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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

sensitivity and stability using standard SRM 612 for trace elements in glass (NIST, Gaithersburg MD), optimising the energy fluence to about 2 J/cm². A semi-quantitative calibration for Te and Se was provided using MASS-1 Synthetic Polymetal Sulfide (USGS, Reston, VA). Samples and the standard were analysed using a 100 µm diameter round spot moving in a straight line at 50 µm s⁻¹. A 15 s laser warm-up preceded 30 s of ablation (1.5 mm) and 15 s delay. ⁸²Se and ¹²⁵Te were monitored for 0.1 s each. Three lines were analysed for each sample or standard. The average count signal over 20 s of the ablation was calculated for each element and subtracted by the average signal over 10 s for the initial gas blank. The standard was used to calculate the concentration (µg g⁻¹)/counts ratio, which was multiplied by the sample counts to estimate concentration.

LIBS data was collected with an Applied Photonics LIBS-8 module equipped with an Innolas SpitLite Compact 200 Q-switched Nd-YAG laser and 8 spectrometers operating in the range 182–1009 nm. The samples was analysed at 180 mJ power with a 1 Hz repetition rate, 1.1 ms integration time, 2 µs delay time and 250 µm spot size. 49 analyses were taken on a 7 × 7 grid. Calibration curves for Se and Te were constructed by comparing the laboratory certified values with the LIBS-determined values of reference standards, with the 49 unknown values analysed against the resulting chemometric regressions.

3. Results

The microscopic studies show that the spheroids contain a range of mineral inclusions, representing concentration of trace elements, including Te and Se. The inclusions are generally micron-scale or smaller, with no distinctive habit except one case where laths are recognized.

- I. SEM study of spheroid cores from both Belt Supergroup localities showed abundant inclusions of tellurides up to micron-scale (Fig. 2). In a sample from Flesher Pass, an iron oxide-rich core contains grains of mercury telluride, copper selenide (with traces of Te), lead selenide and mercury selenide, and also coffinite and barite. The core of a sample from Sieben Ranch shows abundant mercury telluride, copper telluride, lead selenide and rare gold telluride.

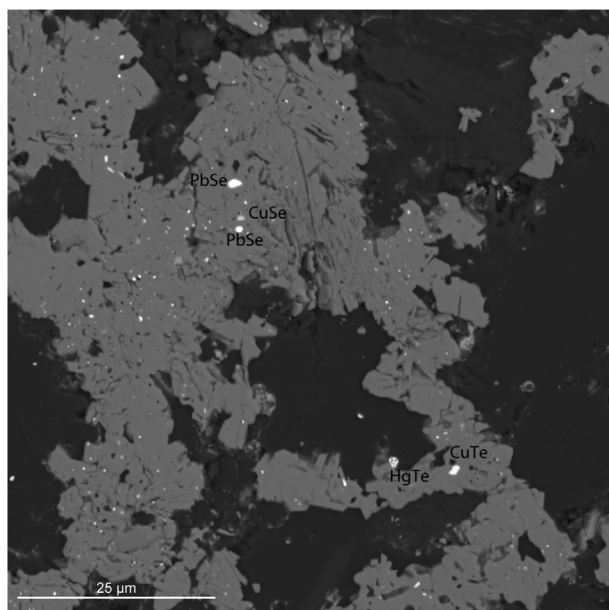


Fig. 2. Scanning electron micrograph of reduction spot core, Belt Group, Montana, showing numerous micro-inclusions (bright) in a matrix of iron oxide. Selected inclusions analyse as lead and copper selenides (upper field) and copper and mercury tellurides (lower field). Field width 100 µm.

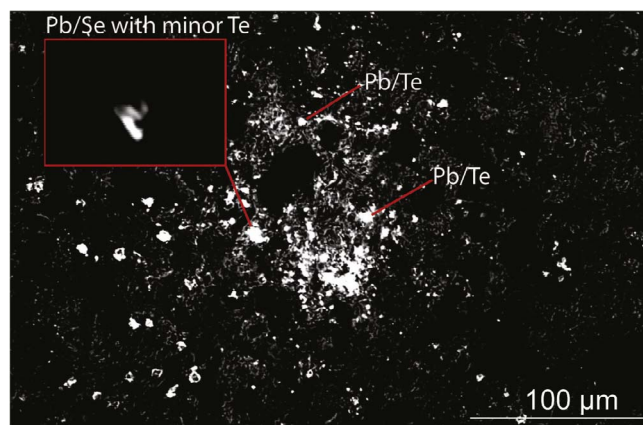


Fig. 3. Scanning electron micrograph of core of reduction spheroid, Sibley Supergroup. Dark matrix is predominantly rocoelite (vanadian phyllosilicate); bright phases in the core are all lead telluride (Pb/Te) and lead selenide (Pb/Se) minerals.

- II. SEM study of spheroid cores from the Sibley Group show a range of authigenic mineral phases. Micron-scale inclusions (Fig. 3) of lead telluride were identified, and also clausthalite (some with traces of Te) and coffinite, in a matrix of rocoelite.
- III. No telluride minerals were detected in a reduction spheroid core from the Stoer Group. However, LA-ICP-MS mapping of the core shows a Te enrichment, increasing towards the centre of the core, where it is 1 to 2 orders of magnitude enriched relative to the core margin. No detectable enrichment was observed for Se, meaning in practice that any enrichment was less than 5 times that at the margin. Thus, Te was enriched relative to Se by an order of magnitude.
- IV. FEG-SEM study of Tawallah Group reduction spheroids shows they contain iron minerals such as siderite and chamosite, but also accessory complex bismuth-selenide-tellurium minerals. These occur as clusters of micron-scale euhedral laths of Bi-Se-Te minerals within the reduction spheroid cores (Fig. 4). The Se/Te ratio in these minerals varies from 1 to 2. There are additionally lead selenides and tellurides.

The very small size of inclusions prohibited precise quantitative analysis, but except where Te occurs as traces in a selenide, the tellurides appear to be pure and so probably of formulae PbTe, HgTe, Cu₂Te and AuTe₂. These minerals indicate that the elements occur mainly as Te²⁻ and Se²⁻ ions.

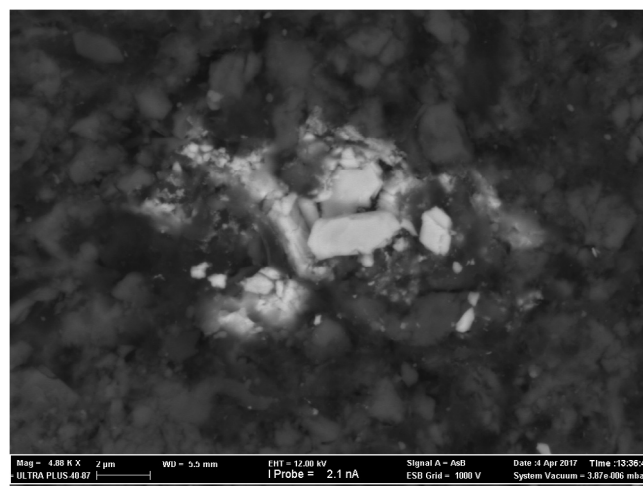


Fig. 4. Scanning electron micrograph of bismuth-selenium-tellurium-bearing phase (bright) in siliciclastic matrix in reduction spheroid, Tawallah Group, Australia.

Table 1
Te/Se ratios for reduction spheroids and reference compositions.

	Te (ppm)	Se (ppm)	Te/Se	Method/Refs.
Spheroids				
Belt Supergroup	32.73	43.00	0.76	LIBS
Sibley Group	0.8	3.0	0.27	LA-ICP-MS
Stoer Group	0.3	1.2	0.25	LA-ICP-MS
Tawallah Group	0.3	0.5	0.60	LA-ICP-MS
Reference				
Bulk Silicate Earth	0.01	0.08	0.14	Wang and Becker (2013)
Siliciclastic sediments	0.03	0.19	0.18	Schirmer et al. (2014)
All sedimentary pyrite	0.63	19.5	0.03	Gregory et al. (2015)
Mesoproterozoic sedimentary pyrite	0.31	12.2	0.03	Gregory et al. (2015)

Quantitative analyses of Te and Se in the cores are reported in Table 1. Cores were measured over an area of about 1 mm², much larger than the inclusions, so there is little significance to the values of Te and Se, but Te/Se ratios indicate relative degrees of enrichment.

4. Discussion

4.1. Concentration of tellurium

Tellurium is a rare element, 3–4 times as rare as gold, at a mean crustal content of about 1 ppb (Rudnick and Gao, 2003). The few measurements available for sedimentary rocks are generally at sub-0.1 ppm level (Belzile and Chen, 2015), excluding slow-growing sea floor crusts (Hein et al., 2003). The occurrence of discrete Te minerals in the spheroids is, therefore, exceptional. Apart from the seafloor crusts, telluride minerals are not widely recorded in other diagenetic environments. However, the incorporation of Te in diagenetic pyrite in black shales (Large et al., 2015) and oil reservoirs (Parnell et al., 2015a), and in secondary alteration minerals (Frost et al., 2009) shows that Te is at least locally mobile in low-temperature environments. Tellurium enrichments in all five localities indicate that Te concentration in this setting is a normal, ubiquitous process.

The concentration of Te has also been recorded in the cores of much younger reduction spheroids, of Palaeozoic and Mesozoic age (Parnell et al., 2016a,b). However, the abundance of discrete Te minerals observed in some of the Mesoproterozoic examples has not been observed in younger samples. A single case of a telluride mineral was recorded in a survey of Triassic-hosted reduction spheroids in the British Isles (Parnell et al., 2015c, 2016b). We cannot be certain that this difference between Mesoproterozoic and younger samples is actually age-related. Nevertheless, it can be concluded that the process by which Te was concentrated in the Phanerozoic was already active a billion years earlier in the Mesoproterozoic. Also, a supply of Te must have been available in either the groundwaters or the host sediment. The occurrence of a gold-bearing phase in a spheroid in the Belt Supergroup is also comparable with gold-bearing phases found in younger spheroids (Parnell et al., 2016b). The oxygen level in the atmosphere at that time was already adequate to allow the weathering of sulphides on the continents, and the liberation of associated trace elements from the sulphides (Reinhard et al., 2009).

The Te/Se ratios of 0.25 to 0.76 measured in the spheroids (Table 1) is greater than recorded in most sedimentary rocks, including siliciclastic sediments (mean ratio 0.18, n = 14) (Schirmer et al., 2014), sedimentary pyrite in black shales (mean ratio 0.03) (Gregory et al., 2015) and the bulk silicate Earth (ratio 0.14) (Wang and Becker, 2013). These data emphasize the relative enrichment of Te in the Mesoproterozoic samples. Notably sedimentary pyrite in Mesoproterozoic black shales, formed in a reducing environment, has a much lower Te/Se ratio

of 0.03 (Gregory et al., 2015) (Table 1). The possible use of the Te/Se ratio as a paleo-redox indicator (Schirmer et al., 2014) was provisionally attributed to surface oxidation of Te (IV) to Te (VI), but no equivalent oxidation of Se (IV), causing preferential enrichment of Te relative to Se (Hein et al., 2003). However, Kashiwabara et al. (2014) determined experimentally that Te(VI) is incorporated into ferrihydrite by co-precipitation, as the Te(VI) octahedron is similar to Fe(III) but unlike the Se(VI) tetrahedron, and Te(IV) is not oxidized by ferrihydrite, indicating that the variations in the Te/Se ratio are yet to be fully understood. From another perspective, at lower oxygenation levels, Te might be more readily sequestered into reducing environments than at higher oxygenation levels. This is consistent with the occurrence of Te enrichments in Proterozoic reduction spheroids reported here. Notably, Fe(III) reducing bacteria that are implicated in the leaching of iron oxide grain coatings, can concentrate both Se and Te (Klonowska et al., 2005; Kim et al., 2013).

There remains the question of why such a rare element as Te should be concentrated to the degree observed. The high concentration could reflect anomalous availability. Tellurium and gold are present at relatively high levels in Archean and Palaeoproterozoic rocks, often together as gold telluride minerals (e.g. Bierlein et al., 2006; Helt et al., 2014; Large et al., 2015; Rezeau et al., 2017). As these older rocks were being eroded into Mesoproterozoic sediments, as evidenced from age data for detrital zircons (Hawkesworth and Kemp, 2006; Parnell and Lindgren, 2016), Te and Au would have been recycled into the surface environment. Although they do not have distinctive habits, the mineral grains are, however, clearly neofomed from groundwaters during burial diagenesis, not simply concentrations of placer minerals eroded from the source rocks. A placer origin for the tellurides can be excluded for multiple reasons, including (i) an absence of the most common heavy minerals such as zircon and garnet; (ii) a selective distribution of tellurides in the cores of reduction spheroids, although the rest of the host rock has the same grain size; (iii) a size range for the telluride grains less than one tenth of the detrital grains in the host rock; and (iv) grains of several different metallic tellurides in close proximity within a single spheroid in the Belt Supergroup samples.

4.2. Red bed reservoir of trace elements

Although the atmosphere was sufficiently oxygenated to cause the formation of red beds containing haematite, the oxygen level may still have been well below 1% PAL (Present Atmospheric Level) in the Mesoproterozoic (Canfield, 2014; Planavsky et al., 2014), and reduction of the haematite would have occurred more readily than in Phanerozoic rocks. This is consistent with the widespread distribution of Mesoproterozoic reduction spheroids and their abundance. Oxygen penetration into the subsurface, where spheroids develop, would have been relatively shallow, promoting redox boundaries. Shallow penetration of oxygen is highlighted by the record of weathering profiles, which shows depths mostly less than 10 m in the mid-Proterozoic (Zbinden et al., 1988; Mitchell and Sheldon, 2009). If redox boundaries were more abundant in the Mesoproterozoic, possibly a greater proportion of the available redox-sensitive elements were precipitated, and thereby fixed, in red beds compared to the Phanerozoic. Reducing conditions at shallow levels would engender an efficient sequestration of redox sensitive elements from near-surface groundwaters.

The composition of Mesoproterozoic seawater can be characterized by trace element contents in pyrite precipitated in marine black shales (Large et al., 2014, 2015). Data for Te in diagenetic pyrite indicate relatively low concentrations during the Mesoproterozoic, between higher levels in the Archean-Palaeoproterozoic and the Neoproterozoic (Large et al., 2015). Gold contents in the Mesoproterozoic oceans were, like Te contents, relatively low (Large et al., 2015), and cycling of the two elements appears to be linked, from deposition through diagenesis to metamorphism. A similar association of Te and Au occurs in Phanerozoic red beds, recorded in reduction spheroids (Parnell et al.,

2016b).

An implication of the enhanced accumulation of Te in Mesoproterozoic red beds is that a relatively low proportion reached the oceans. This possibility would have been amplified by the high continentality at that time (Condie and Aster, 2010), which would reduce the proportion of surface run-off reaching the oceans. Currently, 24% of the world continental surface has interior drainage (Lewis and Berry, 2012), but that proportion would have been greater at times of high continentality. Lower delivery of run-off and associated solute to the oceans is consistent with the lower levels of trace elements measured in marine diagenetic pyrite from this time. This has important consequences for the availability of trace elements required for the flourishing of life, including Se (Lobanov et al., 2007; Long et al., 2015), while the biological role of Te is still emerging (Ba et al., 2009). Limited delivery of trace elements to the oceans may have hindered the development of eukaryotes in marine environments (Anbar and Knoll, 2002; Scott et al., 2008), but concomitantly there would have been greater opportunity for evolution in the terrestrial environment (Parnell et al., 2015b).

5. Conclusions

Study of Mesoproterozoic reduction spheroids shows that, like those in younger rocks, they are enriched in trace elements. Our focus on Te and Se shows that:

- i. The spheroids are markedly and consistently enriched in Te.
- ii. Discrete telluride minerals were precipitated, including tellurides of mercury, copper, lead and gold.
- iii. The abundance of Te relative to Se is greater than in younger spheroids.

We speculate that the occurrence of Te in Mesoproterozoic continental sediments reflects erosion of older basement sources relatively enriched in Te.

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