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The onset of continental weathering recorded in Archean banded iron formations

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ABSTRACT

Early landmass emergence impacted marine chemistry and biosphere evolution by supplying nutrients through continental weathering. However, uncertainties persist regarding the timing of emergence and onset of early continental weathering. We present a compilation of germanium (Ge) and silicon (Si) in banded iron formations (BIFs) to assess Archean weathering. By leveraging the inverse correlation between Ge/Si ratios and Si contents in BIFs, we interpolate the evolution of Archean seawater Ge/Si for the first time. Our analyses reveal a stepwise decrease in Ge/Si, from near-hydrothermal values to those resembling continental input, at ca. 3.5 Ga. Based on a Ge-Si mass balance model, we propose that this shift is attributable to increased riverine fluxes, coinciding with the rapid emergence of continental crust. Significantly, this implies that two crucial prerequisites for the establishment of a marine biosphere were fulfilled in the early Archean: (1) the presence of marginal marine environments suitable for benthic and planktonic communities; and (2) a supply of terrestrially sourced nutrients.

INTRODUCTION

It has been argued that Archean ocean chemistry was dominated by mantle-derived, high-temperature hydrothermal inputs (Shields and Veizer, 2002; Flament et al., 2013). This idea is premised on minimal subaerial weathering due to continental crust being largely submerged at that point in Earth's history (Johnson and Wing, 2020). However, recent studies have proposed that emergent Archean continental weathering may have contributed solutes to the oceans due to the initiation of plate tectonics and crustal growth (Hessler and Lowe, 2006; Satkoski et al., 2016; Roerdink et al., 2022). Importantly, increased nutrient delivery (e.g., phosphorous) could have fueled primary productivity and influenced the evolution of the marine biosphere (Rosas and Korenaga, 2021).

A wide range of estimates throughout the Archean exist for the timing and secular trend in early continental emergence and weathering. Much of this debate has been centered on studying continental materials or their derivatives (e.g., zircons; Wang et al., 2022), but models can also be tested via marine archives (i.e., sinks). For instance, weathering of evolved continental crust over geological time may be traced by analyzing strontium (Sr) isotope ratios ($^{87}Sr/^{86}Sr$) in marine chemical sediments, such as carbonates. This is possible as the marine Sr isotope budget reflects the balance between more-radiogenic riverine input via continental weathering and a less-radiogenic hydrothermal source (Shields and Veizer, 2002). Although there is an extensive seawater Sr isotope record for the Phanerozoic Eon, the Archean record is hindered by a relative scarcity of carbonates. Those few Archean carbonates, characterized by unradiogenic $^{87}Sr/^{86}Sr$ ratios, have been interpreted as recording seawater strongly buffered by hydrothermal fluids (Shields and Veizer, 2002), consistent with positive europium (Eu) anomalies in Archean carbonates and banded iron formations (BIFs) (Wang et al., 2023). A recent Sr isotope compilation (Chen et al., 2022), however, suggests that the $^{87}Sr/^{86}Sr$ curve may have deviated from predicted mantle evolution values by ca. 3.7 Ga, implying that weathering of evolved continental crust could already have begun (Roerdink et al., 2022). Yet, discerning continental weathering's impact so far back in time based solely on Sr isotopes remains challenging (see Supplemental Material[1]).

Germanium/silicon ratios (Ge/Si) in Archean BIFs may provide an alternative means for tracking the continental emergence and the onset of weathering. The Ge/Si ratio, preserved in the chert (SiO_2) endmember of BIFs, is expected to reflect the ratio of seawater from which it precipitated (Hamade et al., 2003). Ge and Si are closely coupled in many geochemical processes (Lugolobi et al., 2010). Due to their similar atomic radii and oxide bond lengths, Ge can substitute for Si in silicates and chert. While there may be a slight fractionation of Ge and Si during igneous processes, leading to higher Ge/Si ratios in mafic magmas, the ratios of mafic and felsic magmas are generally close to that of continental crust (Ge/Si_{mol}: 1.8×10^{-6}) (Ernst et al., 2022). Further, minor fractionation during continental weathering may lead to slightly lower Ge/Si ratios in rivers (Ge/Si_{mol}: 0.6×10^{-6}) (Mortlock and Frohlich, 1987) as Ge is preferentially sequestered in secondary clays (Kurtz et al., 2002). Ge and Si also enter the ocean via hydrothermal fluids generated during seafloor alteration at mid-ocean ridges, with Ge/Si_{mol} ratios between 8×10^{-6} and 14×10^{-6} (Mortlock et al., 1993). Overall, the bulk marine Ge/Si ratio reflects the balance between continental weathering and hydrothermal fluxes.

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[1]Supplemental Material. Supporting discussion, methods, and geochemical data. Please visit https://doi.org/10.1130/GEOL.S.27963849 to access the supplemental material; contact editing@geosociety.org with any questions.

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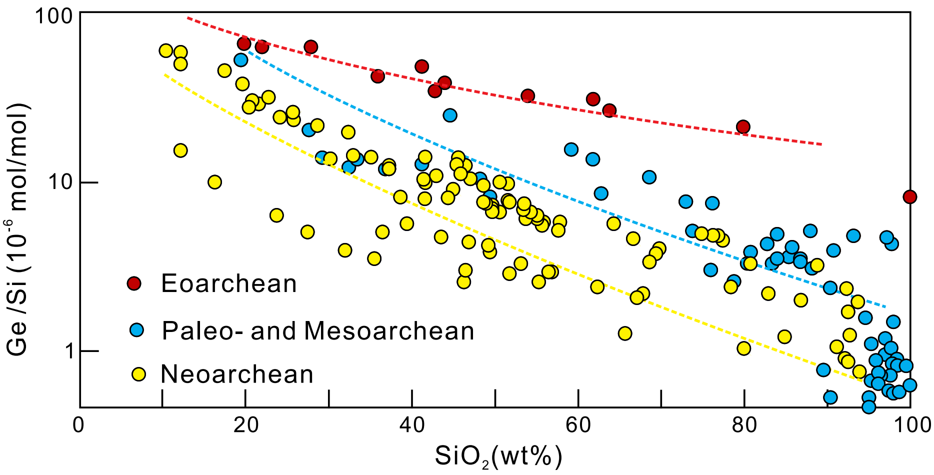

Figure 1. Relationship between SiO_2 (wt%) content and Ge/Si ratio in Archean banded iron formations.

Although Ge and Si concentrations vary, dissolved Ge/Si ratios (Ge/Si_{mol}: 0.7×10^{-6}) exhibit consistency across modern ocean basins (Guillermic et al., 2017). Modern marine Ge/Si_{mol} ratios are similar to those of rivers, indicating continental inputs as the main source, with only minor fractionation (<20%) during estuarine processes (Froelich et al., 1985). Further, there is minimal fractionation between Si and Ge during biogenic or abiotic silica precipitation (Bareille et al., 1998). As such, Ge/Si ratios in seawater can be preserved within Si-rich deposits, such as BIFs, which are composed of 15–40 wt% iron (Fe) and 40–60 wt% SiO_2 (Konhauser et al., 2017).

SAMPLES AND METHODS

We compiled Ge/Si ratios, along with associated aluminum (Al) and Fe contents in either bulk or individual microbands of Archean BIF samples, from literature sources (Table S1 in the Supplemental Material). We also generated new data for bulk BIF samples from Archean intervals with limited existing data. All samples were screened and have undergone minimal alteration (Wang et al., 2023). Samples are predominantly composed of magnetite and quartz, with smaller amounts of Fe(II)-silicates and -carbonates. Age, location, metamorphic grade, and data sources are provided in Table S1. Major elements were determined by X-ray fluorescence (XRF) analyses on fused beads, while trace elements, including Ge, were analyzed by inductively coupled plasma–mass spectrometry (ICP-MS) of powdered samples digested with HF-HCl-HNO_3 (see Supplemental Material).

RESULTS AND DISCUSSION

Evolution of Ge/Si Ratios

Before interpreting Ge/Si ratios in BIFs, it is essential to consider the effects of clastic contamination, diagenesis, and metamorphism. Most Archean BIF samples have <1 wt% Al_2O_3, and there is no correlation between Ge/Si and Al_2O_3 (Tables S1 and S2), suggesting negligible terrigenous input (Konhauser et al., 2017). Although small-scale repartitioning of Ge from Si occurs in modern sediment pore waters (Hammond et al., 2000; King et al., 2000), significant fractionation by chert has not been observed (<5%), and Ge/Si ratios in Si- and Fe-rich mesobands trend toward those in pure chert (Hamade et al., 2003; Bau et al., 2022) (Fig. 1). Further, it is unlikely that diagenetic and metamorphic alteration would have exclusively affected Ge and Si in bulk-rock samples (Bau et al., 2022). BIF samples do not exhibit Eu or light rare earth element (REE) depletion and are characterized by large positive Eu anomalies and consistent shale-normalized REE patterns regardless of metamorphic grade (e.g., Wang et al., 2023), arguing against significant secondary alteration. Therefore, minimal repartitioning of Ge from silica into Fe phases following deposition is expected.

Archean BIF samples show a range of Ge/Si ratios, with increasing Si contents in BIFs corresponding to lower Ge/Si ratios (Fig. 1). A shift toward higher Ge/Si ratios and Ge contents is observed in the relatively Fe-rich endmembers of BIFs, resembling present-day hydrothermal solutions and sediments (Froelich et al., 1985). This shift does not necessarily imply the presence of hydrothermal silica; rather, it suggests a higher concentration of Ge within the Fe phases. This is supported by the positive correlation between Ge and Fe in nearly all BIF samples (Fig. S1) and experimental evidence demonstrating preferential Ge adsorption by Fe(III)-oxyhydroxides (Pokrovsky et al., 2006). A study on Ge-Si in modern hydrogenetic marine Fe-Mn crusts confirms preferential scavenging of Ge by Fe(III) phases (Ernst et al., 2022). Therefore, Ge/Si variations within Archean BIFs are consistent with a two-component mixing scenario between silica and Fe(III)-oxyhydroxide endmembers, as proposed by Hamade et al. (2003).

To construct a plausible trend in seawater Ge/Si evolution, we used the hyperbolic correlation between Ge/Si ratios and SiO_2 for each BIF unit to extrapolate the Ge/Si ratio for the corresponding pure silica endmember. Results show a sharp decline in seawater Ge/Si ratios from $11.3 \pm 2.2 \times 10^{-6}$ prior to 3.5 Ga toward the Neoarchean average of $0.9 \pm 0.3 \times 10^{-6}$ (Fig. 2). This temporal change reflects an evolution in seawater, where Ge/Si ratios transition from marine hydrothermal fluids to values closer to modern continental runoff and seawater.

Onset of Subaerial Crustal Weathering

To decipher the mechanism controlling marine Ge/Si ratios, we constructed a Ge-Si mass balance model. In modern seawater, the major sources of Si are (1) riverine input, including submarine groundwater; (2) low-temperature dissolution of siliceous minerals in seawater and from sediments; (3) subglacial meltwater; (4) eolian dust; and (5) hydrothermal fluids (Tréguer et al., 2021). Among these, riverine (Si_{river}) and hydrothermal (Si_{hy}) inputs account for 70.3% and 11.5% of total Si input fluxes, respectively (Table S3). Germanium has the same sources as Si, but riverine (Ge_{river}) and hydrothermal (Ge_{hy}) inputs account for 25.2% and 71.5%, respectively (King et al., 2000). Marine Si precipitation (Si_{mar}), in the form of clay minerals and opaline silica shells, accounts for nearly 100% of the seawater Si sink. In the case of the opaline silica shells, diatoms effectively scavenge seawater Si, resulting in an average dissolved Si concentration of 70 μM in modern oceans (Tréguer et al., 1995).

Si precipitation in the early Precambrian oceans would have been predominantly driven by inorganic Si precipitation from seawater that was likely saturated with respect to amorphous silica prior to the evolution of silica-secreting organisms (2.2 mM; Maliva et al., 2005). As for Ge, the largest sink is biogenic opal (Ge_{SiO2}). Assuming a steady state, modern input fluxes require a non-SiO_2 sink (Ge_{nos}), which may be authigenic minerals such as Fe(III)-oxyhydroxides and aluminosilicates (King et al., 2000).

Given that riverine and hydrothermal inputs account for ~81.8% of Si and 96.7% of Ge fluxes and would have constituted the most relevant fluxes during continental emergence, we consider only these two sources. A simplified mass balance for Si and Ge, assuming a steady state, can then be expressed as

$$Si_{mar} = Si_{river} + Si_{hy}, \quad (1)$$

and

$$Ge_{SiO2} + Ge_{nos} = Ge_{river} + Ge_{hy}. \quad (2)$$

As there is negligible fractionation between Si and Ge during silica precipitation, which constitutes almost 100% of the marine Si sink, the

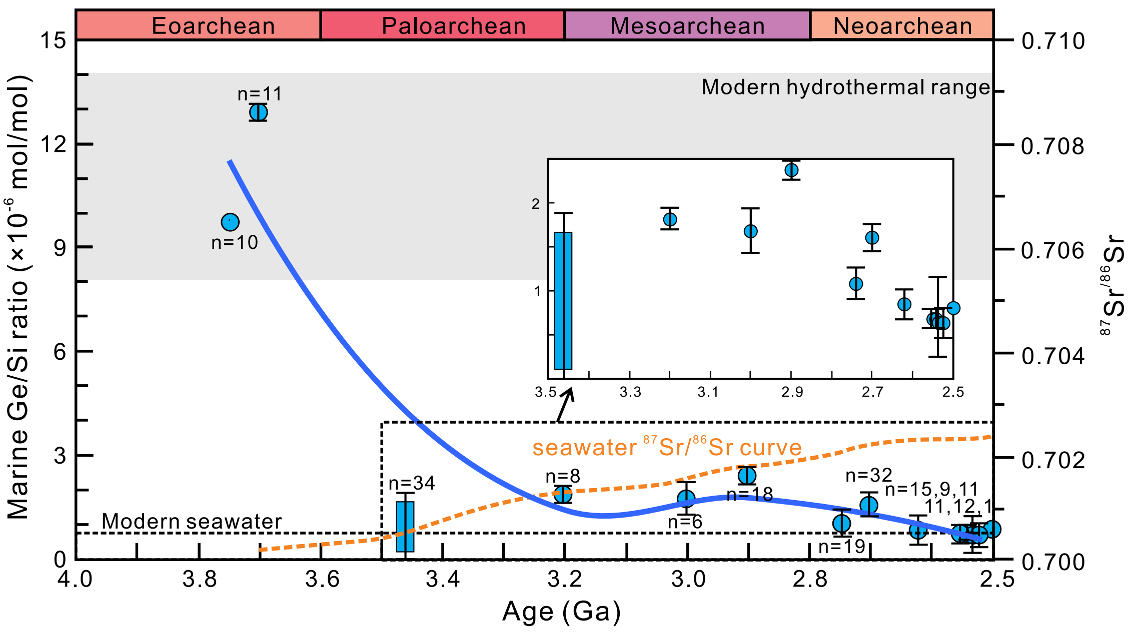

Figure 2. Secular trend in marine Ge/Si ratios (blue line) during the Archean and comparison with published seawater $^{87}Sr/^{86}Sr$ curve (orange dashed line; modified from Chen et al., 2022). Marine Ge/Si ratios (circles) are represented by the pure silica component extrapolated based on the hyperbolic relationship between SiO_2 (wt%) and Ge/Si for each banded iron formation unit. The rectangle represents the data range of the Dresser jaspilite (Dresser Formation, Western Australia). Error bars are 2σ uncertainties on each calculated value. Data, sources, screening criteria, metamorphic grade, and ages are provided in Table S1 (see text footnote 1).

Ge/Si ratio of silica precipitates should mirror that of seawater [$(Ge/Si)_{sw}$]. Therefore,

$$(Ge/Si)_{sw} = (Ge_{river} + Ge_{hy} - Ge_{nos}) / (Si_{river} + Si_{hy}) . \quad (3)$$

Using k to define the relative contribution of Si from riverine and hydrothermal fluxes ($k = Si_{river}/Si_{hy}$), Equation 3 can be rewritten as

$$(Ge/Si)_{sw} = (1 - Ge_{nos}/Ge_T) \times \left[(Ge/Si)_{river} \times k + (Ge/Si)_{hy}\right]/(1+k), \quad (4)$$

where $(Ge/Si)_{river}$ and $(Ge/Si)_{hy}$ are the Ge/Si ratios of river water and hydrothermal fluids, respectively, and Ge_T is the total marine Ge inventory. Equation 4 indicates that low marine Ge/Si ratios require a larger k; i.e., a larger riverine contribution relative to hydrothermal input, and/or a larger non-silica Ge sink (Fig. 3). A sensitivity test indicates (Figs. S2 and S3) that model outcomes are not sensitive to specific $(Ge/Si)_{river}$ and $(Ge/Si)_{hy}$ values.

Given the absence of land plants and eukaryotic soil biota, silicate weathering efficiency was likely lower during the Precambrian (Lenton and Watson, 2004). Consequently, k during the Archean is expected to be smaller than in the Recent (2.4–11.2; Tréguer et al., 2021). When k is less than ∼2.4, marine Ge/Si ratios are highly sensitive to changes in both k and the ratio of Ge_{nos}/Ge_T (Fig. 3).

Previous studies have hypothesized that Archean seawater was buffered by substantial hydrothermal input (Shields and Veizer, 2002; Flament et al., 2013). Further, positive Eu anomalies measured in Archean BIFs indicate a consistently strong hydrothermal flux (Konhauser et al., 2017; Wang et al., 2023). Hence, the observed decline in marine Ge/Si ratios likely reflects an increased riverine flux and extent of continental exposure.

The emergence of land may also have contributed to increased Ge_{nos} burial, leading to a further reduction in seawater Ge/Si. Generally, the burial of non-silica Ge occurs in rapidly accumulating shallow marine sediments deposited near redoxclines, along continental margins and suboxic basins (Hammond et al., 2000; King et al., 2000; Baronas et al., 2016). Today, these authigenic phases are dominated by aluminosilicates (products of reverse weathering) and, to a lesser extent, Fe(III)-oxyhydroxides (Baronas et al., 2016; Ernst et al., 2022). Enhanced authigenic clay formation may have occurred throughout much of the Precambrian, promoted by elevated concentrations of dissolved silica in seawater (Isson and Planavsky, 2018). However, the degree of reverse weathering depends on the extent of exposed continental landmass. If the fraction of exposed continental land was limited, previous modeling suggests a reduction in Archean reverse weathering (Krissansen-Totton and Catling, 2020). Evidence for elevated reverse weathering in the Archean includes the suppression of Ge/Ti ratios in BIFs since ca. 3.5 Ga (Fig. S4), which suggests a decline in authigenic Ge. As the decline in Ge/Ti does not coincide with maximum BIF deposition at ca. 2.5 Ga (Hamade et al., 2003), it is unlikely to be explained by enhanced BIF burial, as Ge/Fe ratios of Archean BIFs remain relatively consistent (Fig. S4). Accordingly, we interpret the decline in seawater Ge/Si during the Archean as indicative of a rapid increase in continental landmass exposure and subsequent subaerial weathering.

This view is consistent with an updated Sr isotope trend (Fig. 2; Chen et al., 2022) and with recent models for continental exposure (Rosas and Korenaga, 2021). The abrupt decline of seawater Ge/Si ratios, shifting from hydrothermal values to those resembling modern seawater, implies that weathering of emerged continental crust began between 3.7 Ga and 3.5 Ga. An early Archean onset of crustal weathering is consistent with Ti isotopic evidence indicating emerged felsic crust at ca. 3.5 Ga (Greber et al., 2017), the presence of exposed land surfaces in the siliciclastic rock record (Buick et al., 1995), epeiric marine deposits (e.g., sandstones and shales) (Drabon et al., 2017), and the existence of felsic crust by 3.5 Ga (Van Kranendonk et al., 2018).

Continental emergence and the onset of crustal weathering in the Archean would have been critical for Earth's nascent biosphere. Emergent continents would have created shallow marine environments conducive to biological innovations, such as the establishment of microbial communities in the form of benthic mats or photic-zone plankton. Moreover, newly emerged landmasses in the Archean would have provided a source of nutrients to the oceans through the establishment of riverine inputs. These nutrient fluxes could have provided an opportunity for the early biosphere to expand into newly available shallow marine environments, making the emergence of continents fundamental to the evolving Archean biosphere.

CONCLUSIONS

Our novel compilation of Ge-Si-Fe data reveals an inverse correlation between Ge/Si ratios and Si in Archean BIFs. We used this correlation to extrapolate Ge/Si ratios for seawater

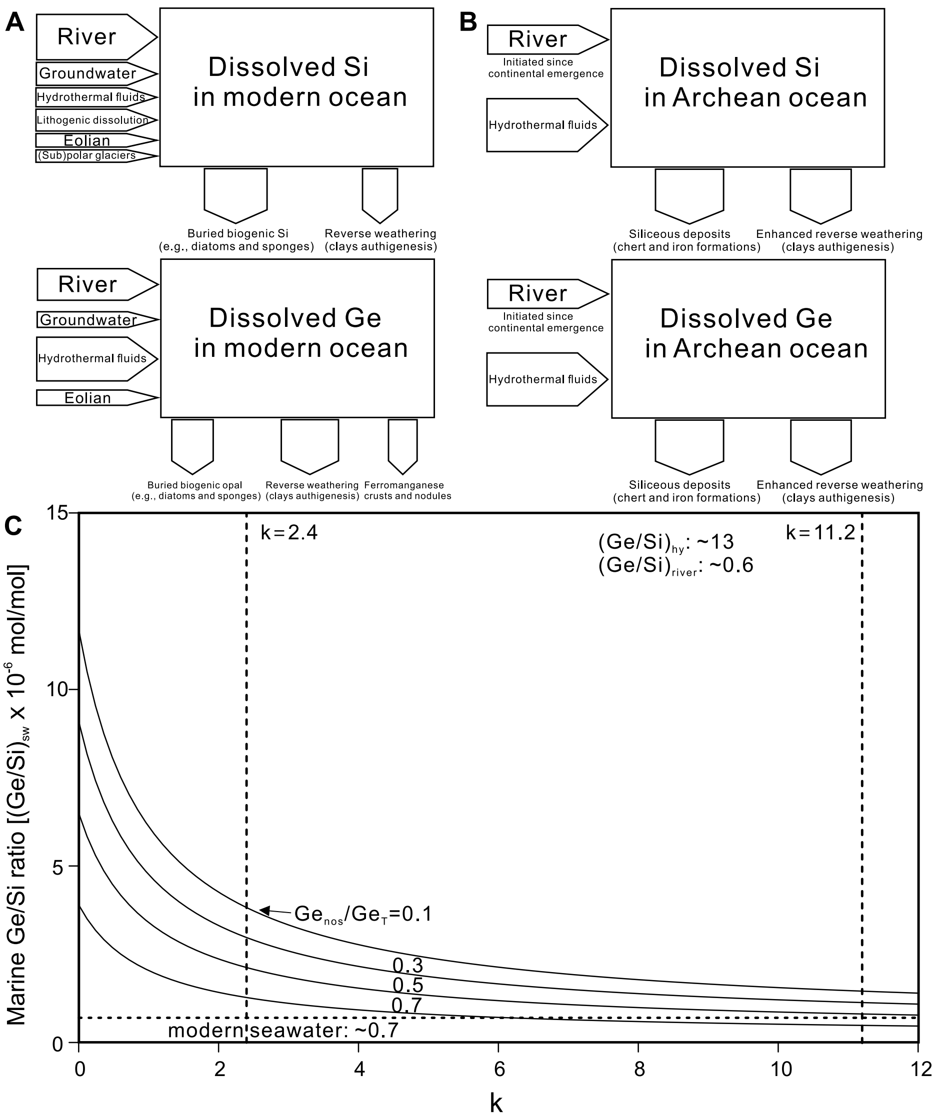

Figure 3. Box models showing modern (A) and Archean (B) marine Ge-Si cycles. (C) Mass-balance model showing the relationship between marine Ge/Si ratios [$(Ge/Si)_{sw}$] and the relative contribution (*k*) of Si from river water (river) and hydrothermal fluids (hy) versus total Ge input (Ge_T) for different non-silica Ge sink (Ge_{nos}) scenarios. Note, for modern seawater, $(Ge/Si)_{sw}$ is 0.7×10^{-6} mol/mol and *k* is 2.4–11.2.

contemporaneous to BIF deposition, where a significant inflection occurs at ca. 3.5 Ga and marks a decline in seawater Ge/Si from the Eoarchean to Neoarchean. This shift is attributed to an increasing continental weathering flux, a consequence of the emergence of continental crust by 3.5 Ga. The exposure of landmasses during the early Archean could imply a change in crustal dynamics that influenced the composition of the oceans and the evolutionary trajectory of the Archean biosphere.

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