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

Ernest Chi Fru¹, Andrea Somogyi², Abderrazzak El Albani³, Kadda Medjoubi³, Jérémie Aubineau³, Leslie J. Robbins⁴, Stefan V. Lalonde⁵, and Kurt O. Konhauser⁶

¹Centre for Geobiology and Geochemistry, School of Earth and Ocean Sciences, College of Physical Sciences and Engineering, Cardiff University, Cardiff CF10 3AT, Wales, UK
²Nanoscopium beamline, Synchrotron SOLEIL, L’Orme des Merisiers Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France
³Institut de Chimie des Milieux et Matériaux de Poitiers, UMR 7285-CNRS, Université de Poitiers, 5 rue Albert Turpin (Bât B35), 86073 Poitiers cedex, France
⁴Department of Earth and Atmospheric Sciences, University of Alberta, Edmonton, Alberta T6G 2E3, Canada
⁵Laboratoire Géosciences Océan, CNRS-UMR6538, European Institute for Marine Studies, Université de Bretagne Occidentale, 29280 Plouzané, France

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, nitrogen, 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.

INTRODUCTION

The Great Oxidation Event (GOE) marks a pivotal point in Earth’s history, when appreciable amounts of O₂ first permanently accumulated in the atmosphere (Lyons et al., 2014). This rise in atmospheric O₂ allowed shallow surface seawater to become globally oxygenated, while sulfide-rich conditions developed in middle-depth continental-margin waters and anoxic iron-rich conditions persisted at depth (Poulton and Canfield, 2011). Abundant mineralogical and geochemical evidence support the timing of the GOE, including the disappearance of detrital pyrite, uraninite, and siderite from fluvial and deltaic deposits, an increase in Fe of detrital pyrite, uraninite, and siderite from subsurface and surface environments, the redox cycling of As follows a simple pathway, determined chiefly by the presence or absence of oxygen and sulfide (Smedley and Kinniburgh, 2002; O’Day et al., 2004; O’Day, 2006). Based on this conservative behavior of the As cycle in nature, we posit that the abundances of As(V) and As sulfides (As-S) in Precambrian marine shales should effectively track As speciation and accumulation in the oxic and sulfide-rich environments that became widespread following the rise of atmospheric oxygen.

METHODS

Drill-core shale samples, aged ca. 2.7–2.0 Ga, are from near-continent-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 (Nagomi-Pembia et al., 2014; Chi Fru et al., 2015). Ferric iron oxide (Fe₂O₃) was determined as the difference between total iron (Fe₂O₃+FeO) and ferrous iron (FeO). FeO was quantified by titration. Banded iron formation data assembled from a literature survey and new chemical analyses are detailed in Table DR2 and supplementary methods in the Data Repository.

RESULTS

We sampled marine shales from 39 deposits across 10 nearshore marine successions 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 an arsenite [As(III)] As(III)/As(V) redox potential close to that of Fe(II)/Fe(III) and NO₃⁻/N₂ (O’Day, 2006), As(V) should have formed readily during the GOE. This would have been amplified by the accumulation of oxidized compounds such as NO₃⁻ and Mn(IV) oxides that, in turn, serve as As(III) oxidants (see Oremland and Stolz, 2003; see also the GSA Data Repository¹). 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.

Whatever on land, in the oceans, or in Earth’s subsurface and surface environments, the redox cycling of As follows a simple pathway, determined chiefly by the presence or absence of oxygen and sulfide (Smedley and Kinniburgh, 2002; O’Day et al., 2004; O’Day, 2006). Based on this conservative behavior of the As cycle in nature, we posit that the abundances of As(V) and As sulfides (As-S) in Precambrian marine shales should effectively track As speciation and accumulation in the oxic and sulfide-rich environments that became widespread following the rise of atmospheric oxygen.

¹GSA Data Repository item 2019089, Table DR1 (sampled formations, ages, and XANES data, Table DR2 (iron formation data and references), and supplementary Figures DR1–DR6, is available online at http://www.geosociety.org/dat arepository/2019/, or on request from editing@geosociety.org.

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 ~1.0 × 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/Ti 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 sulfate 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 the 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_2-rich conditions (e.g., the case of arsenopyrite in Reaction 1).

$$4\text{FeAsS} + 13\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{As}_4 + 4\text{FeSO}_4.$$  \hfill (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:

Anoxygenic photosynthetic and anoxic NO_3^-–dependent chemooautotrophic oxidation of As(III) has been proposed as the most viable mechanisms by which appreciable Archean As(V) production could have occurred (Oremland and Stolz, 2003; Sforza et al., 2014). If these processes were prominent over As(V) reduction,
Figure 2. Distribution of As in iron formations (IFs), spread throughout Earth’s history. A: As/Fe 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.

Figure 3. Conceptual models of principal marine arsenic (As) cycling pathways. A: Proposed Archean As cycle. B: Proposed Paleoproterozoic 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 anoxygenic photoautotrophy and increase in chemoautotrophic 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) regenerated 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).
would have led to a simultaneous buildup of As(V) and depletion of P in seawater that would have negatively impacted marine primary productivity (Chiu 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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