The rise of oxygen-driven arsenic cycling at ca. 2.48 Ga

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ABSTRACT

The Great Oxidation Event (GOE) at 2.45 Ga facilitated the global expansion of oxidized compounds in seawater. Here, we demonstrate that the GOE coincided with a sharp increase in arsenate and arsenic sulfides in marine shales. The dramatic rise of these oxygen-sensitive tracers overlaps with the expansion of key arsenic oxidants, including oxygen, nitrate, and Mn(IV) oxides. The increase in arsenic sulfides by at least an order of magnitude after 2.45 Ga is consistent with the proposed transition to mid-depth continental-margin sulfide-rich waters following the GOE. At the same time, the strong increase in arsenate content, to ~60% of the total arsenic concentration in shales, suggests that the oxidative component of the arsenic cycle was established for the first time in Earth’s history. These data highlight the global emergence of a new selective pressure on the survival of marine microbial communities across the GOE, the widespread appearance of toxic, oxidized chemical species such as arsenate in seawater.

METHODS

Drill-core shale samples, aged ca. 2.7–2.0 Ga, are from near-continental-margin deposits associated with biological activity (Table DR1; Bekker et al., 2004; Canfield et al., 2013; Martin et al., 2015; Chi Fru et al., 2015, 2016a). X-ray absorption near edge spectroscopy (XANES) was performed to evaluate the As speciation (see supplementary methods in the Data Repository). To account for variation in speciation for a given sample, location, or geological age, each sample was measured between five and 60 times. Major elements were measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES), and trace elements by ICP–mass spectrometry (ICP-MS) and ICP–optical emission spectrometry (ICP-OES) as previously described (Ngoombi-Pemba et al., 2014; Chi Fru et al., 2015). Ferric iron oxide (Fe2O3) was determined as the difference between total iron [(FeO)total] and ferrous iron (FeO). FeO was quantified by XANES. Once formed, As(V) could have been reduced back to As(III) in either the water column or sediment pile after interacting with electron donors like H2S and organic carbon.

RESULTS

We sampled marine shales from 39 deposits across 10 nearshore marine successors formed between ca. 2.7 and 2.0 Ga (Table DR1 in the Data Repository). Essentially, the sample suite was chosen based on previous studies demonstrating their usefulness as proxies for Precambrian seawater and atmospheric composition because of limited post-depositional modification (Canfield et al., 2013; Chi Fru et al., 2015, 2016a; see supplementary methods in the Data Repository). These, together with ~800 iron formation samples spanning ca. 3.8 Ga to present, were analyzed for...
As, Ti, and Fe content (Table DR2). The oxidation state of As and associated elements in shale minerals was examined by X-ray absorption near edge spectroscopy (XANES) (Fig. DR1 in the Data Repository) and X-ray fluorescence (Fig. DR2), respectively. After we excluded potential X-ray–induced oxidation of reduced As(III) species to As(V), and As(V) reduction during XANES analysis, our data revealed the following:

1. Early Paleoproterozoic shale As/Fe ratios are mostly within the Neoarchean range, rising from a minimum of $\sim 1.0 \times 10^{-4}$ at the Archean-Proterozoic boundary to a maximum of 4.0 at ca. 2.0 Ga (Fig. 1A).

2. With the exception of one sample, As(III) was exclusively below the XANES detection limit (Table DR1), implying that <15% of total As might be present as As(III). XANES spectra exhibit two prominent peaks in the 11.8695–11.8705 keV range, corresponding to As-S and As(V) species (Fig. DR1).

3. The gradual increase in total As content in marine sediments across the GOE is mainly due to As-S and As(V) enrichment (Figs. 1B–1C).

4. As-S and As(V) enrichment begins at 2.48 Ga, intensifying in the 2.32 Ga Timeball Hill Formation, South Africa (Fig. 1C), consistent with previously reported Cr and U enrichments in iron formations (Konhauser et al., 2011; Partin et al., 2013).

5. As/Ti ratios in iron formations coincide with an increase in the oxidative supply of As from land to the oceans at the GOE (Fig. 2A). A lack of strong variability in As/Fe ratios across the GOE transition (Fig. 2B) suggests that the size of the Fe pool was not a major determinant of sediment As concentration and speciation trends at this time.

6. In the Francavillian shales, Gabon, bulk As concentrations >50 ppm increase with rising Fe-oxide content (Fig. DR3A). However, there is a generally weak correlation between Fe-oxide and As concentration across the Francavillian Series. This is most prominent when As is <50 ppm (Fig. DR3A), along with a correlation between Mo and As in the sulfide-rich FD formation of the Francavillian Series (Figs. DR4 and DR5). This suggests that the rise of near-continental margin sulfidic conditions across the GOE was a critical factor controlling sediment As content and oxidation state.

7. Some Precambrian pyrite-specific As enrichments are significant (Large et al., 2014; Gregory et al., 2015), but may not represent bulk shale As concentrations (Figs. DR3B and DR3C).

**DISCUSSION**

The similar range of As/Fe ratios recorded during the early Paleoproterozoic relative to the Archean in both shales and iron formations suggests that the rise of As(V) and As-S species across the GOE cannot be explained by rapid fluctuations in the sedimentary Fe reservoir (see the Data Repository). Instead we suggest that this change is linked to the intensification of oxidative weathering of a felsic and/or As-S–rich continental crust (Konhauser et al., 2011; Large et al., 2018; see the Data Repository for details), containing up to 1500 ppm of As (Henke, 2009). The peak in As/Fe ratios in iron formations at ca. 2.48 Ga is consistent with a contemporaneous spike in Cr/Ti ratios, interpreted to reflect the onset of terrestrial aerobic sulfide oxidation (Konhauser et al., 2011). The muted GOE iron formation As/Fe signal, relative to Archean ratios, and the knife-sharp rise in the As/Ti trend across the GOE (Fig. 2A) may be related to Snowball Earth glaciations influencing continental As supply patterns (Chi Fru et al., 2015). This hypothesis is supported by the suppression of As/Fe and As/Ti ratios in Neoproterozoic iron formations (Figs. 2A and 2B; Table DR2) that are a product of submarine hydrothermal activity and a result of ice sheets restricting sediment supply and promoting water-column anoxia (Hoffman et al., 1998; see the Data Repository).

Under anoxic conditions, As and S chemistry becomes coupled, such that sulfide production scales with As-S deposition (O’Day et al., 2004; Data Repository). Arsenic sulfides, however, can be oxidized to As(V) in O$_3$-rich conditions (e.g., the case of arsenopyrite in Reaction 1).

$$4\text{AsS}_2 + 13\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{As}_4 + 4\text{FeSO}_4.$$ (1)

In addition, the formation of As(V) only occurs when relevant As(III) oxidants (e.g., O$_2$, MnO$_2$, NO$_3$) are available (Oremland and Stolz, 2003; see the Data Repository). Electron donors are required to regenerate As(III) from As(V), and as today, microbes catalyze both the oxidative and reductive reactions (Oremland and Stolz, 2003). As(V) accumulation, therefore, occurs when production rates are greater than consumption rates, likely explaining the observed rise of As(V) in the data:

Anoxogenic photosynthetic and anoxic NO$_3$-dependent chemoheterotrophic oxidation of As(III) have been proposed as the most viable mechanisms by which appreciable Archean As(V) production could have occurred (Oremland and Stolz, 2003; Sformo et al., 2014). If these processes were prominent over As(V) reduction,
a strong sedimentary As(V) signal would be expected. Our data, however, suggest that anoxic As(III) oxidation of Archean crust was limited, relative to that of post-GOE deposits. To this end, there is a significant increase in As(V) in the 2.32 Ga Timeball Hill Formation, suggesting that As(V) production outpaced consumption, compared to the period before. Further, the prevalence of As-S coincides with significant pyrite deposition in Timeball Hill black shales (Bekker et al., 2004). The strength and reproducibility of the As-S and As(V) signals (Fig. 1C) are consistent with the oxidation of terrestrial minerals containing reduced As to produce soluble As(V) that was then transported to the oceans during the GOE.

In addition to being a strong As(III) oxidant, O₂, as it accumulated in the atmosphere, would have initiated the generation of additional As(III) oxidants, including Mn(IV) oxides and NO₃⁻ (Oremland and Stolz, 2003; Roy, 2006; Zerkle et al., 2017). As expected, the elevated As-S content in shales coincides with the suggested expansion of microbial reduction of sulfate, coincident with the GOE (Kah et al., 2004; Poulton and Canfield, 2011; Planavsky et al., 2012). Neither diagenesis nor the photochemical oxidation of As are likely to have significantly affected our interpretation (see the Data Repository).

Major biogeochemical As cycling pathways in the anoxic Archean oceans are proposed to have been distinct from those operating in the redox-stratified Paleo–Proterozoic seawater column (Figs. 3A and 3B). Accordingly, the oxidative supply of As(V) from land promotes the largescale uptake of As(V) through phosphate transporters by marine phytoplankton. This is followed by intracellular As(V) reduction via cytoplasmic As(V)-reductases and the extrusion of As(III) by membrane transporters (Fig. 3C) (Dyhrman and Halesy, 2011; Wurl et al., 2013, 2015; Yan et al., 2014; Sánchez-Riego et al., 2014; Saunders and Rocap, 2016). The conversion of As(V) to As(III) minimizes phosphate loss, as physicochemical similarities between As(V) and phosphate

![Figure 2. Distribution of As in iron formations (IFs), spread through Earth’s history. A: As/Ti ratio. B: As/Fe ratio. Red symbols are Superior-type IFs; black, Algoma-type IFs; blue, ironstones; and green, Phanerozoic hydrothermal iron sediments. Squares represent bulk sample digests; circles, laser ablation analyses. Light blue diamonds show 100 m.y. time-binned averages, plotted in middle of each bin (e.g., 2.4–2.5 Ga, plotted at 2.45 Ga). Two bins, plotted at 3.25 Ga and 0.55 Ga, were excluded from As/Fe plot as they were represented by single sample each. Ph—Phanerozoic; GOE—Great Oxidation Event.](image)

![Figure 3. Conceptual models of principal marine arsenic (As) cycling pathways. A: Proposed Archean As cycle. B: Proposed Paleo–Proterozoic As cycle. (I)—potential predominant anoxicogenic photosynthetic oxidation of As(III) to As(V) in unstratified Archean oceans with low sulfide content; (II)—potential elevation of As(III) oxidation to As(V) in Great Oxidation Event (GOE) redox stratified oceans, coupled to rise in seawater oxygen, Mn-oxide, and sulfate content; (III)—potential decrease in As-dependent anoxicogenic photosynthesis and increase in chemosynthetic nitrate-dependent oxidation of As(III) to As(V) after GOE; (IV)—As(III) regeneration by anaerobic dissimilatory As(V) reduction with organic matter. White, blue, red, and orange arrows represent As(III) regeneration in sediments and water column through anaerobic As(V) reduction, As(V) production by As(III) oxidation, As-sulfide formation pathways, and hydrothermal As(III) release, respectively. Arrow size represents hypothesized size of pool for each As species reaction pathway. C: A microbial cell performing As(V) detoxification: (i)—phosphate transporter (red); (ii)—cytoplasmic As(V) reduction to As(III); (iii)—extrusion of As(III) through As(III) efflux pump (orange). D: Conceptual model depicting behavior of As(III) and As(V) in modern fully oxygenated ocean (Cutter et al., 2001; Maher and Butler, 1988).](image)
would have led to a simultaneous buildup of As(V) and depletion of P in seawater that would have negatively impacted marine primary productivity (Chu Fru et al., 2016b; Hemmingsson et al., 2018).

The rise in As-S and As(V) appears some 30 m.y. before the loss of S-MIF, providing compelling evidence that the GOE was protracted rather than instantaneous. This rise in marine As-S and As(V) across the Archean-Proterozoic boundary overlaps with the expansion of major As oxidants during the GOE. We propose that this radical change enabled the expansion of a global As cycle reminiscent of the modern, and is related to the onset of abundant As-S and As(V) species in sulfidic and oxygenated environments, respectively. The emergence and impact of these toxic species have yet to be considered despite this knowledge forming a critical prerequisite for understanding how life adapted to the new redox landscape that emerged with the GOE.

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