Trace element content of sedimentary pyrite as a new proxy for deep-time ocean–atmosphere evolution

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Abstract

Sedimentary pyrite formed in the water column, or during diagenesis in organic muds, provides an accessible proxy for seawater chemistry in the marine rock record. Except for Mo, U, Ni and Cr, surprisingly little is known about trace element trends in the deep time oceans, even though they are critical to developing better models for the evolution of the Earth’s atmosphere and evolutionary pathways of life. Here we introduce a novel approach to simultaneously quantify a suite of trace elements in sedimentary pyrite from marine black shales. These trace element concentrations, at least in a first-order sense, track the primary elemental abundances in coeval seawater. In general, the trace element patterns show significant variation of several orders of magnitude in the Archaean and Phanerzoic, but less variation on longer wavelengths in the Proterozoic. Certain trace elements (e.g., Ni, Co, As, Cr) have generally decreased in the oceans through the Precambrian, other elements (e.g., Mo, Zn, Mn) have generally increased, and a further group initially increased and then decreased (e.g., Se and U). These changes appear to be controlled by many factors, in particular: 1) oxygenation cycles of the Earth’s ocean-atmosphere system, 2) the composition of exposed crustal rocks, 3) long term rates of continental erosion, and 4) cycles of ocean anoxia. We show that Ni and Co content of seawater is affected by global Large Igneous Province events, whereas redox sensitive trace elements such as Se and Mo are affected by atmosphere oxygenation. Positive jumps in Mo and Se concentrations prior to the Great Oxidation Event (GOE1, c. 2500 Ma) suggest pulses of oxygenation may have occurred as early as 2950 Ma. A flat to declining pattern of many biologically important nutrient elements through the mid to late Proterozoic may relate to declining atmosphere O$_2$, and supports previous models of nutrient deficiency inhibiting marine evolution during this period. These trace elements (Mo, Se, U, Cu and Ni) reach a minimum in the mid Cryogenian and rise abruptly toward the end of the Cryogenian marking the position of a second Great Oxidation Event (GOE2).

1. Introduction

Whole rock variation of trace elements (TE) — in particular Mo, U, V, Cr and Ni — in black shales deposited in marine environments have been successfully used to interpret palaeo-redox conditions on the ocean floor (Lyons et al., 2003; Tribovillard et al., 2006; Reinhard et al., 2013), including temporal changes in oxygenation of the global ocean (Holland, 1984; Anbar et al., 2007; Scott et al., 2008; Partin et al., 2013). Most of the redox sensitive TE, as well as multitude of other TE in black shales, are concentrated in early-formed pyrite (Huerta-Diaz and Morse, 1992; Large et al., 2007, 2009; Gregory et al., in press). Laser Ablation-Inductively Coupled Plasma Mass Spectrometer (LA-ICPMS) techniques developed to study zonation in the composition of pyrite (FeS$_2$) in various ore systems (Danyushevsky et al., 2011) have demonstrated how this information can be used to study potential sources of metals (Meffre et al., 2008), track changes in the chemistry of hydrothermal fluids (Large et al., 2009), determine the evolution of...
ore deposits (Thomas et al., 2011) and establish the effectiveness of pyrite as a trap for TE in contaminated sediments (Gregory et al., 2013, in press). We suggest here, that in the same way that hydrothermal pyrite tracks changes in chemistry of ore fluids, sedimentary pyrite, which is a common trace mineral in carbonaceous marine black shales (Fig. 1a–d), can be used to track first-order changes in the chemistry of seawater and ultimately oxygenation of the ocean–atmosphere system. Whereas bulk shale studies require samples of particular palaeo-redox facies (Lyons et al., 2003; Scott et al., 2008; Algeo and Rowe, 2012), the focus on early-formed pyrites developed here allows sampling of a wider range of redox conditions, enabling a more complete record of seawater variation. For this study we have analysed over 1880 sedimentary pyrites from 131 black shale samples covering 77 time intervals from 3515 Ma to present day (Supplementary Tables 1–4).

2. TE analysis of sedimentary pyrite as a proxy for seawater chemistry

2.1. Incorporation of TE in sedimentary pyrite

Sedimentary pyrite forms in seafloor muds when H₂S, produced by the microbial reduction of marine sulfate, reacts with iron to form pyrite (FeS₂), arguably by way of an iron monosulfide precursor, such as mackinawite or greigite (Rickard and Luther, 1997; Rickard, 2012). Experimental studies (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993) have shown that many TE are incorporated into the precursor iron monosulfide at an early stage, including As, Hg, Mo, Co, Cu, Mn, Ni, Cr, Pb, Zn and Cd, which are absorbed from seawater and local pore waters in seafloor muds (Larget et al., 2007, 2009; Gregory et al., in press). This TE enrichment process is controlled by the amount of pyrite produced and the amount of trace metals available from seawater and pore waters (Huerta-Diaz and Morse, 1992). However it is recognised that microbially controlled reduction and sequestration of TE and sulfate on the seafloor are complex biochemical processes. Variables like Eh/pH conditions in the sediment/water column, degree of bio-productivity and availability of preferred electron acceptors will influence which TE the microbes reduce and co-precipitate with pyrite at any given time (Kulp and Pratt, 2004; Mitchell et al., 2012).

Various textural forms of pyrite are typical of syngenetic/diagenetic sedimentary origins, including framboids, microcrystalline clusters, small nodules and layers of fine crystals (Fig. 1a–d). Late diagenetic pyrites typically overgrow earlier pyrite generations (Thomas et al., 2011; Rickard, 2012) and commonly have a rounded anhedral surface which may be expressed as elongate nodules or various spheroidal and nodular forms (Large et al., 2007, 2009). Recent studies have shown that many of the TE originally thought to be present in the structure of pyrite, are actually present as micro-inclusions (Ciobanu et al., 2009; Large et al., 2009; Deditius et al., 2011) abundant in early forms of pyrite (Fig. 1a–c). Whereas Ni, Co, and Se are commonly present in the pyrite structure, As, Cu, Zn, Pb, Bi, Sb, Ti, Mo, Ag, Cd, Mn, Hg, and Te may be either in the structure or as sulfide micro-inclusions, and Ti, V, U, Ba, Sn, W, and Cr, are invariably present within micro-inclusions of matrix material. This earliest formed inclusion-bearing sedimentary pyrite is the most TE rich, and subsequent, more crystalline generations with fewer inclusions (late diagenetic to early metamorphic) may contain lower TE concentrations and trend toward a pure FeS₂ composition (Huerta-Diaz and Morse, 1992; Large et al., 2007; Large et al., 2009; Rickard, 2012). Trace elements that are loosely held in the pyrite structure or occur as nano-inclusions (e.g., Zn, Cu, Pb, Ag, Mo) are readily expelled from the pyrite during metamorphic recrystallisation, whereas TE
that are stoichiometric in the pyrite structure (e.g., Co, Ni, As, Se) tend to remain and even become enriched during metamorphism (Large et al., 2007, 2011b).

2.2. Sample selection, rationale and analysis

In this study, samples of sedimentary pyrite were selected on the basis of: (1) metamorphic grade of the host shale, (2) texture of pyrite and (3) Co/Ni ratio of pyrite, as outlined below.

1. Black shales of mid greenschist facies or below were chosen. Post lithification metamorphism and/or hydrothermal activity leads to recrystallisation of earlier pyrite forms and commonly results in pyrite overgrowths with euhedral outer surfaces and well developed crystal growth zones with alternation of TE chemistry (Large et al., 2009, 2013; Thomas et al., 2011). These latter euhedral and zoned pyrite types have been studiously avoided in this current study, as their chemistry reflects the composition and conditions of the metamorphic or hydrothermal fluids rather than the precursor seawater chemistry during sedimentation. Samples with pyrrhotite were also rejected, as previous studies have shown a marked loss of TE during conversion of pyrite to pyrrhotite (Thomas et al., 2011).

2. Pyrite was selected that retained textures indicative of synogenesis or formation during early diagenesis. Textures indicative of diagenetic pyrite include: framboïds, microcrystalline pyrite in clouds in the shale, microcrystalline pyrite aligned parallel to bedding, small cubic euhedral and bladed crystals, small porous patches and rounded or elongate zoned nodules (Fig. 1a–d) (Huerta-Diaz and Morse, 1992; Large et al., 2007, 2009; Guy et al., 2010). Pyrite textures indicative of metamorphic and/or hydrothermal growth, including medium and large sized euhedral crystals (> 1 mm), clear crystals without inclusions, and pyrite which cuts across the bedding as blebs or veins, were not selected for analysis. Textural discrimination between diagenetic and metamorphic pyrite textures was assisted by etching pyrite with nitric acid (Large et al., 2007), coupled with the LA-ICPMS mapping technique when required (Fig. 1e–j, Supplementary Fig. 7) (Large et al., 2009, 2013; Thomas et al., 2011).

3. Chemical screening of the pyrite was undertaken following LA-ICPMS analysis. On a Co versus Ni plot, samples which showed a linear array parallel to Co/Ni = 1, and with Co/Ni < 2 were selected as suitable. This is based on previous work (Bajwah et al., 1987; Large et al., 2009) that have shown diagenetic pyrite commonly has Co/Ni < 2, whereas hydrothermal pyrite has higher Co values that trend away from the Co/Ni = 1 line. More than 80% of our data was deemed acceptable on this basis.

All LA-ICPMS analyses of pyrite were performed at the Centre for Ore Deposit and Exploration Science (CODES), University of Tasmania (see Supplementary Information for LA-ICPMS methodology). LA-ICPMS element maps clearly show those TE that are evenly distributed through the pyrite (e.g., Se in Fig. 1e), compared with those that are zoned (Cu, Fig. 1h), those with a patchy distribution (As, Fig. 1i), and those dominated by inclusions (Mo and Zn, Fig. 1f–g). The time-resolved signal of an individual LA-ICPMS analysis (Fig. 1k) provides information on the likely form of elements incorporation in the pyrite (Large et al., 2009; Thomas et al., 2011). Removal of the effects of matrix micro-inclusions leads to the pyrite compositions measured on various pyrite grains from the same black shale sample commonly exhibiting a variation of less than one order of magnitude (ppm scale), compared with the overall dataset variation of up to four orders of magnitude for any given TE (see example in Supplementary Fig. 1).

2.3. Proof of concept

Five separate lines of evidence support our contention that variations in the TE composition of early-formed sedimentary pyrite in black shales are a good first order proxy for TE variations in the ocean through time (Table 1). The physical/chemical connection between early-formed sedimentary pyrite and seawater underpins our first line of evidence. Syngenetic pyrite which forms in euxinic water columns adsorbs TE from the seawater (Huerta-Diaz and Morse, 1992) is an obvious proxy for seawater TE chemistry (Berner et al., 2013). However, diagenetic pyrite in anoxic to dysoxic bottom water conditions forms by biogenic reduction of sulfate in the pore waters of seafloor muds within the first few centimetres of the seafloor (Wilkin et al., 1996). In this environment the muds contain from 60 to 85% seawater (Baldwin and Butler, 1985; Harrold et al., 1999) and thus ensure a strong connection between pyrite chemistry and seawater chemistry, even though sedimentary clays and organic matter are likely to play a role in partitioning TE into pyrite. The seawater content of seafloor muds remains over 40% in the top 100 to 200 m (Baldwin and Butler, 1985) and thus diagenetic pyrites forming at considerable depth will maintain a seawater connection influenced by matrix interactions. The significance of matrix/pore water interaction in affecting a change in sedimentary pyrite chemistry can be evaluated from data on pyrite TE depth profiles in recent sedimentary environments from Huerta-Diaz and Morse (1990, 1992). Their data, collected from a range of anoxic to euxinic sedimentary environments in the Gulf of Mexico, shows that most TE in sedimentary pyrite increase with depth from 0 up to 100 cm depth. However, the increase is variable, depending on sedimentary environment and the TE measured, and is commonly in the range of 1.4 to 6 times (less than one order of magnitude), compared to the 2 to 4 orders of
The magnitude variation exhibited by sedimentary pyrite in our samples from different epochs and eras through time.

The second line of evidence comes from a study of the LA-ICPMS composition of a range of different textural and paragenetic pyrite types, from syngenetic, through diagenetic to metamorphic, in the Neoproterozoic Khomolkho Formation in the Lena Goldfield, Siberia (Large et al., 2007). This study demonstrated a general trend of steady to decreasing mean TE content in pyrite with time, from syngenetic to diagenetic to metamorphic through the paragenesis (Fig. 2a). The changes during diagenesis for all five TE are substantially less than one order of magnitude. This suggests that the first order (2 to 4 orders of magnitude) temporal changes are unlikely to relate to diagenesis in the seafloor muds, but more likely reflect the changes in TE content of seawater within and overlying the muds.

The third line of evidence, based on our framboid data from the Permian black shale from the Perth Basin, Western Australia, shows there is no substantial difference in the TE range (ppm) of small (\(\leq 5 \mu m\)) syngenetic framboids, compared with larger (6 to 35 \(\mu m\)) pyrite framboids (Fig. 2b). All sizes of framboids in this Late Permian black shale sample show similar TE contents (40 to 800 ppm Ni and As; 3 to 80 Mo and Se; Fig. 2b) suggesting that early-formed sedimentary pyrite is a first order recorder of TE variations irrespective of its framboid size and mode of origin (syngenetic or diagenetic).

The fourth line of evidence is exhibited in Fig. 3, which demonstrates a first order positive relationship between the LA-ICPMS TE composition of sedimentary pyrite from an actively forming sedimentary basin the Cariaco Basin on the Venezuela shelf (Lyons et al., 2003; Piper and Perkins, 2004), and the TE composition of
The current ocean enrichment in Mo, As, Ni, Zn, Cu and Se which are enriched in between 5 and 8 orders of magnitude (Supplementary Table 1). Relative to seawater, TE in Cariaco Basin pyrite are enriched in modern ocean water (http://www.mbari.org/chemsensor/summary.html). Trace elements Mo, As, Ni, Zn, Cu and Se which are enriched in between 5 and 8 orders of magnitude (Supplementary Table 1). Relative to seawater, TE in Cariaco Basin pyrite are enriched in modern ocean water (http://www.mbari.org/chemsensor/summary.html). Trace elements Mo, As, Ni, Zn, Cu and Se which are enriched in between 5 and 8 orders of magnitude (Supplementary Table 1). Relative to seawater, TE in Cariaco Basin pyrite are enriched in modern ocean water (http://www.mbari.org/chemsensor/summary.html). Trace elements Mo, As, Ni, Zn, Cu and Se which are enriched in between 5 and 8 orders of magnitude (Supplementary Table 1). Relative to seawater, TE in Cariaco Basin pyrite are enriched in between 5 and 8 orders of magnitude (Supplementary Table 1).

The final proof of concept for the approach proposed here involves comparing our data on the TE composition of pyrite with the TE content of whole rock black shale samples, particularly for Mo, which is commonly used to interpret palaeo-ocean conditions and changes in oxygenation of the atmosphere/ocean system through time (Lyons et al., 2003; Tribovillard et al., 2006; Scott et al., 2008). A small group of black shale samples from the Devonian Popovich Formation, Nevada, reveal similar down-hole trends (Fig. 4); those TE concentrated in pyrite such as Mo and Se are commonly between 10 to 100 times the whole rock value, depending on the percentage of sedimentary pyrite and organic matter in the sample.

In order to evaluate the deep time variability of TE in sedimentary pyrite in black shales, we compare Mo data on whole rock euxinic and/or organic-rich black shales from Scott et al. (2008) with our data on the Mo content of sedimentary pyrite in black shales over the same time interval (Fig. 5a and b). The two data patterns are remarkably similar, with several times more Mo in pyrite compared with the whole rock values, even though Mo is present both in the sedimentary matrix and in the sedimentary pyrite (Fig. 1) (Chappaz et al., 2014). A second comparison is made with the Ni/Fe ratio measured on whole rocks and minerals in marine Banded Iron Formations (BIFs) (Konhauser et al., 2009) (Fig. 5c and d). Again the two datasets show similar patterns, although the Konhauser et al. (2009) plot contains no Phanerozoic data due to the lack of BIFs in this era. In summary, our pyrite TE plots have reproduced the temporal trends in the previous whole rock data and confirm the value of sedimentary pyrite as a proxy for deep time variations of TE in the oceans.

3. Temporal trends in TE from sedimentary pyrite

Individual TE time curves derived from LA-ICPMS analysis of 1885 pyrite spots on 131 black shale samples are given in the Supplementary Information (Supplementary Tables 2 and 3; Supplementary Figs. 3–5). We have selected a subset of the TE to focus our discussion; Mo, Ni, Co, As and Se measured in sedimentary pyrite, and U and Cr measured in the sedimentary matrix (Figs. 6–8). In the summary figures to follow, we use a rolling TE mean to highlight the long-term TE trends (Fig. 6b–f, see also Supplementary Fig. 2) at the expense of the variation in individual sample sets (Fig. 6a). In general terms (see Mo, Ni, Co, As and Se in Fig. 6b–f), most TE exhibit significant cyclic variation of several orders of magnitude in the Archaean and Phanerozoic, but less variation on longer wavelengths in the Proterozoic. In the Precambrian, there are four general TE trends:

- Trend 1: a flat-to-broadly increasing pattern through the Archaean and Proterozoic: only Mo, Zn, Mn, and Cd show this pattern. Although this pattern is not unidirectional, it suggests that supply of these TE to the ocean has exceeded drawdown into seafloor muds through most of the Precambrian.
- Trend 2: A variable, but generally decreasing pattern through the Archaean and Proterozoic: Ni, Co, As, Te, Ti, Hg, Sb, Pb, Bi, Cr, Sn, and W. This pattern suggests drawdown has exceeded supply for the Precambrian.
- Trend 3: a general increase through the Mesoarchaean to early Paleoproterozoic followed by a decrease through the Mesoproterozoic: Se, U, and V. In the first half of the period supply exceeded drawdown, with reversal in the second half.
- Trend 4: a relatively flat pattern with no obvious trend through the Archaean and Proterozoic: Cu, Ag, and Ba. In this case TE supply and drawdown were roughly matched through the period but with perturbations.
All TE show high frequency and high amplitude variations through the Phanerozoic suggesting geologically rapid changes in ocean chemistry over this latter period of Earth history. It should be emphasised that the four trends discussed above are a first attempt to group the data, but in fact each TE shows its own individual pattern (Supplementary Figs. 3 and 5), that is probably controlled by a number of factors, which are beyond the scope of analysis here. A brief discussion of the temporal trends of the five TE shown in Fig. 6, and comparison between these pyrite TE trends and those previously published for whole rock datasets follows below.

Molybdenum (Trend 1) is a conservative TE in the current ocean, present as the soluble MoO$_4^{2-}$ species (Helz et al., 1996). The general rise in the Mo time curve (Fig. 6b) is attributed to oxygenation of the atmosphere, particularly in the Neoproterozoic and Phanerozoic, leading to increased continental oxidative weathering such that supply of Mo to the oceans exceeded the drawdown into seafloor sediments (Anbar et al., 2007; Scott et al., 2008; Dahl et al., 2011). Our time curve shows that Mo in pyrite commenced at a relatively low 0.5 to 1 ppm at 3500 Ma and increased through a series of steps to reach 10 to 70 ppm at 1000 Ma. The step up at around 2500 Ma likely corresponds to the Great Oxidation Event (GOE1) (Farquhar et al., 2001; Holland, 2006) when oxygen rose to significant levels that ultimately supported the rise in pyrite over the period 3000 to 1800 Ma; 2) followed by a rise to just under 1000 ppm through the Precambrian to 660 Ma, but most of the drop occurred in the Archaean, decreasing from around 2500–10,000 ppm to just under 1000 ppm through the Palaeoproterozoic. This pattern, also seen in Ni/Fe ratio in BIFs (Fig. 5c), is attributed to cooling upper mantle and decreased eruption of Ni-rich komatiite ultramafic rocks from about 2700 Ma (Konhauser et al., 2009).

Nickel (Trend 2) is a nutrient TE present as Ni$^{2+}$ in the modern ocean. The Ni time curve (Fig. 6c) shows an overall decrease through the Precambrian to 660 Ma, but most of the drop occurs in the Archaean, decreasing from around 2500–10,000 ppm to just under 1000 ppm through the Palaeoproterozoic. This pattern, also seen in Ni/Fe ratio in BIFs (Fig. 5c), is attributed to cooling upper mantle and decreased eruption of Ni-rich komatiite ultramafic rocks from about 2700 Ma (Konhauser et al., 2009). Cobalt (Trend 2) shows a similar pattern to Ni, but with more variation (Fig. 6d). Most of the segments on the time curve when Ni and Co in pyrite exceeds 1000 ppm and 500 ppm respectively, overlap with episodes of Large Igneous Province (LIP) eruptions of mafic lavas and associated intrusives, both subaereal and submarine (Prokoph et al., 2004) (Fig. 7). The komatiitic LIPs of the Archaean are particularly enriched in Ni and Co, and thus contributed to the sustained high levels of Ni and Co to the global oceans and sedimentary pyrite (Fig. 7). The highest Phanerozoic Ni and Co were measured in sedimentary pyrite of 250 Ma from the Perth Basin Western Australia; values up to 48,000 ppm Ni and 16,000 Co were recorded, indicating the likelihood of widespread enrichment of the global ocean in Ni and Co due to the Siberian Trap eruptions. It is noteworthy that these Siberian eruptions are associated with the largest nickel ore bodies on Earth, Norilsk and Talnack.

Arsenic (Trend 2) (Fig. 6e) also exhibits a declining trend through the Precambrian. However, the As pattern has two segments; 1) a continuous decrease from a mean of 5000 to 300 ppm in pyrite over the period 3000 to 1800 Ma; 2) followed by a rise to 10,000 ppm at 1400 Ma and fall to the Cryogenian TE trough, rising again at GOE2 around 660 Ma. The cause for the sharp decline in As through Late Archaean and Early Proterozoic is not source-rock controlled, as unlike Ni and Co, As is not enriched in ultramafic or mafic rocks (Reimann and Caritat, 1998), and alternative As-bearing Archaean source rocks are not known. A possible explanation for the As trend relates to the fact that As forms a soluble arsenate complex (HAsO$_4^{2-}$) in oxic to anoxic ocean conditions and soluble polysulphide complex (H$_2$AsS$_3$) in euxinic ocean conditions (see Supplementary Table 5). Thus higher levels of volatile elements, S and As, associated with a degassing Earth in the Archaean, may have contributed to stable arsenic polysulphide complexes in the mainly H$_2$S-bearing Archaean ocean, which declined in concentration through the Early Proterozoic as H$_2$S levels in the ocean dropped and As was drawn-down into seafloor pyrite. An increase in As through the Mesoproterozoic (Fig. 6e) supports a switch to anoxic conditions as the SO$_4^{2-}$/H$_2$S ratio of the ocean continued to increase, followed by an As decline as euxinic conditions took hold again in the Neoproterozoic (Poulton and Canfield, 2011).

Selenium (Trend 3) (Fig. 6f), like Mo, is sourced from the oxidative weathering of continental pyrite, with release of selenite and selenate species (SeO$_3^{2-}$ and SeO$_4^{2-}$; see Supplementary Fig. 6), which accumulate in the ocean. Selenium is a nutrient TE, with
significant biological uptake and eventual accumulation on the seafloor in both organic matter and by substitution for S in sedimentary pyrite (Diener and Neumann, 2011; Mitchell et al., 2012). Se shows strong narrow peaks around 3000 and 2500 Ma, rising to a flat trend between 2500 and 1700 Ma, with a major perturbation from 1800 to 1300 Ma, then declines to a trough at 900 to 660 Ma, before rising again at GOE2. The stoichiometric substitution of Se for S in pyrite, its homogeneous distribution in sedimentary pyrite (Fig. 1e, Supplementary Fig. 7), high enrichment in pyrite versus the black shale matrix (Supplementary Table 4), low variability in pyrite from the same sample (Supplementary Fig. 1), and tendency to remain in pyrite even after significant recrystallisation (Large et al., 2007; Thomas et al., 2011), indicate the Se content of sedimentary pyrite may be a superior oxygenation proxy compared to other commonly used proxies, as further discussed below.

3.1. Selenium as a proxy for deep time atmosphere–ocean oxygenation

In Fig. 8 we compare the temporal trend of Se in pyrite with Mo, U and Cr, three of the commonly employed whole rock proxies for atmosphere–ocean oxygenation (Anbar et al., 2007; Scott et al., 2008; Partin et al., 2013; Reinhard et al., 2013). All four redox-sensitive TE show related trends through the Archean and Proterozoic.

The temporal trend of U (Fig. 8c) is broadly similar to Se (Fig. 8b), stepping up through the late Archean and Early Proterozoic to a broad peak around 1700–1400 Ma, and then decreasing into the Cryogenian TE trough from 1000 to 660 Ma. The broad U peak around the mid Proterozoic may relate to the abundance of hot U-bearing granites in the Paleo- and Mesoproterozoic (Wilson and Akerblom, 1982; Wyborn et al., 1992) that would have presented an enriched source rock of U for the contemporary oceans. Chromium (Fig. 8d), like Ni and Co (Fig. 7), is elevated in the
Fig. 7. Intervals of major LIPs (Prokoph et al., 2004), juxtaposed with the time curves for Co and Ni. Most highs for Ni and Co in sedimentary pyrite coincide with the periods of high numbers of LIPs (green bars). The extreme minimum in Ni and Co around 400 Ma is a good match for a period of minimum LIP activity from 300 to 500 Ma, whereas the maximum at 250 Ma matches the Siberian Trap LIP eruptions.

Archean due to the abundant ultramafic/mafic crustal components and shows a decline from 2200 to 1200 Ma before rising to a plateau around 800 Ma. The Cr data shows a very similar trend to that recently published for organic-rich shales using whole-rock analytical techniques (Reinhard et al., 2013).

Through the Archean, Se (Fig. 8b) averages around 10 ppm in pyrite but with a spike at 2970 Ma and steps upwards between 2650 and 2500 Ma. The latter steps, to over 100 ppm Se, are many tens of millions years earlier than the accepted position of GOE1 between 2450 to 2300 Ma (Farquhar et al., 2001; Holland, 2006; Pufahl and Hiatt, 2012) and suggest earlier oxygenation pulses (Anbar et al., 2007; Wille et al., 2007; Scott et al., 2008). The spike at 2970 Ma, which is from pyrite in black shales from the Witwatersrand Basin, may define the first pulse of global oxygenation, and supports other recent evidence for an oxygenation pulse determined by Cr isotopes and redox sensitive TE in the Pongola Supergroup (Crowe et al., 2013). From 1700 to 700 Ma, Se shows a gradual decline (Fig. 8b). This trend suggests the possibility of a gradual drop in atmosphere oxygen through the Meso- and Neoproterozoic but with minor perturbations (particularly at 1700 to 1300 Ma). Our U and Cr curves measured on the black shale matrix (Fig. 8c and d) show a similar decreasing trend during this period, consistent with published whole-rock data (Partin et al., 2013). Reinhard et al. (2013) have calibrated the palaeoredox proxies Cr and Mo in the Proterozoic to delineate anoxic settings, where Cr is reduced and buried, compared to euxinic settings, where both Cr and Mo are reduced/sulfidised and buried. On this basis, our data (Fig. 8a and d) may be interpreted to suggest that anoxic settings were dominant in the Proterozoic from 2150 to 700 Ma, whereas euxinic settings (anoxic + H2S) were dominant from 1200 to 800 Ma. This interpretation fits with the concept of decreasing atmosphere oxygenation through the Meso- and Neoproterozoic, with minimum O2 levels around 800 Ma, corresponding to the Cryogenian TE trough.

Fig. 8. Temporal trends of a, Mo in sedimentary pyrite, b, Se in sedimentary pyrite, c, U in shale matrix, and d, Cr in shale matrix; measured by LA-ICPMS displayed as a 19 point rolling mean.

3.2. TE deficiency in the Meso- to Neoproterozoic Oceans

Anbar and Knoll (2002) present the hypothesis that under the conditions of a deep sulfidic ocean for most of the Meso- and Neo-
proterozoic (Canfield, 1998) nutrient TE would be scarce, thus limiting the ecological distribution of eukaryotic algae and adversely effecting marine evolution. Our data on the biologically important nutrient TE (Mo, Zn, Co, Cd, Se, Ni, Ag, Mn, U, V and Cr; Supplementary Figs. 3–5) supports this hypothesis and shows that although these TE exhibit various trends in detail, they all show a relative depletion from 1200 to 700 Ma compared to their early Phanerozoic values, and in most cases their Neoarchean to Palaeoproterozoic values. For the redox sensitive TE that are employed as atmosphere–ocean oxygenation proxies, Mo, U, Cr and Se there are two possible causes for these trends; (1) low values of these TE represent gradual drawdown of these elements in a predominantly sulfidic deep ocean (Anbar and Knoll, 2002; Reinhard et al., 2013), with limited renewal by continental erosion due to low levels of tectonic activity over the period 1800 to 700 Ma. Atmospheric oxygen remains constant in this scenario (Canfield, 2005; Holland, 2006) Alternatively, (2) the decline in these redox sensitive TE signal a gradual decrease in atmosphere oxygenation from 1800 to 800 Ma, with the lowest O2 levels forming the Cryogenian TE trough between 800 and 660 Ma, prior to the rise at GOE2. Other workers (Shen et al., 2003; Planavsky et al., 2011; Poulton and Canfield, 2011; Partin et al., 2013) provide evidence for sustained low levels of O2 during the mid Proterozoic, although none have suggested a significant O2 decline during this period.

In considering these two scenarios, there is little evidence to support a static tectonic regime, as this period of the middle to late Proterozoic saw the amalgamation (1300–1000 Ma) and breakup (900–700 Ma) of the super continent Rodinia (Li et al., 2008; Condie et al., 2011). Active erosion during these events would involve a continuous supply of nutrient TE to the oceans. However the normalised $^{87}$Sr/$^{86}$Sr curve of riverine runoff compared with mantle influence (Shields, 2007), indicates a decline in erosive supply of Sr which parallels the Se and U time curves. On the other hand, low O2 may have caused the nutrient deficiency, which is corroborated by carbon isotope evidence for low productivity (Anbar and Knoll, 2002). Canfield (2005) suggests that atmospheric oxygen rose to a level of 5 to 10% Present Atmospheric Level (PAL) around 1800 Ma and remained constant until about 700 Ma. Planavsky et al. (2011) suggest a lower level of 1 to 10% PAL throughout the Meso- and Neoproterozoic. Based on our data, and these previous estimates, we speculate that atmospheric O2 may have decreased from a level around 10–20% PAL at 1800 Ma to the Cryogenian TE trough at 1–5% PAL between 800 and 660 Ma (Fig. 9).

4. Strengths, weaknesses and caveats of sedimentary pyrite proxies for ocean chemistry

The TE variation in sedimentary pyrite, determined by LA-ICPMS, has the potential to enable the development of several ocean–atmosphere proxies through time including: ocean TE chemistry, ocean pH, ocean sulfate content, ocean–atmosphere oxygenation, ocean anoxic events, ocean productivity and ocean hydrothermal activity. Although there are strengths associated with this approach, there are also several weaknesses and caveats.

4.1. Strengths

Sedimentary pyrite concentrates many of the redox sensitive and nutrient TE, in particular, Se, Mo, Cu, Ni, Ag, As, Cd, Co, Mn, Sb well above their content in the sedimentary matrix of black shales (Fig. 4, Supplementary Information). This means, that by using the LA-ICPMS technique, the minimum (down to ppb levels) and maximum (over wt% levels) of TE in pyrite can be measured accurately, enabling proxies for both maximum and minimum levels of TE in the oceans to be developed. This has not been previously possible. The LA-ICPMS technique used here enables 22 TE to be analysed simultaneously. This enables the trends of a suite of redox sensitive elements (e.g., Mo, Se, U, Ni, Ag and Cr) to be compared on the same sample set. Furthermore, TE in both the pyrite and sedimentary matrix are quantified, and thus TE concentrated in the matrix, (e.g., U, V, W, Sn and Ba) can also be tracked through time.

Pyrite analyses involve only one mineral, and thus there are less complications than whole rock analyses of black shales, where TE are partitioned amongst a number of minerals and organic matter, of varying proportions, plus seawater and pore fluids. Sedimentary pyrite forms in black shales from sub-oxic to euxinic environments, and thus sampling is not restricted to a particular redox facies in order to apply the technique. This enables a much larger population of black shales to be included in deep time research. A detailed petrographic study of sedimentary pyrite allows the effects
of late diagenesis, metamorphism and hydrothermal overprints to be fully assessed and thus avoided in sample selection.

4.2. Weaknesses

Sedimentary pyrite develops both in the water column (syngenetic) and in the sea floor muds (diagenetic), and yet the technique proposed here does not take into account the modification of seawater TE chemistry by interaction with minerals, other than pyrite, in the muds. Our analyses are a mixture of syngenetic and early diagenetic framboidal pyrites plus nodular pyrites that developed during late diagenesis, probably several meters below the seafloor. Diagenetic nodular pyrite that forms during late diagenesis, commonly contains lower TE concentrations (Fig. 2; Large et al., 2007), but no more than an order of magnitude less than syngenetic and early diagenetic pyrite in the same sedimentary unit. We argue that seawater is the principal component of pore fluids, and as framboidal pyrite develops in the top few centimetres of the muds, when seawater is >60% of the muds, then a strong chemical connection between pyrite and seawater is maintained. These assumptions apply in the use of strontium, carbon and oxygen isotopes of sedimentary carbonate as a proxy for their respective isotope variations in the palaeo-ocean (Veizer et al., 1999; Shields and Veizer, 2002).

The TE in early formed (syngenetic and early diagenetic) pyrite can be strongly modified by later diagenetic, metamorphic or hydrothermal processes and thus have little relationship to the original seawater chemistry. This is a major issue, especially for those elements loosely held in the pyrite structure, such as Mo (Chappaz et al., 2014). However, the approach proposed here is to undertake petrographic studies of pyrite textures in order to screen out samples with evidence of metamorphic and hydrothermal influences (e.g., Thomas et al., 2011). Selenium in pyrite is very robust to metamorphic influences and is the best of the redox sensitive TE (Fig. 9). Black shales and associated pyrite are of little use as seawater proxies for samples above middle greenschist facies due to major TE exchange with metamorphic fluids (Pitcairn et al., 2006; Large et al., 2011b).

Our data indicate a wide variation in the TE content of sedimentary pyrite from the same sample. However, many TE show a variation of less than one to two orders of magnitude. This degree of variation could be considered to relate to ocean TE variation, or to the inherent variability of syngenetic and early diagenetic pyrite, and the effects of diagenesis and low-grade metamorphism. The variation of one order of magnitude in a single sample is significantly less than the variation of up to 4 orders of magnitude in the full dataset through time. Studies on single drill core (Supplementary Fig. 1) show the variation in individual samples compared to the mean variation through a stratigraphic section, and clearly demonstrate that robust trends in the TE are related to stratigraphic position.

In addition to the concentrations of TE in seawater, a number of other factors may have an effect on the TE content of diagenetic pyrite, including: the matrix composition of the sediment, the amount of pyrite produced, pH of pore fluids, degree of biodegradivity and preferred electron acceptors. Although these factors are assumed here to have a second order effect, they each need further evaluation.

4.3. Caveats

The most coherent TE data on early-formed sedimentary pyrite is obtained by the analysis of pyrite framboids, and these must be the first priority in any analytical strategy. However many black shales of greenschist facies do not contain framboidal pyrite, but may contain diagenetic nodules or partially recrystallised framboids. Great care is required to record the textural and paragenetic changes in pyrite in order to undertake analyses on the early-formed pyrite or their partially recrystallised equivalents.

In order to place pyrite TE analyses in a temporal context, high quality geochronology is required. For Phanerozoic samples, fossil assemblages can yield detailed chronological resolution. In Precambrian settings, the U–Pb analysis of zircon can provide high quality constraints on the timing of eruption of tuffs and/or maximum depositional ages for silt- and sand-dominated strata that may be interbedded with black shale sequences. U-bearing authigenic mineral phases also provide at least a minimum age of deposition of the host rocks, and in some cases may date diagenesis. Where available, we have preferred chronological constraints based on these techniques in order to minimise uncertainties related to whole rock dating methods, however the age resolution and uncertainties vary significantly (Supplementary Table 2). A major caveat of any temporal analysis such as this is the accuracy and resolution of chronological constraints.

5. Conclusions

The use of sedimentary pyrite as a proxy for TE trends in the palaeo-ocean has opened a new window into deep time, and presents exciting possibilities. Several lines of evidence indicate that for any particular black shale depositional environment, syngenetic pyrite that forms in the water column and diagenetic pyrite that forms in the top few meters of the seawater-saturated muds, will have a similar first order TE composition that relates to the TE composition of the seawater at that time. Processes during diagenesis do not substantially change the mean first order TE content of sedimentary pyrite. However, metamorphic processes that cause recrystallisation of pyrite and conversion to pyrrhotite at moderate to high metamorphic grades, may be accompanied by major changes in many TE concentrations. Therefore, this study has concentrated on early-formed (syngenetic to diagenetic) pyrite and avoided samples with obvious metamorphic or hydrothermal pyrite and/or pyrrhotite.

Our data suggest that for most TE, temporal variations in concentration have been over 2 to 4 orders of magnitude. The concentrations of some TE, like Ni, Co and Cr, generally decrease through time, but with significant variation, commonly related to changes in the composition of the exposed crust. Other redox sensitive TE like Mo and Se, generally increase through time, and are principally controlled by oxygenation trends in the ocean-atmosphere system.

A schematic diagram of our major findings is given in Fig. 9. This figure uses the Se content of sedimentary pyrite as a proxy for variations in atmosphere oxygenation. This proxy is based on the premise that oxidative weathering of pyrite in continental rocks leads to the release of selenium as both the selenate and selenite species. Under neutral to alkaline oxygenated conditions the selenate species remains highly soluble, where it can be readily transported via river systems to the ocean. However under low oxygen conditions, continental weathering releases little soluble Se, because the reduced forms of Se (selenide, elemental Se0 and organo-selenium complexes) are relatively insoluble. Thus significant increases in atmospheric oxygen, accompanied by active erosion, can lead to a major increase in the supply of soluble Se to the ocean, to be subsequently trapped in sedimentary pyrite in seafloor muds.

The Se curve derived from sedimentary pyrite, along with curves for other redox sensitive TE (e.g., Mo, U, Ti, Mn, Cd, Ag), show significant increases in TE abundance of one to two orders of magnitude at GOE1 and GOE2 (Fig. 9). However our data for some TE shows sharp rises prior to GOE1, suggesting pulses of...
oxygenation commenced as early as 2970 Ma. Through the Proterozoic, TE variations in sedimentary pyrite are subduced, compared with the Archaean, suggesting steady state or declining oxygen levels reaching a minimum in the Cryogenian prior to GOE2. From 1800 to 700 Ma a number of biologically important TE (e.g., Se, Cr, Mo, Cu, Ni, Mn) show a flat to decreasing trend suggesting that nutrient TE deficiency may be the reason for limited eukaryotic development and radiation, thus adversely affecting marine evolution during the middle to late Proterozoic. This period ended with the Sturtian glaciation, and from 700 to 540 Ma many of the redox sensitive TE rose by 1 to 2 orders of magnitude in response to GOE2, accompanied by diversification of photoplankton and the appearance of eukaryotic clades (Shields-Zhou and Och, 2011); the prelude to the Cambrian Explosion.

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Appendix A. Supplementary material

Supplementary material related to this article can be found on-line at http://dx.doi.org/10.1016/j.epsl.2013.12.020.

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References


