Cycles of nutrient trace elements in the Phanerozoic ocean

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A R T I C L E   I N F O
Article history:
Received 19 June 2015
Received in revised form 27 June 2015
Accepted 27 June 2015
Available online xxx
Handling Editor: M. Santosh

Keywords:
Sedimentary pyrite
Palaeo-ocean chemistry
Mass extinction
Ocean nutrients
Metalliferous shales
Evolution

A B S T R A C T
Availability of nutrients in the ocean can be a major factor affecting bioproductivity, burial of carbon and release of oxygen. However, the nutrient trace element (TE) composition of the palaeo-ocean cannot be measured directly. Here we present a comprehensive global dataset on the TE content of marine sedimentary pyrite in black shales, dating back 700 million years, and demonstrate a systematic cyclic evolution of pyrite TE composition with time. The nutrient TE, molybdenum, selenium, cadmium and thallium measured in pyrite, and phosphorus measured on whole rock, rise sharply at 560 to 550 Ma followed by several cycles of TE variation through the Palaeozoic and into the Mesozoic. A number of factors could explain the trends. We suggest that variations in continental uplift, erosion and nutrient flux rates were possible drivers of the oceanic nutrient cycles. The cyclic patterns through the Phanerozoic suggest periods of nutrient-rich oceans that fostered key evolutionary events, followed by nutrient-poor oceans that encompass several major mass extinction events.

1. Introduction
The concentrations of bio-essential trace elements (TE) in the ocean have had a major influence on evolutionary processes through time (Saito et al., 2003; Williams and Frausto Da Silva, 2003; Knoll et al., 2006; Morel, 2008). However, little data is available on the composition of the palaeo-ocean because it cannot be studied directly. Some constraints on the composition of the palaeo-ocean have been obtained from bioinformatic analyses of modern bacteria (Dupont et al., 2006, 2010), thermodynamic modelling (Saito et al., 2003; Zerkle et al., 2005; Anbar, 2008) and analyses of ancient marine sedimentary shales (Scott et al., 2008; Partin et al., 2013). Thermodynamic modelling combined with shale geochemistry provides a continuous, but approximate, history of some TE, highlighting the control by oxygen concentrations in the ocean/atmosphere system (Anbar, 2008) (Fig. 1A, B). The model of a two-step atmosphere-ocean oxygenation (Canfield, 1998, 2005), predicts significant changes in concentration of redox sensitive TE at the start and end of the Proterozoic (Zerkle et al., 2005; Anbar, 2008) (Fig. 1B). Between these periods of change, TE concentrations are assumed to vary little due to an absence of direct constraints on composition of the palaeo-ocean and also a lack of detailed knowledge on atmosphere pO2 variations (Lyons et al., 2014). On the other hand, availability of nutrient elements in the ocean may have a major impact on productivity and oxygenation of both the ocean and atmosphere. Recent modelling of atmosphere oxygen in the Proterozoic (Laakso and Schrag, 2014) suggests that modern biogeochemical cycling of carbon in a phosphorus limited ocean can result in significant divergence of pO2 from the current value of present atmosphere level (PAL). For example; a reduction in the phosphorus ocean input flux to one tenth of the modern value will drive pO2 to less than 0.1 PAL, whereas a 10 times increase in phosphorus input flux drives pO2 to 2.5 times PAL; a 4 times increase in pyrite weathering drives pO2 to 0.5 PAL; a 10 times increase in volcanic outgassing drives pO2 to 9 times PAL. Therefore low pO2 conditions can be developed if the flux of phosphorus to the oceans is greatly reduced, and high pO2 conditions require a dramatic increase in phosphorus flux (Laakso and Schrag, 2014). The nutrient elements are supplied to the ocean by weathering and erosion of the continents, and periods of increased P supply have been linked to events of continental collision, supercontinent assembly, orogenesis and magmatism (Campbell and Allen, 2008).

Many palaeo-ocean studies investigate the TE composition of black shales as a proxy for TE nutrients in seawater (Scott et al., 2008; Konhauser et al., 2009; Partin et al., 2013; Reinhard et al., 2013), however the bulk concentrations represent mixed signals from terrigenous
material, organic matter, absorption from seawater plus diagenetic interaction of the various sediment minerals and seawater. Sedimentary pyrite is formed either in an euxinic water column or shortly after deposition by the biomediated reaction of seawater sulphate with reactive iron (Rickard, 2012). The remarkable property of pyrite to incorporate many redox-sensitive TE during growth, means that the TE content of the pyrite provides an amplified signal compared to the content of the TE in the bulk rock shales (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993; Rickard, 2012; Large et al., 2014). Measurement of TE down to parts-per-billion levels is now routine by Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS), providing an opportunity for high spatial resolution and precise quantification of a suite of important TE throughout the geological record (Large et al., 2014). In order to obtain more direct constraints on compositions of seawater and investigate the TE variations in the oceans we have developed LA-ICPMS analytical protocols to simultaneously measure 25 TE in sedimentary pyrites of different ages that can be used to track TE ocean chemistry. This has enabled us to build a comprehensive database of sedimentary pyrite chemistry in suboxic to euxinic black shales from around the globe that are well constrained by geochronology (Supplementary Information, Tables S1–S2). Here we present the data for 15 trace elements that are concentrated in pyrite, based on over 2270 individual analyses of pyrite from 192 black shale samples from 700 Ma to present day (Tables S1–S2). This current Neoproterozoic–Phanerozoic database includes 1040 additional pyrite analyses and supplements our previous database and discussion that focused on the Archean and Proterozoic (Large et al., 2014; Gregory et al., 2015a).

2. Analytical methods

Trace element analysis of sedimentary pyrite was performed using Laser Ablation-Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). All analyses were conducted at the ARC Centre of Excellence in Ore Deposits, University of Tasmania. Instrumentation used involved a 213 nm solid-state laser microprobe (UP213, NewWave Research) coupled to an Agilent 7500a quadrupole mass-spectrometer, and a 193 nm solid-state laser microprobe (UP193ss, NewWave Research) coupled to Agilent 7700s quadrupole mass-spectrometer. Laser microprobes are equipped with custom-made constant-geometry ablation cells. The following analytical parameters and conditions were used: laser beam diameter of 8–40 μm, depending on the size of pyrite grains; laser beam fluence ~ 3.5 J/cm² at the sample for UP213 and ~ 2 J/cm² for UP193ss; laser pulse rate 5 Hz; ablation occurred in the atmosphere of pure He flowing at a rate of 0.8 l/min; immediately past the ablation point within the cell, He carrier gas was mixed with Ar (0.85 l/min) for improved efficiency of aerosol transport; both ICP-MS instruments were optimized to maximize sensitivity on mid- to high-mass isotopes (in the range 80–240 amu). Further details on the LA-ICPMS method can be found in Large et al. (2014)

The porous nature of syngenetic and diagenetic pyrite resulted in a variable amount of silicate matrix being ablated together with pyrite. Quantification of the mixed pyrite/matrix signal was achieved by analysing all major elements in the mix and normalizing the total of the analysis to 100% (g/g). The composition of the silicate matrix was determined in each sample by analysing several spots around the diagenetic pyrite. With the composition of the silicate matrix known, the compositions of diagenetic pyrite were derived from the analysis of the mix using a standard mass-balance approach. Concentrations of all major silicate elements, but Fe (i.e., Al, Mg, K, Na, Si, Ti) were used to estimate the proportion of matrix in each analysis by a least squares method. All analyses with the amount of silicate matrix over 50%, or analyses where the least squares method for estimating the amount of matrix gave large errors, were excluded from the data set. Pyrite data that showed large inclusions of other sulphides was also excluded.

Fig. 1. Comparison between thermodynamic modelling estimates of Co and Mo in palaeo-ocean and mean values for each eon measured in marine pyrite. A: Variation in modelled atmospheric pO₂ (Canfield, 1998). B: Variation of Co and Mo in the oceans from thermodynamic modelling (Saito et al., 2003; Zerkle et al., 2005; Anbar, 2008). C: Variation of Co and Mo in the oceans from marine pyrite proxy measurements, based on data in Large et al. (2014) and this study.
from the dataset when Zn and Pb > 10,000 ppm, Cu > 30,000 ppm, As > 10 wt.% or Fe/S < 1.2. Analyses of recrystallized and chemically modified parts of pyrite grains that had lost most of their TE, were also removed from the dataset using the Co content, as Co is tightly held in the pyrite structure and only released after significant recrystallization (Large et al., 2007). Whole rock phosphorus was analysed by ICP-MS using an aqua regia digest at ALS Laboratories, Brisbane. The powder analysed was drilled from the same polished mounts that were used for the pyrite LA-ICPMS analyses. The lower limit of detection for P was 10 ppm.

3. Results

3.1. Cyclic trace element variations in the Phanerozoic

The variation in concentrations of redox sensitive trace elements Se, Mo, Cd and Tl measured in sedimentary pyrite show somewhat similar trends through the late Neoproterozoic and Phanerozoic (Fig. 2A, C, D). Although the measured TE variation in any given sample is considerable (Fig. 2), the mean and median values (Fig. 3B) exhibit a consistent cyclic pattern. Cobalt exhibits a very different pattern in Phanerozoic sedimentary pyrite (Fig. 2B), with Co maxima corresponding with Se, Mo, Tl and Cd minima. This is most clearly evident through the Late Devonian and Early Carboniferous, when a broad minimum in Se, Mo, Cd and Tl correlates with a broad maximum in Co (Fig. 2). This pattern is confirmed by the Spearman correlation coefficients for the pyrite dataset shown in Table 1. The Spearman correlation coefficient ($r_s$) is used here rather than the Pearson’s correlation coefficient ($r$), as the TE data relationships are not linear, nor normally distributed, but are monotonic. Se shows positive $r_s$ with Mo (0.60), Cd (0.69), Sb (0.52) and Tl (0.31), but a negative correlation with Co ($-0.37$). On the other hand, Co has all negative $r_s$ correlations with Mo ($-0.38$), Se ($-0.37$), Cd ($-0.27$), Sb ($-0.17$) and Tl ($-0.58$). In fact these are the only significant negative correlations ($<-0.2$) present in the 15 element matrix (Table 1). Although these correlations may be considered only weak to moderate, probably due to the scatter in the analytical data (Fig. 2), they are nevertheless very consistent; all five TE showing positive correlations with Se, but negative correlations with Co. Thus the opposite trends in Mo and Co in the ocean previously predicted using thermodynamic modelling (Zerkle et al., 2005; Anbar, 2008), have been replicated at the billion-year scale in the Precambrian (Fig. 1B–C), and the million-year scale in the Phanerozoic (Fig. 2B, C and Supplementary Information Fig. S2) by our studies using the TE content of marine pyrite.

Through the late Neoproterozoic, those TE with a positive correlation (Mo, Se, Cd, Tl), show a minor increase of about one order of magnitude in concentration around 640 Ma off a relatively flat background, and then rise steeply, between 560 and 540 Ma, by one to two orders of magnitude (Fig. 2). This rise represents the start of several cycles of TE increase and then decrease through the Phanerozoic. Three cycles of the order of 100 million years duration are present through the Palaeozoic, followed by two poorly defined cycles in the Mesozoic. The peaks of each cycle,
Based on Se and Mo maximum concentrations (Fig. 2) are at 520 Ma (early Cambrian), 390 Ma (early-middle Devonian), 320 Ma (Late Mississippian), 210 Ma (Late Triassic), 130 Ma (Early Cretaceous) and present day. TE minima occur at 455 Ma (Late Ordovician), 370 Ma (Late Devonian), 250 Ma (Permian-Triassic boundary), 200 Ma (Triassic-Jurassic boundary) and 90 Ma (Late Cretaceous). Modern levels of these TE suggest we are currently in the first phase of a sixth cycle. Selenium best typifies the cyclic pattern as it is tightly held in the pyrite structure, replacing S, and has the smallest sample variation of all the nutrient TE (Fig. 2). In addition to Se and Mo, other bio-essential TE show depletion at the end of cycle periods, including Cu, Zn, V, Mn and Ni (Table 2, Supplementary Information Fig. S1). Cobalt on the other hand is counter-cyclical, commonly exhibiting enrichment when the other nutrient TE are depleted, compared with mean Phanerozoic concentrations (Table 2).

3.2. Linking pyrite chemistry to ocean chemistry

Marine sedimentary pyrite, that forms in seafloor muds in anoxic to euxinic environments, has recently been proposed as a first order proxy for studying temporal variations in ocean TE chemistry (Large et al., 2014). The technique requires careful selection of samples that have suffered minimal metamorphic or hydrothermal overprints, such that the pyrite retains its original syngenetic or diagenetic form. There are several important assumptions and caveats involved in using the technique, the most important of which are discussed below.

Experimental and field studies have demonstrated that a large range of TE (As, Ni, Cu, Co, Zn, Pb, Mo, Se, Cd, Tl and Hg) are incorporated into marine pyrite during growth, by adsorption from seawater and local pore waters in seafloor muds (Huerta-Diaz and Morse, 1992; Morse and Arakaki, 1993; Large et al., 2009; Rickard, 2012; Gregory et al., 2014). Previous work (Large et al., 2007, 2014; Berner et al., 2013) has demonstrated that late diagenetic and metamorphic processes may reduce the effectiveness of pyrite as a proxy for seawater chemistry, especially for elements that are weakly held in the pyrite structure (e.g., Mn, Pb, Cu, Zn, Ag, Cd). In contrast elements that are strongly held as stoichiometric replacements for Fe or S, are little affected by later processes (e.g., Se, Ni, Co, As).

Large et al. (2014) outlined five separate lines of evidence to support the contention that variations in the TE composition of early formed
Table 1
Spearman correlation coefficients for TE in sedimentary pyrite, phosphorus in shale matrix, Sr isotopes in marine carbonates (Viezer et al., 1999) and modelled atmosphere O2 from Berner (2009).

| Spearman | P ppm | O2 by Berner | 87/86 Sr | Mn ppm | Co ppm | Ni ppm | Cu ppm | Zn ppm | As ppm | Se ppm | Mo ppm | Ag ppm | Cd ppm | Sb ppm | Te ppm | Ti ppm | Pb ppm | Bi ppm |
|----------|-------|--------------|----------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| P ppm    | 1     | 0.45         | 0.21     | 0.31   | 0.073  | 0.41   | 0.31   | 0.25   | -0.03  | 0.34   | 0.14   | 0.27   | 0.31   | 0.085  | 0.3    | 0.11   | 0.11   | 0.21   |
| O2 by Berner | 0.45  | 1             | 0.29     | 0.32   | -0.05  | 0.27   | 0.24   | 0.24   | 0.19   | 0.25   | 0.23   | 0.33   | 0.31   | 0.26   | 0.2    | 0.33   | 0.26   | 0.1    |
| 87/86 Sr | 0.21  | 0.29         | 1        | 0.055  | -0.22  | 0.17   | 0.023  | 0.069  | 0.071  | 0.14   | -0.009 | 0.28   | 0.043  | 0.33   | 0.023  | 0.37   | 0.17   | 0.058  |
| Mn ppm   | 0.31  | 0.32         | 0.055    | 1      | 0.079  | 0.2    | 0.59   | 0.75   | 0.14   | 0.26   | 0.37   | 0.38   | 0.45   | 0.16   | 0.53   | 0.05   | 0.29   | 0.55   |
| Co ppm   | 0.073 | -0.05        | -0.22    | 0.079  | 1      | 0.36   | 0.23   | 0.15   | -0.063 | -0.35  | -0.39  | 0.03   | -0.24  | -0.19  | 0.27   | -0.58  | 0.5    | 0.5    |
| Ni ppm   | 0.41  | 0.27         | 0.17     | 0.2    | 0.36   | 1      | 0.47   | 0.26   | 0.064  | 0.3    | 0.15   | 0.52   | 0.26   | 0.31   | 0.32   | 0.032  | 0.38   | 0.22   |
| Cu ppm   | 0.31  | 0.24         | 0.023    | 0.59   | 0.23   | 0.47   | 1      | 0.66   | 0.19   | 0.36   | 0.22   | 0.65   | 0.47   | 0.28   | 0.63   | -0.016 | 0.5    | 0.58   |
| Zn ppm   | 0.25  | 0.24         | 0.069    | 0.75   | 0.15   | 0.26   | 0.66   | 1      | 0.12   | 0.34   | 0.39   | 0.46   | 0.53   | 0.21   | 0.61   | 0.027  | 0.31   | 0.66   |
| As ppm   | -0.03 | 0.19         | 0.071    | 0.14   | -0.063 | 0.064  | 0.19   | 0.12   | 1      | 0.22   | 0.35   | 0.2    | 0.67   | 0.29   | 0.3    | 0.11   | 0.12   |
| Se ppm   | 0.34  | 0.25         | 0.14     | 0.26   | -0.35  | 0.3    | 0.36   | 0.34   | 0.22   | 1      | 0.62   | 0.53   | 0.69   | 0.55   | 0.41   | 0.31   | -0.084 | 0.12   |
| Mo ppm   | 0.14  | 0.23         | -0.009   | 0.37   | -0.39  | 0.15   | 0.22   | 0.39   | 0.62   | 1      | 0.19   | 0.61   | 0.33   | 0.29   | 0.42   | -0.15  | -0.037 | 0.42   |
| Ag ppm   | 0.27  | 0.33         | 0.28     | 0.38   | 0.03   | 0.52   | 0.65   | 0.46   | 0.35   | 0.53   | 0.19   | 0.1   | 0.51   | 0.62   | 0.56   | 0.26   | 0.42   | 0.47   |
| Cd ppm   | 0.31  | 0.31         | 0.043    | 0.45   | -0.24  | 0.26   | 0.47   | 0.53   | 0.2    | 0.69   | 0.61   | 0.51   | 1      | 0.47   | 0.41   | 0.31   | 0.033  | 0.23   |
| Sb ppm   | 0.085 | 0.26         | 0.33     | 0.16   | -0.19  | 0.31   | 0.28   | 0.21   | 0.67   | 0.55   | 0.33   | 0.62   | 0.47   | 1      | 0.3    | 0.41   | 0.18   | 0.2    |
| Te ppm   | 0.3   | 0.2          | 0.023    | 0.53   | 0.27   | 0.32   | 0.63   | 0.61   | 0.29   | 0.41   | 0.29   | 0.56   | 0.41   | 0.3    | -1     | 0.092  | 0.4    | 0.73   |
| Ti ppm   | 0.11  | 0.33         | 0.37     | 0.05   | -0.58  | 0.032  | -0.016 | 0.027  | 0.3    | 0.31   | 0.42   | 0.26   | 0.31   | 0.41   | -0.092 | 1      | -0.13  | -0.3   |
| Pb ppm   | 0.11  | 0.26         | 0.17     | 0.29   | 0.5    | 0.38   | 0.5    | 0.31   | 0.11   | -0.084 | -0.15  | 0.42   | 0.033  | 0.18   | 0.4    | -0.13  | 1      | 0.64   |
| Bi ppm   | 0.21  | 0.1          | 0.058    | 0.55   | 0.5    | 0.22   | 0.58   | 0.66   | 0.12   | -0.037 | 0.47   | 0.23   | 0.2    | 0.73   | -0.3   | 0.64   | 1      |
sedimentary pyrite in black shales are a good first order proxy for TE variations in the ocean through time: (1) Previous published data (Huerta-Diaz and Morse, 1992; Wilkin et al., 1996) indicate that pyrite framboïds develop within the top few centimetres of anoxic seawater-saturated muds, and that their TE contents exhibit second order variations with depth, which are far less than the overall variation of first order the earliest syngenetic pyrites in the same sample, diagenetic and early metamorphic pyrite types (Large et al., 2007, 2009; Gregory et al., 2015b).

(2) in a detailed study of syngenetic, early diagenetic, sedimentary pyrite in our samples from different epochs and eras through time; and (3) sedimentary pyrite concentrates many important TE used as palaeo-environmental proxies, with parallel trends but at several orders of magnitude higher than whole rock values.

Individual black shale samples show scatter in TE values in pyrite commonly up to one and rarely two orders of magnitude (Fig. 2). This high variability is not surprising considering the multiple pathways of pyrite formation (Rickard, 2012) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010). Other factors related to pyrite growth at the micro-scale are also likely to give rise to TE variability, including: a) exchange of TE between syngenetic pyrite and diagenetic pore waters in the seafloor muds (Berner et al., 2013), b) late diagenetic and early metamorphic recrystallization of sedimentary pyrite which releases certain TE from the pyrite structure (Large et al., 2014), c) and natural variability of trace element concentrations in the world ocean (Nozaki, 2010).
content of As, Mo and Sb, whereas framboidal pyrite interpreted to form during diagenesis has a different composition with a high content of Cu, Ni, Co, Pb, Bi and Tl. However statistical treatment of our greater than 3000 pyrite analytical dataset demonstrated that there is no significant systematic difference between framboidal and small euohedral varieties of pyrite in black shales (Gregory et al., 2015b).

Even after careful screening, including exclusion of samples with a metamorphic grade above lower greenschist (chlorite facies), significant scatter remains in the LA-ICPMS data for pyrite grains in individual shale samples. In order to display the micro-scale TE scatter and also focus on longer-term temporal trends between samples, the geometric mean values have been overlain on the time series plots (Fig. 2). The Se in pyrite geometric mean, arithmetic mean and median values for given time intervals, compared with the raw spot-data for all samples shows similar trends and cycles (Fig. 3B) and provides confidence in the TE trends discussed here.

Another issue we have considered is whether the measured pyrite chemistry reflects just local TE ocean variations or is a first order representation of the global ocean chemistry at the time of shale deposition. We have addressed this question by comparing the pyrite TE data from black shales of similar age (within 5 to 20 million years), but from widely different global locations, taking into account supercontinent arrangements at the relevant times. This exercise shows first order TE agreement for most samples of similar age irrespective of their local location (Fig. 3C; Table S3). For example, samples in the 540–550 Ma interval, from north west Tasmania and Massachusetts USA have the following comparison of mean values; Se (12 and 13 ppm), Mo (31 and 4 ppm), Co (363 and 654 ppm) and Ni (1040 and 581 ppm). Samples from the 370–380 Ma interval located in north Western Australia and the Yukon Canada have Se (4 and 21 ppm), Mo (43 and 35 ppm), Co (371 and 217 ppm) and Ni (214 and 586 ppm). Table S3 shows a more comprehensive list and indicates a TE variation, in widely located pairs of similar age, of commonly less than one order of magnitude (and well within the one standard deviation).

Micronutrient TE and phosphorus

Micronutrient elements that are critical for life in the oceans include Fe, Zn, Cu, Co, Mn, Mo, Se, Cd and Ni (Sunda, 2010). Other than Fe, temporal trends in the other micronutrients have been inferred from this study of marine pyrite chemistry (Figs. 2 and S1). As mentioned previously, the most robust micronutrient TE data is obtained for Se, Co and Ni as these are relatively tightly held in the pyrite structure. However, over and above these micronutrients, phosphorus is of crucial biological importance due to its role in fundamental biochemical reactions involving genetic material (DNA, RNA) and energy transfer in cells (Sunda, 2010). Phosphorus and the micronutrients are principally sourced by chemical weathering and physical erosion of the continents related to tectonic uplift (Paytan and McLaughlin, 2007; Ruttenberg, 2010). River systems deliver the dissolved and particulate nutrients to the oceans, where they stimulate biological productivity, and are eventually buried with organic matter and pyrite on the ocean floor. Unlike the other nutrients, phosphorus does not reside in pyrite and is thus not measured by the LA-ICPMS technique used here. An alternative method, whole-rock solution ICPMS, was used to measure the P concentration of an area of black shale matrix adjacent to the pyrites analysed by LA-ICPMS (see Methods). The temporal trend through the Late Neoproterozoic and Phanerozoic of the P content of the shale matrix (Fig. 2F) compared with other nutrient TE (Se, Co, Mo, Cd and Tl) concentration in marine pyrite indicates the peaks in P correspond with peaks in the micronutrient TE (Fig. 2A–G). Statistical analysis (Table 1), shows a weak to moderate positive Spearman correlation between P in the shale matrix and nutrient TE in sedimentary pyrite ($r_s$: Se 0.34; P: Ni 0.41; P: Mo 0.14, P: Cd 0.31, P: Cu 0.31 and P: Zn 0.25), but a lack of correlation between P: Co (0.07).

Apatite, organic matter, ferric oxyhydroxides and some clay minerals are the potential hosts for P in the black shale matrix (Ruttenberg, 2010). In our shales, limited whole-rock geochemistry, suggests that the P is present in organic matter, REE phosphate minerals and apatite. The P concentration in sedimentary rocks is controlled by sedimentary environment, and a substantial fraction of P redissolves in pore waters and cycles back to the ocean. Consequently the P-content of sediments is difficult to link to the P-content of contemporaneous seawater (Follini, 1996). However P concentrations in the ocean show good correlations with several nutrient elements (Se, N, Ba), with a particularly good correlation with Cd (Elderfield and Rickaby, 2000; Bryan and Marchitto, 2010). The positive Spearman correlations between Se, Cd, Ni and Cu in marine pyrite with P in the shale matrix (Table 1), coupled with the positive correlations between P, Se and Cd in the modern ocean, suggest that our measure of temporal trends of Se in marine pyrite may serve as a first order proxy for both P and micronutrient TE concentrations in the ocean. On this basis, using Se in pyrite as the general nutrient proxy (Fig. 4), we may divide the Phanerozoic ocean into three periods; 1) nutrient-rich periods (above the geometric mean plus one multiplicative standard deviation for Se), 2) average nutrient concentration periods (geometric mean $+/−$ one standard deviation), and 3) nutrient-poor periods (below the geometric mean minus one standard deviation).

The nutrient-rich periods are (Fig. 4): Latest Ediacaran to Late Cambrian, Early–Middle Devonian, Middle to Late Carboniferous, Middle Permian and Oligocene to present. The nutrient-poor periods, which in many cases include mass extinction events, are; Mid to Late Ordovician, Late Devonian to Early Carboniferous, Early Jurassic to Early Cretaceous and Late Cretaceous. The counter-cyclical nature of Co means that the nutrient-rich oceans contain low Co and nutrient-poor oceans contain high Co. Considering our full list of nutrient TE, not all nutrients follow the same patterns of enrichment and depletion. For example in the Latest Ediacaran to Middle Cambrian, Se, Ni, Zn, Mo, Cd and V are all enriched well above their mean values, whereas in the Early–Middle Devonian only Se, Ni and V are enriched above their mean values (Table 2). Our general lack of sedimentary pyrite samples through the Mesozoic and Cenozoic, compared with the Palaeozoic means that our interpretations of this latter period are less robust.

Ocean residence times

The residence time for a TE is the amount of time that a TE resides in the ocean before it becomes fixed in the seafloor sediments. It is calculated by dividing the total amount of the given TE in the ocean, by the rate of input by rivers. Residence time is thus directly related to the solubility of an element in the ocean. The four redox sensitive micronutrient TE (Mo, Se, Cd, Tl) are soluble under oxic ocean conditions as chemical species (Nozaki, 2010) $\text{MoO}_4^{2−}$, $\text{SeO}_4^{2−}$ and $\text{Se}_2\text{O}_7^{2−}$, $\text{CdCl}_2^−$, and $\text{Tl}^+$ with long residence times of 760,000 years (Mo), 50,000 years (Cd), 26,000 years (Se) and 21,000 years (Tl) (Monterey Bay Aquarium Research Institute, 2014). All these residence times are well in excess of the global mixing time of the modern ocean (~1000 years) and suggest a relatively homogenous distribution of these TE was likely throughout the Phanerozoic ocean on the scale of sample time intervals used here. However Co, which in oxic conditions exits as the less soluble $\text{Co}^{2+}$ species, has a much shorter residence time (340 years) (Monterey Bay Aquarium Research Institute, 2014), indicating relatively rapid deposition upon entering an oxic ocean like the present (Figs. 1, 2; Supplementary Information). Thus Co content of pyrite will most likely record a local basin signal, whereas Se, Mo, Cd and Tl will record a global ocean signal.

Supply and burial of TE

The TE cycles recorded in marine pyrite through the Phanerozoic, resulting from regular periods of nutrient enrichment followed by
nutrient depletion, are likely due to a number of complex inter-related factors that may be considered simply as supply factors and burial factors. Nutrient-rich periods result when TE and P supply exceeds TE and P burial, and similarly nutrient-poor periods result when burial exceeds supply. Two key supply factors are 1) physical erosion rates, related to eustatic uplift and climate, and 2) chemical weathering rates related to rock composition, atmosphere composition and environmental conditions. A third supply factor, seafloor hydrothermal flux, is considered relatively insignificant for most TE compared to the first two factors (Elderfield and Schultz, 1996; Laakso and Schrag, 2014; Jeandel and Oelkers, 2015). Burial rates include a number of interrelated factors; rates of biological productivity, residence times for nutrients, rates of biological uptake of nutrients, solubility of nutrient species, inorganic scavenging rates, and rates of organic matter and pyrite burial. In the thermodynamic models used to estimate nutrient TE trends in the palaeo-oceans (Saito et al., 2003; Zerkle et al., 2005), only the solubility of TE relative to their sulphides, was considered.

Considering supply factors, Sr isotopes in marine carbonates have been previously suggested as a proxy for continental uplift, chemical weathering and erosion rates (Brass, 1976; Palmer and Elderfield, 1985; Veizer et al., 1999). The marine Sr isotope ratio represents a balance between continental and seafloor hydrothermal flux of Sr, as well as the Sr isotope composition of the predominantly weathered continental Sr (Veizer et al., 1999; Tripathy and Singh, 2010). A comparison of the Sr isotope record with our marine pyrite Se curve (Fig. S4) shows some points of similarity, but in general a poor correlation exists between Sr isotopes in marine carbonates and Se in marine pyrite (Spearman correlation rs = 0.14), indicating that other factors, such as the Sr isotope record with our marine pyrite Se curve (Fig. S4) shows some points of similarity, but in general a poor correlation exists between Sr isotopes in marine carbonates and Se in marine pyrite (Spearman correlation rs = 0.14), indicating that other factors, such as the Sr isotope composition of the predominantly weathered continental crust, are involved in effecting the Sr isotope ratio, which may be proxies for silicate weathering (independent of redox), compared with the trace elements from pyrite, which may be a better proxy for oxidative sulphide weathering, particularly from mafic rocks.

Changes in oxygen content of the atmosphere, is another factor that may contribute to the flux of nutrient TE. This possibility is indicated by the fact that redox sensitive TE (Se, Mo, Ti, Cd), which are released from pyrite during oxidative weathering, become more soluble and easily transported under oxidised conditions. They have a long residence time in the modern oxygenated ocean and all show a positive Spearman correlation the late Neoproterozoic and Phanerozoic. However other nutrient TE, particularly Co, which becomes immobilised during pyrite oxidation due to absorption by Fe and Mn oxyhydroxides, and has a short residence time in the ocean, have a negative Spearman correlation with the other redox sensitive TE (Table 1). This suggests the possibility that O2 levels in the atmosphere are a contributing factor promoting an increase in oceanic abundance of readily oxidised TE (Mo, Se, Cd, Sb, Ti), whilst at the same time promoting a decrease in the poorly oxidised and scavenged TE (Co, Mn).

Although pyrite is readily oxidised under all likely pO2 levels in the Phanerozoic, it is the solubility of the redox sensitive species that controls their flux to the ocean. The flux of mobile Co2+ decreases as O2 rises whereas the flux of the oxidised species of Mo, Se, Cd, Sb and Ti increases as O2 rises, assuming constant erosion rates (see Supplementary Information).

4. Discussion

In order to better understand the TE cycles in the Phanerozoic it is necessary to step back into the Neoproterozoic where major oxygenation and TE variation likely began, following the relatively stable period of the Mesoproterozoic (Brasier and Lindsay, 1998; Brasier and Lindsay, 2014). Most geochemical and isotopic proxies point towards a global oxygenation event in the late Neoproterozoic to Precambrian–Cambrian transition (Fike et al., 2006; Canfield et al., 2007; Scott et al., 2008; Och and Shields-Zhou, 2012; Sahoo et al., 2012) as the most important trigger for the evolution of life on Earth (Nursall, 1959; Canfield and Teske, 1996; Catling et al., 2005), notwithstanding some researchers who maintain the opposite view that...
evolution of life was responsible for the rise in oxygen (Butterfield, 2009). The driver behind this major oxygenation is thought to be the fragmentation of the supercontinent Rodinia and assembly of Gondwana during the late Neoproterozoic (Donnadieu et al., 2004; Halverson et al., 2007), interrupted by two global glaciations (so called “Snowball Earth” events) that temporarily drove oceans to anoxic conditions (Kirschvink, 1992). Oxygenation during Rodinia breakup is thought to reflect the low-latitude arrangement of the continental masses at this time, concentrating nutrient delivery along newly developing passive margins via intense tropical weathering of uplifted cratonic margins (Halverson et al., 2007). Through the Neoproterozoic the Se, Mo and Cd micronutrients and the P macronutrient all show a rise at 600 Ma (Fig. 2), followed by 50 million years of relatively rapid variation, including the Marinoan Snowball Earth period, then fall to lower levels at 600 Ma. At 560 Ma most redox sensitive micronutrients and P rise rapidly to a peak in the Early Cambrian at 520 Ma, before falling to strongly depleted values between 470 and 445 Ma at end Ordovician. The inference here is that the nutrient-rich oceans coincide with elevated atmosphere O₂, and the nutrient-poor oceans coincide with reduced levels of atmosphere O₂. The rapid rise in nutrients (both redox sensitive TE and P), of commonly more than an order of magnitude, from 560 to 520 Ma, coincides with the latter period of development of the one of largest orogenic belts on the planet, the East African-Antarctic orogen, which formed by the collision of different parts of proto-East and West Gondwana. The orogenic belt is over 8000 km long and 1000 km wide, extending north–south through the centre of Gondwana (Stern, 1994; Jacobs and Thomas, 2004). Weathering and erosion during uplift of this giant orogen, and other major Gondwana-forming orogenic belts of Pan-African age, may well account for the order of magnitude increase in global oceanic nutrients at 560 to 520 Ma, promoting a dramatic increase in productivity and release of O₂ to the atmosphere, and eventually stimulating the Cambrian Explosion (Squire et al., 2006; Campbell and Squire, 2010). During the late Cambrian, a period of global ocean euxinia and carbon isotope excursion (Steptoean Positive Carbon Isotope Excursion or SPICE) at around 500 Ma (Gill et al., 2011) immediately follows the peak in ocean nutrients at 520 Ma, and may relate to a period when burial of carbon and nutrients exceeded continental supply following the end of the East African-Antarctic orogenetic event.

Within the Phanerozoic, the periods of nutrient-rich oceans (Fig. 4) correspond with global scale plate collision and continent up-lift events, major bio-evolutionary events and carbon- and TE-rich marine sedimentation (Table 2, Fig. 5). The peak of the first nutrient-rich ocean around 555–510 Ma corresponds with the East African-Antarctic orogenic event, the onset and peak of the Cambrian explosion exemplified by the Chengjiang (c. 520–515 Ma; Zhang et al., 2008) and Burgess Shale faunas (c. 510–505 Ma; Marshall, 2006), and strongly metalliferous and carbonaceous Cambrian shale deposition (e.g., southern China, Sweden, and NE Australia; Table 2). The peak in the second nutrient cycle around 410–380 Ma in part corresponds with the termination of main phase of orogenesis in Appalachian–Caledonian system the major evolutionary rise of tetrapods and deposition of metalliferous carbonaceous Early Devonian shales (e.g., Popovich Formation, Great Basin USA and the Canol Formation, Yukon Canada; Table 2). The third nutrient cycle peak at 330–310 Ma corresponds with the early Pangea assembly, the Appalachian (Hercynian) orogenetic event, the radiation of amphibians and a period of widespread deposition of metalliferous carbonaceous Carboniferous shales in North America (e.g., Linton Formation, Sikiilik Forma-
tion, Heath Formation, Mecca Quarry Shale, USA; Table 2). The next nutrient peak at 280–260 Ma relates to the main phase of Pangea assembly — including widespread orogenesis in marginal regions (e.g., Central Asian orogenic belt and Terra Australis Orogen), diversification of reptiles, and deposition of metalliferous and phosphorus-rich shales in the Middle to Late Permian (Kupferschiefer, northern Europe; Phosphoria Fm., USA.), and the fifth peak around 150 Ma in the Late Jurassic coincides with the Alpine orogenetic event, the appearance of the first birds, and Oxfordian metalliferous carbonaceous shale deposition typified by the Bazhenovskaya Formation in Russia. The final nutrient-rich ocean is at the present day, corresponding to start of Amasia (also termed Neo-Pangea) assembly, and the first members of the genus Homo.

Nutrient TE depletion at the end of each Phanerozoic cycle corresponds closely with the timing of major Phanerozoic mass extinction events (Fig. 4), particularly those coinciding with severe Se-depletion during the Late Ordovician, Middle–Late Devonian and at the Triassic–Jurassic boundary, where micronutrients may have dropped below critical thresholds necessary for sustaining most marine life (Long et al., in review). Bio-essential trace elements that become deficient at these same times, to levels of at least one order of magnitude below mean Phanerozoic ocean levels, include Se, Mo, Cu, Zn, V, and Mn (Tables 2, S2). As outlined above all significant Phanerozoic TE-, P- and carbon-rich shales studied by us have ages close to or coinciding with nutrient-rich oceans. Black shales with deposition ages within the nutrient poor periods are commonly TE-, P-poor compared with the Phanerozoic mean values (Tables S2, S3).

Models of ancient global O₂ cycles involve geochemical proxies such as carbon, sulphur or their isotope ratios, and incorporate estimations of carbon and sulphur, burial rates and various other factors (Berner et al., 2000; Bergman et al., 2004; Falkowski et al., 2005). The most long-standing model (Berner and Canfield, 1989; Berner, 2009) shows variation in O₂ in the atmosphere during the Phanerozoic period to have ranged between 0.7 to 1.7 PAL (1 PAL = 20.1 wt.% O₂), following a broad sinusoidal cycle, with an increase at ~300 Ma assumed to be related to the rise in vascular land plants, followed by a decrease to a minimum at ~180 Ma and then a rise to the present day (Fig. 3A). This modelled oxygen curve (Berner, 2009) shows a somewhat similar pattern to our Se time series curve (Fig. 3A), taking into account the variable spacing of our data. The four major oxygen minima in the Berner model (at 470, 380, 240 and 180 Ma) correspond within 10 million years to the Se minima in our pyrite data (Fig. 3A). The standout oxygen maxima in the Berner model in the mid Permian, at 270–310 Ma, overlaps with the two Se peaks at 320 Ma and 270 Ma. The other Se cycle maxima correlate with the modelled second order O₂ peaks at 520, 410 and 220 Ma. Notwithstanding these visual similarities, the Spearman correlation coefficient is only 0.25 (Table 1), suggesting a complex interplay of factors affecting atmosphere O₂ that are not fully captured by the Se in pyrite proxy.

Recent modelling of atmospheric oxygen in the Proterozoic (Laakso and Schrag, 2014) shows that the flux of O to the ocean has a very marked effect on long term pO₂ levels. Order of magnitude changes in pO₂ result from order of magnitude changes in continental erosion rates or weathering rates of pyrite. This research emphasised a factor that is very relevant to the discussion here; low pO₂ conditions can be developed if the flux of nutrients to the oceans is greatly reduced, and high pO₂ conditions require a dramatic increase in nutrient flux (Laakso and Schrag, 2014).

5. Conclusions

Our dataset of 3020 marine pyrite analyses in black shales from around the globe reveals that the redox sensitive trace elements, particularly Se, Mo, Sb, Cd and Tl exhibit a first order cyclic pattern of variation through the Palaeozoic and into the Mesozoic. We interpret this variation to be a global ocean phenomenon. The trace element nutrients exhibit fairly constant minimum levels in the ocean through much of the Neoproterozoic, but rise abruptly at around 560 Ma by one to two orders of magnitude to reach peak values around 520 Ma. They then remain elevated through the Cambrian and Early Ordovician, before plunging to a minimum in the Late Ordovician (~550 Ma). This pattern of rise and fall is repeated several times through the Phanerozoic.

We suggest that this first-order cyclic variation of nutrients in the ocean, may be driven by cycles of continent uplift, associated with continental plate collisions and increased weathering and erosion rates (Fig. 5). Increased erosion related to major tectonic events, is an
effective way to deliver a higher nutrient flux to the oceans, promoting planktonic productivity and related oxygen release (Fig. 5A). The downward flux of organic-matter, P and TE burial in seafloor muds produces widespread anoxia with ultimate deposition of metalliferous and P-bearing organic-rich sediments in continental margin basins, promoting a further increase in atmosphere $p_{O_2}$. Our data suggests these coupled mechanisms may have produced nutrient-rich oceans favourable for critical evolution events and species radiation, with peaks at 520 Ma (Early Cambrian), 390 Ma (Early Devonian), 330 Ma (Late Mississippian), 280 Ma (Mid Permian) and the present day. Based on previous modelling (Berner, 2009; Laakso and Schrag, 2014), the oxygen peaks of each cycle were probably between 1.25 and 1.5 PAL, and may have resulted from a 2 to 3 times increase in the nutrient flux from the eroding continents. We suggest that the tipping point promoting a drop in nutrients may be caused when the continuing increase in TE- and P-drawdown by organic matter to the seafloor, exceeds the TE supply from continental erosion (Fig. 5B). This may lead to a relatively rapid decline in ocean nutrients, and associated productivity, causing a drop in carbon burial and consequent drop in atmosphere oxygen. Minima in the Se cycles represent periods of widespread nutrient, and consequently O2, deficiency and in extreme cases, marine mass extinction at end Ordovician, Late Devonian and the Triassic–Jurassic boundary. Modelling (Laakso and Schrag, 2014), suggests that a drop in nutrient supply by 70% will cause a drop in $p_{O_2}$ to 0.6 PAL, in keeping with Berner’s minimum values for the Phanerozoic. Recovery from this $O_2$ minimum state is probably due to the fact that although a condition of stagnation
prevailed in the oceans, erosion continued on land, thus leading to gradual nutrient build-up in the oceans that activated a rebound of marine life.

Finally, although the peaks and troughs in the TE cycles represent maxima and minima in nutrient supply, they both coincide with periods of global ocean anoxia. At the peak of nutrient supply, anoxia is driven by the rise in organic productivity, whereas in the trough of nutrient supply, anoxia is a consequence of low pO2 conditions across both atmosphere and oceans during periods of low organic productivity. This model predicts that the cycle peak anoxic events are accompanied by deposition of organic Te- and P-rich (metalliferous) shales, whereas Te-poor shales accompany the cycle trough anoxic events.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.gj.2015.06.004.

Acknowledgment

Information on the black shale samples and pyrite trace element LA-ICPMS data reported in the paper is presented in the Supplementary Tables S1–S2. The following colleagues are gratefully acknowledged for providing black shale samples toward this project: Clive Calver, Tim Lyons, Stuart Bull, Robert Scott, Sean Johnson, John Slack, Karen Kelley, Ray Coveney Jr., Marcus Kunzman, Jerry Sharrow, Kirill Ivanov, V. Lisenko and Rüdiger Stein. Critical comments on earlier drafts by five reviewers including B. Kamber and P. Cawood are very much appreciated. Funding was provided by an ARC Centre of Excellence grant L0014436, ARC Discovery Grant DP 150102578 and AMIRA International project grant P923 to RRL. PWH publishes with the permission of the Executive Director, Geological Survey of Western Australia.

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Javaux, I.M., Lisenko and Rüdiger Stein. Critical comments on earlier drafts by five reviewers including B. Kamber and P. Cawood are very much appreciated. Funding was provided by an ARC Centre of Excellence grant L0014436, ARC Discovery Grant DP 150102578 and AMIRA International project grant P923 to RRL. PWH publishes with the permission of the Executive Director, Geological Survey of Western Australia.

Geochemistry, Geophysics, Geosystems 11, Q01005.


