSIRO Australian Resource Research Centre (ARRC) Advanced Characterisation Facility, in Perth, Australia. Samples were mounted on slides and analysed by energy-dispersive X-ray spectroscopy at ~6 mm working distance. Standard analytical conditions were an accelerating voltage of 10–20 kV and a beam current of 690 pA. Data were collected and processed with the Bruker Esprit Quantax software package.

LA-ICP-MS analysis of a Stoer Group spheroid was performed using a UP213 laser ablation (LA) system (New Wave, Fremont, CA) coupled to an Agilent (Wokingham, UK) 7500ce inductively coupled plasma mass spectrometer (ICP-MS). LA-ICP-MS was tuned for maximum

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