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Barite, BIFs and bugs: evidence for the evolution of the Earth's early hydrosphere[☆]

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Abstract

The presence of relatively abundant bedded sulfate deposits before 3.2 Ga and after 1.8 Ga, the peak in iron formation abundance between 3.2 and 1.8 Ga, and the aqueous geochemistry of sulfur and iron together suggest that the redox state and the abundances of sulfur and iron in the hydrosphere varied widely during the Archean and Proterozoic. We propose a layered hydrosphere prior to 3.2 Ga in which sulfate produced by atmospheric photolytic reactions was enriched in an upper layer, whereas the underlying layer was reduced and sulfur-poor. Between 3.2 and 2.4 Ga, sulfate reduction removed sulfate from the upper layer, producing broadly uniform, reduced, sulfur-poor and iron-rich oceans. As a result of increasing atmospheric oxygenation around 2.4 Ga, the flux of sulfate into the hydrosphere by oxidative weathering was greatly enhanced, producing layered oceans, with sulfate-enriched, iron-poor surface waters and reduced, sulfur-poor and iron-rich bottom waters. The rate at which this process proceeded varied between basins depending on the size and local environment of the basin. By 1.8 Ga, the hydrosphere was relatively sulfate-rich and iron-poor throughout. Variations in sulfur and iron abundances suggest that the redox state of the oceans was buffered by iron before 2.4 Ga and by sulfur after 1.8 Ga.

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1. Introduction

Variations in the amount of free atmospheric oxygen through geologic time have been the sub-

ject of considerable debate since Cloud [1] suggested that the Archean atmosphere contained much less oxygen than at present. He observed that uraninite and pyrite, unstable in an oxygen-rich atmosphere, are present as detrital grains in Archean conglomerates. Subsequent work on Archean and early Proterozoic soil profiles indicates that iron, immobile in an oxygen-rich atmosphere, was mobile [2,3]. Although disputed by some [4], most workers accept that these geologic observations indicate that Archean atmospheric oxygen levels were substantially lower than at present [1,2].

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It is tempting to infer that because Archean atmospheric oxygen levels were low, the coexisting hydrosphere was reduced. However, the presence of syngenetic sulfate in the early Archean suggests at least local oxidizing redox conditions in the hydrosphere¹ [5]. These deposits, along with the abundance of banded iron formation (BIF), an indicator of reduced bottom waters [6] in the late Archean and early Proterozoic, suggest the redox state of seawater may have varied substantially.

A substantial body of literature exists regarding the evolution of the atmosphere and hydrosphere during the early part of the Earth's history, a topic that still receives a large amount of research, and perhaps more than its fair share of controversy. In the pursuit of research interests outside this general field, we have inferred a number of geological and geochemical anomalies that are not explained by current models for the evolution of the Earth's atmosphere and, particularly, hydrosphere. As discussed below, these anomalies include the *abundance* of bedded barite deposits, and the temporal distribution and geochemistry of BIFs.

In this paper we use temporal distributions of sulfate deposits and iron formations along with the aqueous geochemistry of iron, sulfur, and barium to present a unifying concept for the evolution of the Earth's hydrosphere before 1.0 Ga. This model builds on previous models, but presents important, although in some cases subtle, differences in an attempt to account for the anomalies mentioned above. The model also places *quantitative* constraints on variations in the abundance and redox state of aqueous components such as sulfur and iron, parameters that are not well established in many current models. Although previous models invoking layered

oceans [7,8] partly explain our observations, the data suggest a more complex evolution of the hydrosphere through time. We intend to show that changes in the oxidation state of the atmosphere and the resulting impact on weathering had a profound and perhaps unexpected impact on the hydrosphere. In particular, we hope to show that changes occur in both availability of sulfate and iron through time and that the dominant multivalent ions that help buffer oxidation states of the hydrosphere varied in a surprising way.

2. The temporal distributions of sulfate and iron formation

The geologic record contains various sediments and deposits that reflect the oxidation state of the hydrosphere and/or the atmosphere. We have reviewed the temporal and spatial occurrences of the key sediment types (see [Tables 1 and 2²](#)), the details of which are summarized below. [Fig. 1](#), which is based on [Tables 1 and 2²](#), illustrates the distributions of bedded sulfate deposits and BIFs prior to 1.0 Ga. These tables were compiled from existing literature. [Table 2²](#) is extensively updated from compilations by James [9], Walker et al. [2], Isley [10] and Isley and Abbott [11]. It provides more constrained ages for many BIFs and includes data for BIFs not presented in the previous compilations. In [Table 2²](#), BIFs are classified as either Algoma- or Superior-type. Algoma-type BIFs are generally small in size and associated with contemporaneous volcanic suites. In contrast, Superior-type BIFs (Hamersley-type in Australia) are laterally extensive, generally in a shelf environment without a volcanic association [12].

Before 3.2 Ga, bedded barite deposits are relatively common (18 in [Table 1²](#)), whereas other bedded sulfates are not known and BIFs, although present, are not common and are exclusively of Algoma-type. Between 3.2 and 2.4 Ga, the geologic record is characterized by abundant BIF and a paucity of bedded sulfate deposits (only two known). The period between 2.4 and

¹ Unless stated otherwise, comments relating to redox conditions refer only to the hydrosphere. No inference should be made about atmospheric conditions, unless specifically stated. By the term 'oxidizing' we imply that sulfate was the dominant hydrous sulfur species. By the term 'reduced' we imply that H₂S and/or HS⁻ were the dominant sulfur species. Under disequilibrium conditions with intermediate redox, sulfite may be important.

² See the online version of this article.

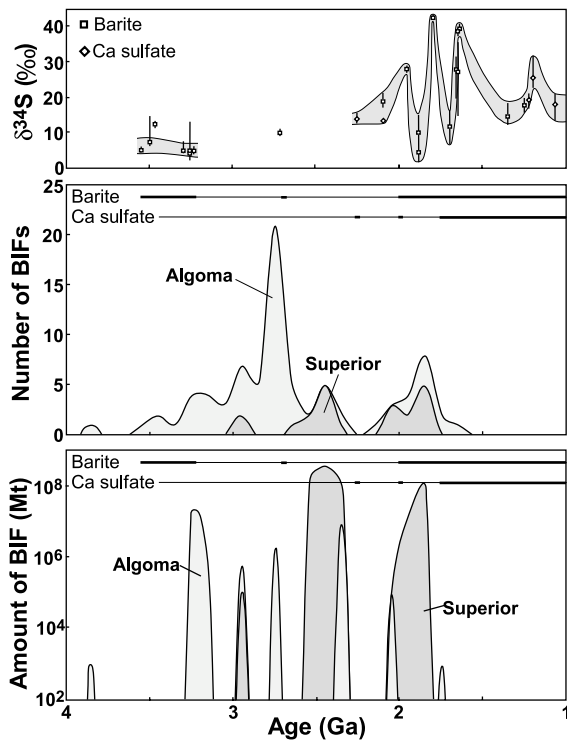


Fig. 1. Variations in the abundances of bedded sulfate deposits and BIF and of $\delta^{34}\text{S}$ through time (based on Tables 1 and 2).

1.8 Ga is characterized by abundant BIF, and increasingly abundant sulfate deposits, with gypsum and anhydrite becoming more common. Between 3.0 and 1.8 Ga, both Superior- and Algoma-type BIFs are present, but the Superior-type deposits account for the vast majority of BIF. The period between 1.8 and 1.0 Ga lacks BIF but contains abundant sulfate deposits. Although BIFs of late Proterozoic and Phanerozoic ages are known (e.g. Rapitan), these deposits are the products of either unusual geologic conditions (e.g. global glaciation [13]) or hydrothermal venting.

As both the style and the abundance of BIF vary with time, it is unlikely that these variations are solely controlled by tectonic preservation. In addition, the true frequency of bedded sulfate deposits is likely to be understated in the older rocks as these rocks are less likely to be preserved [14].

3. Sulfur isotope variations through time

Prior to 2.4 Ga, $\delta^{34}\text{S}_{\text{sulfate}}$ is relatively uniform (Fig. 1) with average values for all deposits in the range of 3.8–5.4‰ (all $\delta^{34}\text{S}$ values are reported relative to the CDT standard), bar the Big Stubby and Geco volcanic-hosted massive sulfide (VHMS) deposits. Moreover, with the exception of the Dresser deposits [15], coexisting sulfide minerals have a narrow range of $0 \pm 4\%$ [16]. Sedimentary sulfide elsewhere has $\delta^{34}\text{S}$ in the range of $0 \pm 10\%$ [13,17]. In contrast, deposits younger than 2.4 Ga have higher and more variable $\delta^{34}\text{S}_{\text{sulfate}}$, ranging from 4 to 39‰ (Fig. 1), similar to values in the late Proterozoic and Phanerozoic [18]. Sedimentary sulfides also have a large range in $\delta^{34}\text{S}$, from -30 to 60‰ [13,19,20].

Farquhar et al. [21] showed that the fractionation of ^{33}S relative to ^{32}S also changes at about 2.4 Ga. Syn- or diagenetic sulfate and sulfide minerals deposited before 2.45 Ga show mass-independent fractionation of ^{33}S , interpreted to result from gas-phase photolysis of SO_2 , yielding a large range of oxidized and reduced sulfur-bearing species [22]. Between 2.45 and 2.09 Ga ^{33}S fractionation shifted from mass independent to mass dependent. The lack of mass-independent fractionation after 2.09 Ga suggests that photochemical reactions ceased to be important, with biogenic and redox reactions controlling sulfur speciation. These observations have been independently supported by Mojzsis et al. [23].

4. The low-temperature geochemistry of sulfur, iron and barium

Fig. 2 illustrates the stability of Fe–S–O minerals and barite, and the solubility of iron as a function of sulfur content and redox at pH (7.8) and salinity of modern seawater (3% NaCl). These diagrams were calculated for 25 and 75°C to illustrate constraints on deposition of BIF and barite.

At 25 and 75°C, magnetite is only stable at sulfur levels below 10^{-5} and 10^{-3} that of modern seawater. Iron is most soluble in the magnetite stability field and least soluble in the pyrite field.

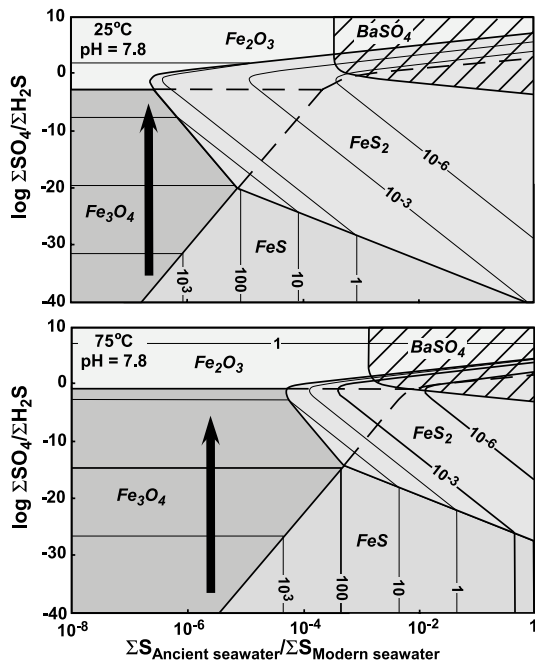


Fig. 2. $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$ versus total sulfur diagrams calculated at 25 and 75°C at modern oceanic pH and salinity showing Fe–Ba–S–O mineral stabilities and Fe solubilities (calculated using data generated from HCh [24]). Total sulfur concentrations are normalized to the level in modern open ocean seawater.

In the magnetite field, iron solubility locally exceeds 100 ppm and decreases as $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$ increases. Even if slow reaction rates inhibit pyrite formation, and the magnetite field expands to higher sulfur levels (dashed lines in Fig. 2), sulfur concentrations must still be much lower than that of modern seawater. Under reduced conditions at current seawater sulfur levels, the maximum iron solubility in the pyrite field is only $\sim 10^{-3}$ ppm, some five orders of magnitude lower than that in the magnetite field. Although iron solubility exceeds 1 ppm at the base of the hematite field, it decreases with increasing $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$. Therefore, under sulfur-rich, highly oxidized conditions characteristic of modern seawater, iron is highly insoluble. Magnetite is only stable under reduced conditions ($\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S} < 10^{-2.5}$ at 25°C), and high iron solubility is only possible under very low ambient sulfur concentrations.

In the presence of even low concentrations of aqueous sulfate, barium is insoluble, forming bar-

ite. Therefore, barite deposition indicates relatively oxidized conditions ($\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S} > 10^{-2}$), even for fluids with low sulfur levels (at most 10^{-3} current seawater concentrations). In contrast, the solubilities of gypsum and anhydrite are much higher: a high degree of evaporation is required to precipitate gypsum. Although barite is the only sulfate mineral reported prior to 3.2 Ga, the initial workers on the Dresser barite deposit suggested that the barite replaced original evaporative gypsum [25,26]. However, recent work [27] suggests that most sulfate precipitated originally as barite from low-temperature hydrothermal emanations analogous to white smokers.

Thus, the distributions of bedded sulfate minerals and iron formations plus constraints based on the aqueous geochemistry of iron, sulfur and barium set limits for $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$, total sulfur, and iron abundances in ancient seawater. These data require that before 1.8 Ga, ancient seawater had much lower total sulfur and higher iron abundances than modern seawater. Furthermore, total sulfate levels between 3.2 and 2.4 Ga must have been extremely low, although before 3.2 Ga sulfate levels may locally have approached modern levels. Variations in the abundances of the elements may be linked to the evolution of the atmosphere and hydrosphere, as suggested by Walker and Brimblecombe [28].

5. The origin of bedded sulfate deposits

Interpretation of the genetic significance of the distribution of bedded sulfate deposits through geologic time requires an understanding of how these deposits formed. Of particular interest are the barite deposits: barite is the dominant or only sulfate mineral in bedded sulfate deposits formed prior to 2.4 Ga.

Because of the highly insoluble nature of barite, formation of this mineral requires two discrete sources, one for barium and another for sulfate. Jewell [29] suggests that barite can form in three ways: (1) diagenetic replacement, (2) hydrothermal exhalation, or (3) biological precipitation. The first two mechanisms are most important, particularly in the Archean.

Diagenetic replacement of original bedded gypsum has been proposed at Dresser in the Pilbara Craton and several occurrences in the Kaapvaal Craton [25]. However, the most common origin for barite in the Archean appears to be hydrothermal exhalation. Barite precipitates when a reduced fluid carrying Ba^{2+} mixes with a fluid carrying SO_4^{2-} . In Phanerozoic VHMS deposits, barium-bearing hydrothermal fluid mixed with sulfate-bearing seawater at or just below the seafloor. As a consequence, barite concentrated toward the top of VHMS deposits [30].

It is tempting to draw a direct analogy between Phanerozoic VHMS barite and Archean barite, but given the controversy regarding the redox state of the Archean hydrosphere, other alternatives should be considered. The most likely alternative is that an oxidized, sulfate-bearing hydrothermal fluid mixed with barium-bearing, reduced seawater. Hydrothermal sulfate can be derived either from leaching of sulfate in evaporative, sedimentary rocks or by disproportionation of magmatic SO_2 [31]. As evaporative sulfate minerals form by the evaporation of sulfate-bearing seawater, the only alternative that is not ultimately derived from seawater is magmatically derived sulfate.

However, a number of characteristics of Archean barite-bearing deposits favor seawater over a magmatic source for sulfate. Firstly, barite deposits were more abundant before 3.2 Ga, whereas magmatic activity was more abundant between 3.2 and 2.4 Ga, a period of extensive formation of continental crust [32]. The formation of much of the Yilgarn, Slave and Superior provinces between 3.0 and 2.6 Ga involved extensive volcanism. If magmatic derived sulfate was important in forming Archean barite deposits, more deposits should have formed between 3.2 and 2.4 Ga.

Secondly, the isotope characteristics of the barite deposits are also inconsistent with a magmatic sulfate source. In Phanerozoic deposits where disproportionation of magmatic SO_2 has been demonstrated, sulfate tends to be 15–30‰ enriched in ^{34}S relative to the parent SO_2 [31]. Hence, unless magmatic $\delta^{34}\text{S}$ values during the Archean were substantially lower than the general range of $2 \pm 5\%$ [33], the $\delta^{34}\text{S}$ of Archean barite is not

consistent with derivation from disproportionated magmatic SO_2 . Moreover, the mass-independent ^{33}S fractionation observed in Archean barite indicates that the sulfate formed in the atmosphere [21,23], which, again, is inconsistent with a magmatic source.

Thirdly, Huston et al. [34] interpreted that regional alteration in the 3.24 Ga Panorama VHMS district involving increases in $\text{Fe}_2\text{O}_3/\text{FeO}$ of volcanic rocks indicated extensive inorganic reduction of seawater sulfate. Moreover, early Archean VHMS deposits have similar mineral zonation to Phanerozoic deposits, suggesting similar depositional mechanisms, including interaction with sulfate-rich seawater.

In summary, the temporal distribution, sulfur isotope characteristics and alteration/mineralization associated with bedded Archean barite-bearing deposits all point to seawater being the source of sulfate. Hence we take the presence of bedded barite to indicate the presence of sulfate in contemporaneous seawater.

6. The origin of BIF

Cloud [35] and Holland [36] first suggested that iron and silica, the main components of BIFs, were derived from seawater. This concept is now generally accepted, although some disagreement still exists as to the ultimate origin of these components. Holland [36] suggested that Fe^{2+} could be provided either from terrestrial weathering in an anoxic environment, volcanic emanations into the ocean, or bottom waters. Low-temperature weathering and high-temperature alteration [37] of the ocean floor could also be sources of iron.

The concept that the iron and silica in BIFs were derived from high-temperature alteration of rocks below the seafloor stems from comparing the rare earth element patterns of BIFs with those from modern hydrothermal fluids venting on the seafloor. Both the BIFs and the venting fluids are characterized by positive europium anomalies, which are indicative of high-temperature alteration of volcanic rocks [37–39]. Although this model is generally accepted, systematic differences in the intensity of the europium anomaly exist

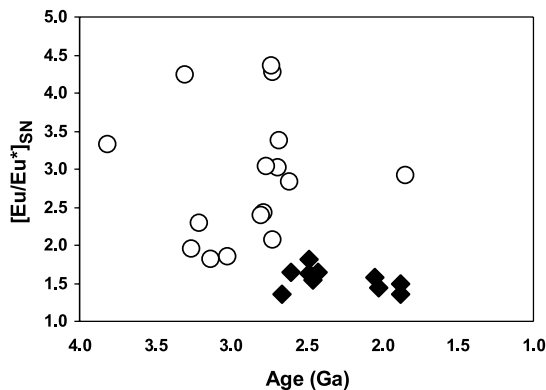


Fig. 3. Variations with time of the average NASC-normalized europium anomaly for Algoma- (open circles) and Superior-type (solid diamonds) BIFs. Table 2 presents the data, which were culled to minimize clastic input, used to make this diagram.

between Algoma- and Superior-type BIFs (Fig. 3).

Algoma-type BIFs are characterized by much larger europium anomalies (>1.8) than Superior-type BIFs (<1.8). This difference suggests that there is a much larger component of volcanic-related hydrothermal emanations in Algoma-type BIFs, consistent with their close association with greenstone belts. The smaller europium anomalies that characterize Superior-type BIFs suggest a lower input from volcanic-related hydrothermal emissions and a higher contribution from other sources, including oceanic bottom waters. Therefore the distribution and characteristics of Superior-type BIFs are a more accurate record of background processes that controlled the overall chemistry of Archean and Proterozoic oceans.

Isley [10] and Isley and Abbott [11] demonstrated that major BIF depositional events correlate strongly with global plume events. This analysis was extended by Abbott and Isley [40] to consider Algoma- and Superior-type BIFs separately. Inspection of their diagrams confirms that peaks in Algoma-type BIF deposition correspond to major global plume events, but that not all plume events correspond to Algoma-type BIF deposition. The largest peak in Algoma-type BIFs corresponds to a major plume event at 2.75–2.70 Ga, which can be related to extensive crustal

growth in many Archean greenstone belts. However, although Abbot and Isley [40] also suggested a correlation between mantle plumes for Superior-type BIFs, the updated age constraints provided in Table 2 indicate more complicated relationships. These constraints suggest that the ~ 2.463 Ga Superior-type BIF peak identified by Abbot and Isley [40] includes at least three discrete events over a period of at least 163 million years, and these BIF events do not all correlate directly to identified plume events. Moreover, the ~ 1.890 Ga Superior-type BIF event occurs toward the end of a ~ 700 million year period of pulsed plume activity. Therefore, although some link between mantle plume events and Superior-type BIFs is probable, that link is not direct. Rather, hydrothermal activity associated with superplume events, along with other processes, contributed iron to an oceanic reservoir, which deposited iron during upwelling [2] or oxidation events not directly related to the plume events.

7. A model for the geochemical evolution of the hydrosphere prior to 1.0 Ga

Temporal variations in the abundances of iron formations and bedded sulfate, together with variations in $\delta^{34}\text{S}_{\text{sulfate}}$, suggest that the evolution of the hydrosphere before 1.0 Ga can be divided into four periods: (1) >3.2 Ga, (2) 3.2–2.4 Ga, (3) 2.4–1.8 Ga, and (4) 1.8–1.0 Ga. The geologic and isotopic characteristics, along with the low-temperature geochemistry of sulfur, iron and barium, suggest that the evolution of the hydrosphere was more complex than generally thought [7,13]. Figs. 4 and 5 present our model for this evolution, which accounts for most of the constraints outlined above.

7.1. >3.2 Ga: sulfur-poor, stratified oceans

The presence of barite and iron formation prior to 3.2 Ga indicate variable seawater sulfur contents and redox conditions. Magnetite, the main mineral in iron formations, only forms at low temperatures under reduced redox conditions and low sulfur levels. Barite forms at higher sulfur

levels, but only under oxidized conditions. The widespread occurrence of barite before 3.2 Ga suggests that sulfate-bearing seawater was a global, not local, phenomenon.

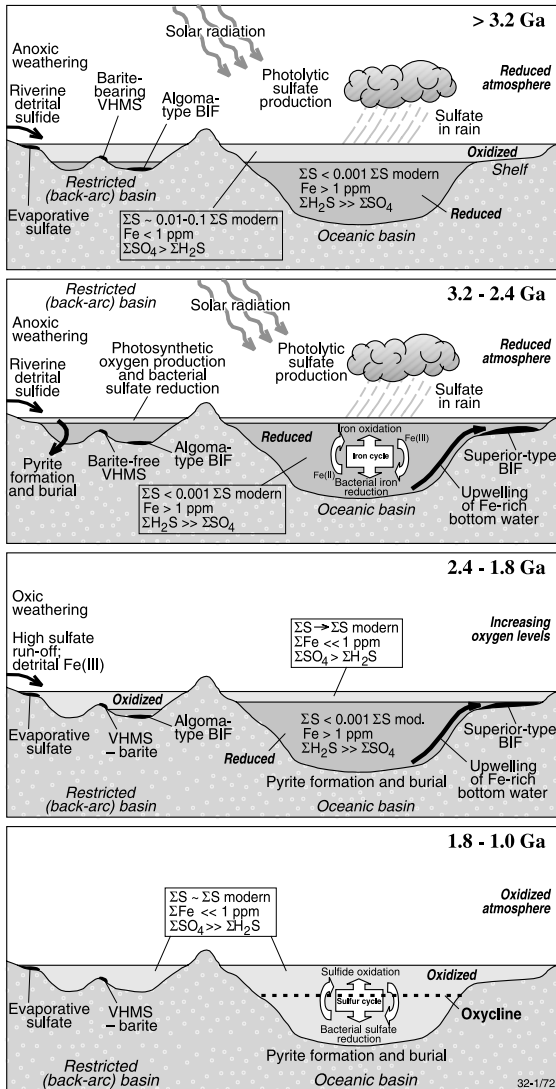


Fig. 4. Model for hydrosphere evolution prior to 1.0 Ga. Photochemical sulfate oxidation effectively shuts down between 2.4 and 1.8 Ga and is not displayed in the diagram after 2.4 Ga. The term oxidized refers to the presence of oxidized species such as sulfate and does not imply the presence of free oxygen. Low levels of oxygen would have been present in the photic zone and a significant oxycline may have developed by 1.8 Ga.

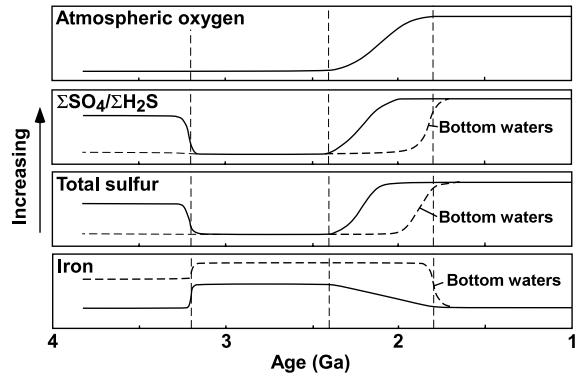
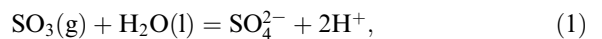
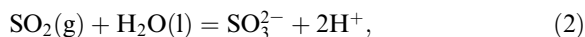


Fig. 5. Schematic diagram illustrating inferred changes in atmospheric oxygen levels and oceanic $\Sigma\text{SO}_4/\Sigma\text{H}_2\text{S}$, total sulfur and iron abundances.

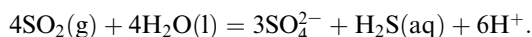
The variable redox condition could be explained by a stratified ocean, with barite deposits forming in an oxidized upper layer, and Algoma-type BIF forming from Fe^{2+} -rich hydrothermal emanations in the reduced lower layer (Fig. 4). The presence of an upper oxidized layer covering shelf areas may have prevented iron deposition and suppressed Superior-type BIF. This may have been further influenced by lack of shelf environments early in Earth's history. Differences in the operation of plate tectonics may have limited the extent of some of the environments displayed in Fig. 4 compared to later periods.

As argued by a number of authors [1], the Earth's early atmosphere was oxygen-poor and reduced. Such conditions would stabilize gases such as H_2S and SO_2 , both of which can undergo photolytic reactions, producing mass-independent sulfur isotope fractionation and oxidized sulfur-bearing gases such as SO_3 [21]. Modelling by Pavlov and Kasting [22] suggests that the products of these photolytic reactions will be incorporated into the hydrosphere through a combination of 'rainout' and dissolution at the surface of the ocean, with SO_3 and SO_2 being the two most important oxidized sulfur-bearing gases. These gases would be dissolved into the hydrosphere by hydrolysis and disproportionation reactions, as follows:





and



These processes would produce an upper oceanic layer enriched in sulfate (cf. [41]), and possibly sulfite [42]. The presence of sulfate in this layer would then have allowed deposition of bedded sulfate minerals in hydrothermal and evaporative environments, or possibly at the interface between the oceanic redox layers. Many Paleoproterozoic barite deposits are interpreted to have formed in shallow water [25,26,43], and analogies with modern arc-related black smoker deposits suggest depths of less than 2000 m for the VHMS deposits. Moreover, reduced atmospheric conditions would allow the ^{33}S anomalies noted by Farquhar et al. [21].

However, below this sulfate-enriched oxidized upper layer, the ocean was reduced. Inorganic sulfate reduction processes, where sulfate (and possibly sulfite) from this upper layer was reduced hydrothermally via interactions with Fe^{2+} in rock below [34], and biological sulfate (or sulfite [42]) reduction, which may have evolved by ~ 3.4 Ga [15], combined to reduce sulfate produced by photochemical reactions, eventually forming a steady state. These interactions buffered seawater redox, sulfur abundances and $\delta^{34}\text{S}$. During this period, $\delta^{34}\text{S}_{\text{sulfate}}$ and $\delta^{34}\text{S}_{\text{sulfide}}$ were both close to zero, consistent with crustal values. These interpretations are consistent with those of Veizer et al. [44], who suggested that many aspects of Archean oceanic chemistry were buffered by equilibrium with basaltic oceanic crust.

7.2. 3.2–2.4 Ga: sulfur-poor, reduced oceans

The period from 3.2 to 2.4 Ga differs from the earlier period in lacking bedded sulfate deposits and having abundant BIFs, including abundant Superior-type BIFs. This suggests that the oceans at this time lacked a significant sulfate-bearing layer (Figs. 3 and 4). Moreover, the abundance of BIF suggests that the ocean was generally more reduced than the previous period, allowing high concentrations of Fe^{2+} in the bottom waters,

which may have been supplemented by hydrothermal emanations as recorded in Algoma-type iron formations.

As mass-independent ^{33}S fractionation is recorded during this period [21,23], photochemical reactions with atmospheric sulfur-bearing gases were still important. As the atmosphere was still reduced during this period, the oxidative weathering of terrestrial pyrite to sulfate would not have supplied significant levels of sulfur to the oceans. Importantly, the advent of sulfate-reducing bacteria, in combination with hydrothermal inorganic sulfate reduction, would help to keep the oceans virtually sulfate-free because in waters with low sulfate concentrations biological sulfate reduction rapidly removes sulfate, precipitating iron sulfides from iron-rich ocean waters. Because of low atmospheric oxygen levels, the terrestrial weathering of sulfides would not have supplied sulfate at the rate of removal, and the oceans would effectively be scrubbed of sulfur through iron sulfide precipitation. By 3.2 Ga sulfate deposits were virtually absent and photolytic reactions were the main process of sulfate production [21,23]. We infer that biological sulfate reduction may have been an important process by 3.2 Ga and that this led to the removal of sulfate as a significant component within ocean waters between 3.2 and 2.4 Ga. This process may have been assisted or even initiated by a major meteorite bombardment at ~ 3.2 Ga [46], which would have perturbed the steady-state layered hydrosphere inferred prior to 3.2 Ga. Like the period before 3.2 Ga, the $\delta^{34}\text{S}$ composition of preserved sulfates and sulfides from 3.2 to 2.4 Ga was limited to that of crustal average [17,45].

Biogeochemical evidence for oxygenic photosynthesis exists in sediments as old as 2.7 Ga [47]. Eukaryotic steroids have a biosynthetic requirement for free oxygen, these steroids being preserved as steranes, which have been found in 2.7 Ga sediments [48]. This helps set a lower limit for oxygen levels in the photic zone to at least 1% PAL at this time [49]. Upwelling of reduced, Fe-bearing waters into the photic zone would result in extensive iron precipitation to form Superior-type BIF [2], as shown in Figs. 2 and 4.

Further supporting evidence for sulfate-poor

seawater may also come from a global excursion in the $\delta^{13}\text{C}$ of kerogen between 2.8 and 2.5 Ga [50]. A model involving significant rates of methanogenesis coupled with methanotrophy has been proposed by Hayes [54,55] to explain this excursion. For a methane cycle to be of global significance it would require that other modes of organic matter recycling, such as microbial aerobic respiration, and bacterial sulfate reduction may not have been as important within the water column and upper sediments. Such a situation would certainly be the case in anoxic, sulfate-poor and Fe^{2+} -rich waters.

7.3. 2.4–1.8 Ga: transition to sulfur-rich, oxidized oceans

The rise of atmospheric oxygen levels, which started at 2.4–2.2 Ga [3], initiated one of the most sweeping changes in geologic processes affecting Earth's history. This rise initiated conditions that influenced the evolution of the hydrosphere over the next 600 million years (Figs. 3 and 4). The rise in atmospheric oxygen levels has been linked to the increased sequestration of reduced carbon by burial [50], to the loss of hydrogen to space in a methane-rich atmosphere [51], to changes in the redox of volcanic gases and/or hydrothermal fluid that interacted with the crust [52,53], or to a major continental growth period at the Archean–Proterozoic boundary [45]. Much higher levels of methanogenesis suggested for the previous period of Earth's history may have driven atmospheric methane levels and thus initiated the loss of hydrogen [51].

The most significant consequence of the rise of atmospheric oxygen levels was the initiation of oxidative weathering [3]. An increasingly oxygen-rich atmosphere has important ramifications for the geochemistry of sulfur and iron [28]. The mobility of these elements reverses: sulfur becomes increasingly mobile as oxidative weathering of terrestrial sulfides produces soluble sulfate, increasing sulfate levels in seawater. The earliest known examples of bedded calcium sulfate deposits are the 2.26 Ga anhydrite lenses in the Gordon Lake Formation in Ontario [56]. From this time the abundance of bedded sulfate deposits in-

creased, so that by 1.8 Ga, these deposits were relatively common (Table 1).

The rise of atmospheric oxygen also would have ended photochemical oxidation of reduced sulfur-bearing gases. Farquhar et al. [21] interpreted the decrease in mass-independent fractionation of ^{33}S between 2.45 and 2.09 Ga as having resulted from 'either a change in atmospheric composition or actinic flux'. The first alternative is consistent with our data, and suggests that atmospheric oxygenation destabilized reduced sulfur gases, shutting down the photochemical reactions responsible. During this period, the increasing flux of sulfate derived from oxidative weathering swamped the buffering capacity of atmospheric and volcanic sulfur reservoirs. Biological sulfate reduction, coupled with higher seawater sulfate levels led to a larger range in $\Delta^{34}\text{S}_{\text{sulfate-sulfide}}$.

The consequences of the oxygenation of the Earth's atmosphere did not proceed uniformly in time or space. The processes alluded to above probably occurred at different rates, and the rate of change differed in different geologic environments. For instance, sulfate concentrations would have risen more quickly in a small, closed basin relative to an open oceanic basin (Fig. 4). As a consequence, the effects of the oxygenation of the atmosphere would have led to both temporal and spatial variations in the distribution of sulfate and sulfides.

The cessation of significant BIF at about 1.8 Ga is one of the last consequences in the hydrosphere of the oxygenation of the atmosphere. The final increase in the oxidation state of bottom waters would result in extensive deposition of BIF, which may account for the spike in the quantity of iron formation between 1.9 and 1.8 Ga (Fig. 1).

During the period between 1.9 and 1.8 Ga, at least 1.2×10^8 Mt of BIF was deposited (Table 2: [9]), which equates to 3.6×10^7 Mt of iron assuming an average BIF iron content of 30%. Given that the mass of seawater in the Proterozoic was similar to current day, the average iron concentration in Proterozoic seawater required to precipitate this iron is 25 ppm. This value, or a value of two or three times higher, is consistent with con-

straints on iron levels for a reduced ocean indicated in Fig. 2. Even if the amount of BIF produced was a factor of two or three more than that preserved, the concentration of iron required is consistent with the values indicated in Fig. 2.

The presence of sulfate deposits between 2.4 and 1.8 Ga indicates that the shallower parts of the oceans became progressively sulfate-rich, yet the production of iron formations suggests that the bottom waters were reduced and sulfur-poor. Like the time prior to 3.2 Ga, this suggests a redox stratified ocean. Several processes could cause this inferred stratification. Photosynthetic production of organic matter and its oxidative destruction by microbial aerobic respiration, bacterial sulfate reduction or even bacterial Fe^{3+} reduction would also play important roles in defining the redox gradients within ocean waters. Moreover, Fe^{2+} introduced via hydrothermal emanations would also have maintained high iron levels in bottom waters. Biological sulfate reduction would have been an active process in ocean waters and the sulfide produced would have been titrated by the Fe^{2+} -rich bottom waters, keeping the lower ocean virtually sulfate-free.

7.4. 1.8–1.0 Ga: sulfur-rich, oxidized hydrosphere

The abundance of bedded sulfate deposits combined with the lack of iron formation between 1.8 and 1.0 Ga suggests that the hydrosphere was sufficiently oxidized and sulfur-rich to suppress iron solubility. Moreover, $\delta^{34}\text{S}$ variations reflect biogenic sulfate-reducing reactions [13]. Once the flux of sulfate from terrestrial weathering of sulfides was high enough to swamp hydrothermal Fe^{2+} flux, biogenic sulfate reduction could then begin to titrate iron from ocean waters. The greatly increased flux of sulfate from weathering compared to the supply of Fe^{2+} in the hydrosphere ultimately led to the removal of Fe^{2+} from the oceans [28]. This reverses the way that iron titrated sulfur between 3.2 and 2.4 Ga. The chemistry of the hydrosphere between 1.0 and 1.8 Ga was more like modern day seawater, in comparison to the period before 2.4 Ga. However, sulfidic bottom water and redox gradients may have had a profound effect on the distribution

of redox-sensitive bio-essential elements [7,8,57,58].

7.5. Redox buffering of the hydrosphere

Data presented in this paper suggest not only that there were large variations in the redox state and sulfur concentrations in the hydrosphere, but that the element that buffers the redox state changed with time. Sulfur is presently the most abundant multivalent element in seawater, its oxidation state buffering the redox state of seawater. As sulfate is virtually the only sulfur species in seawater in the open ocean, this seawater is geochemically oxidizing. To appreciably change the redox state of seawater requires the conversion of sulfate to sulfide, as happens biologically in anoxic basins or thermochemically in seafloor hydrothermal systems. However, if the total sulfur content of seawater was low, and the iron content was high, the speciation of iron would govern the redox state of seawater. Moreover, the presence of high Fe^{2+} would also prevent a rise in total sulfur concentrations as sulfur could be titrated by bacterial sulfate reduction. Therefore, the sulfur cycle prior to 2.4 Ga would be governed by high iron concentrations along with the low rate of sulfate production coupled to rapid bacterial consumption. Prior to 3.2 Ga, bacterial sulfate reduction may not have been a global phenomenon and seawater did contain sulfate in the upper ocean.

The rise in atmospheric O_2 led to oxidative weathering and an increased flux of sulfate to the ocean. Bacterial sulfate reduction would have led to the titration of Fe^{2+} from the global oceans. The O_2 rise may have had its roots in low-sulfate, high- Fe^{2+} oceans, where methanogenesis would have been a key component of the carbon cycle. This may have provided the methane-rich atmosphere where hydrogen loss gradually led to O_2 increase [51].

8. Implications of hydrosphere evolution to mineralization

In addition to BIFs and barite deposits, a number of other mineral deposit types have restricted

distributions in time [59,60]. For instance, paleo-placer uranium deposits, which require a reduced atmosphere and hydrosphere to form, are found only in rocks older than ~ 2.0 Ga, whereas unconformity-related uranium deposits formed after this time. In addition, sediment-hosted copper and shale-hosted zinc–lead (e.g. Mt Isa-type) deposits entered the geologic record at 2.0 and 1.7 Ga, respectively [60]. The unifying theme of the latter three deposit types is the inference that they formed from oxidized, sulfate-rich ore fluids. As pointed out by Lambert et al. [60], Veizer [59] and others, the oxygenation of the atmosphere, which began at 2.4–2.2 Ga, allowed the generation of such oxidized fluids. Another type of deposit which appears to require oxidized fluids for either metal transport or deposition is iron oxide-hosted Cu–Au deposits, including the giant Olympic Dam deposit in South Australia. The oldest, and one of the better studied districts – Tennant Creek in the Northern Territory, Australia – has been dated at about 1.83 Ga [61]. Again the emergence of this class of deposit appears to be linked to the development of an oxygenated atmosphere and hydrosphere.

9. Implications of hydrosphere evolution to lead isotope growth

The oxidation of the hydrosphere also influenced temporal changes in the crust and mantle, including Th/U ratios and the growth of lead isotopes. Modelling by Kramer and Tolstikhin [62] suggested that the ‘future’ paradox of lead isotopes can be resolved by oxidation of the atmosphere (and hydrosphere) at about 2.0 Ga, a process which mobilized uranium into the oceans and oceanic crust. Collerson and Kamber [32] suggested that subduction of oceanic crust resulted in a decrease in depleted mantle Th/U ratios, beginning at between 2.2 and 1.8 Ga.

Our analysis suggests that many of the consequences of atmospheric oxidation proceeded unevenly across the Earth’s surface. This may also apply to the introduction of uranium into the crust. This hypothesis is illustrated by considering lead from mineral prospects in the Pilbara Craton

(cf. [63]). In this region, crust was formed from the early Archean (~ 3.5 Ga) to the very earliest Proterozoic (~ 2.4 Ga), with mineralizing events spanning virtually this entire history and continuing to even younger periods. Fig. 6 shows the changes in the isotopic ratios of ore leads from this region relative to a theoretical lead isotope evolution curve calculated using the Wabigoon–Uchi model of Thorpe et al. [64]. The ore leads deviate from the model evolution curve toward lower $^{208}\text{Pb}/^{206}\text{Pb}$ values at a model age of around 2.4 Ga, which indicates κ ($^{232}\text{Th}/^{238}\text{U}$ integrated to present day) decreased and that uranium was introduced into the source rocks of the ores at this time.

As all of the deposits sampled are small in size, it is likely that the source of Pb was local. Therefore, we hypothesize that uranium was introduced into the Pilbara upper crust by circulation of oxidized surficial fluids during incipient oxidation of the atmosphere and hydrosphere. This model is consistent with the suggestion by Powell et al. [65] that BIFs in the Hamersley Province were upgraded by oxidized fluids at 2.2 Ga. However, we are not implying that the uranium introduction recorded by Pilbara lead isotopes is a global event. Rather, the inferred uranium metasomatism of the upper crust is probably a local phe-

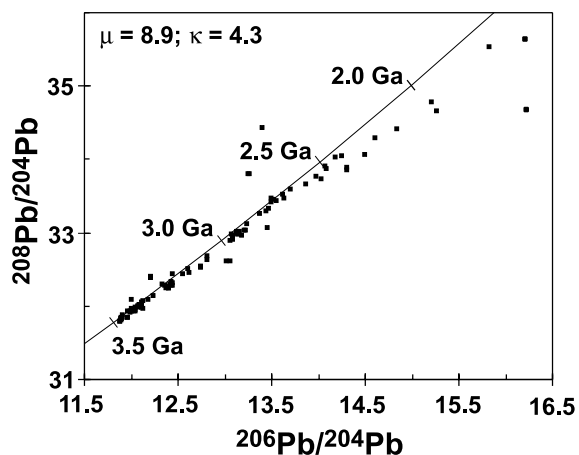


Fig. 6. $^{208}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$ diagram showing the isotopic composition of ore leads from the Pilbara Craton. At ~ 2.4 Ga the data progressively deviate from the Wabigoon–Uchi growth curve of Thorpe et al. [64] to lower κ values.

nomenon, with pandemic introduction of uranium into the crust and upper mantle at ~ 2.0 Ga [32,62].

10. Conclusions

1. Bedded barite deposits are common in the Paleoarchean (> 3.2 Ga), but virtually lacking in the Meso- and Neoproterozoic (3.2–2.4 Ga).
2. Variations in europium anomalies between Superior- and Algoma-type BIFs indicate hydrothermal emanations are not as important an iron source for Superior-type deposits.
3. The evolution of the hydrosphere prior to 1.0 Ga is complex, as follows:
 - 3.1. > 3.2 Ga: The oceans were mostly reduced and sulfur-poor, although a sulfate-enriched upper layer was present. Sulfate in this upper layer was sourced from atmospheric photolytic reactions.
 - 3.2. 3.2–2.4 Ga: The oceans were relatively uniform, reduced, sulfur-poor and iron-rich, although oxyclines may have existed near the surface. These conditions allowed the extensive development of Superior-type BIFs. Although atmospheric photolytic sulfate production still occurred, this sulfate was rapidly reduced by biogenic and hydrothermal activity, preventing the maintenance of a sulfate-rich upper layer.
 - 3.3. 2.4–1.8 Ga: Increasing atmospheric oxygen levels allowed oxidative weathering, which added sulfate to the oceans. This process proceeded at varying rates across the globe, producing layered oceans and an increasing number of sulfate deposits in the geologic record, and culminating with the deposition of extensive BIF at 1.9–1.8 Ga as the final oxidation of the hydrosphere scrubbed the oceans of iron. Because the oxidation of the atmosphere removed reduced sulfur gases, photolytic sulfate reduction progressively shut down.
 - 3.4. 1.8–1.0 Ga: The oceans were uniformly sulfate-enriched and iron-poor. Bedded sulfate deposits became common and BIFs rare.
4. Prior to 2.4 Ga, Fe^{2+} was the main oceanic redox buffer. After 1.8 Ga, sulfate was the main redox buffer. From 2.4 to 1.8 Ga, the redox buffer shifted from Fe^{2+} to sulfate at various rates across the globe depending on basin size and environmental factors.
5. The evolution of the hydrosphere had major impacts on the types of mineral deposits formed. Oxidized fluids became important between 2.4 and 1.8 Ga, which allowed the formation of sediment-hosted copper, Mt Isa-type zinc–lead and iron oxide-hosted copper–gold deposits. Moreover, the presence of these oxidized fluids allowed upgrading of BIFs to form iron oxide deposits.
6. The introduction of uranium into the mantle by subduction of oxidized oceanic crust, thereby decreasing mantle Th/U ratios, was a global process between 2.2 and 1.8 Ga. Lead isotope data from the Pilbara Craton suggest that uranium addition to the upper crust may have occurred locally at ~ 2.4 Ga in response to the initial oxidation of the hydrosphere and atmosphere.

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