

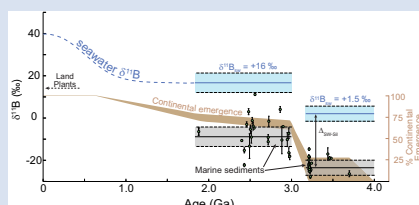
Boron isotopes in Archean-Proterozoic marine deposits trace continental emergence

A. Abbo^{1,2*}, H.R. Marschall^{1,2}, A. Gerdes^{1,2}



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Abstract



Emergence of continental crust profoundly impacted Earth's evolution by enriching oceans with nutrients enabling evolution of complex life. Crustal growth models indicate significant continental volume increases between 3.0–2.5 Ga, marking this period as critical, possibly linked to the transition towards subduction tectonics.

We present a novel approach to trace continental emergence by reconstructing the oceanic boron isotope composition from marine deposits (chert, iron formations and shales). Boron enrichment in continental crust means runoff directly influences ocean boron concentration and isotopic composition, with continental runoff representing the largest boron source on the modern Earth.

Our Archean-Proterozoic marine B isotope record reveals a major compositional shift at 3.0 Ga: pre-3.0 Ga deposits show mean $\delta^{11}\text{B}$ values of -23.5 ± 3.6 ‰, projecting to seawater $\delta^{11}\text{B}_{\text{sw}} = +1.5 \pm 3.6$ ‰, whereas post-3.0 Ga sediments exhibit mean $\delta^{11}\text{B}$ of -8.8 ± 4.6 ‰, projecting to seawater $\delta^{11}\text{B}_{\text{sw}} = +16.1 \pm 4.6$ ‰. The rapid change at this time likely reflects enhanced emergence and subaerial erosion after 3.0 Ga, substantially increasing the boron flux to the ocean. A second elevation to modern values ($\delta^{11}\text{B}_{\text{sw, modern}} = +39.6$ ‰) occurred throughout the Phanerozoic due to increased chemical weathering and fractionation following land plant appearance, also reflected in the $\delta^7\text{Li}$ record.

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Introduction

The reconstruction of the secular growth and accumulation of continental crust on Earth is crucial for understanding planetary differentiation and the evolution of the hydrosphere, atmosphere and biosphere. It thus attracts both major research efforts together with lively controversy (e.g., Dhuime *et al.*, 2018; Palin *et al.*, 2020; Stern and Gerya, 2024). The emergence of continental crust above sea level ensued continental erosion and the enrichment of ocean water with nutrients. This created conditions that enabled biomineralising marine microorganisms to evolve and flourish, setting the stage both for the evolution of complex life and for the oxygenation of Earth's atmosphere (Bindeman *et al.*, 2018). The accumulation of continental crust on Earth is also linked to changes in the tectonic style, *i.e.* the transition from stagnant/squishy lid vertical tectonics to modern style subduction driven horizontal lithospheric motions and interactions at plate boundaries (Spencer *et al.*, 2017; Palin *et al.*, 2020).

Although there is still no consensus on the onset of modern style plate tectonics on Earth, many studies point to 3.0–2.5 Ga (Archean-Proterozoic transition) as the time when subduction became dominant on Earth (Palin *et al.*, 2020). Most continental growth studies rely on compilations of records coming from fine grained sediments (shale) or from resilient minerals within them, such as zircon, and analyses of stable and radiogenic isotope systems such as Sr, Nd, Hf, and O that may indicate the separation of Earth reservoirs into

mantle and crust (e.g., Roerdink *et al.*, 2022). Such studies typically involve the compilation of large data sets based on extensive analytical work that required many years to gather. Uncertainties in these studies arise from potential representation bias of different source rocks in these sediments or their detrital mineral load (Andersen *et al.*, 2019). Alternatively, Archean-Proterozoic crustal rocks are investigated directly, but these are rather scarce on Earth with increasing age (Fig. 1), and each sample represents its regional/local environments and results are more difficult to extrapolate to the global regime. Notably, radiogenic isotopes are less powerful discriminators of crustal growth further back in Earth history, as the crust-mantle system diverged over time. This is not the case for stable isotopes, which follow the same fractionation laws independent of age.

Besides uncertainties on the composition and growth curve of continental crust, it remains unclear what was the extent of exposure of Archean crust above sea level. Estimates of crustal emergence through time are both scarce and variable. Recently Mineart *et al.*, (2025) reconstructed the oxygen isotope composition of seawater deduced from Archean-Proterozoic altered oceanic complexes, to propose modern-like emergence was achieved by *ca.* 1720 Ma, albeit involving complex calculations for the deduction. Complications in evaluating emergence rise from the scarcity and uneven spatial distribution of Archean-Proterozoic exposure (Fig. 1), and from the variable metamorphic alteration in many of these rocks, which may have overprinted their original geochemical signals.

1. Institut für Geowissenschaften, Goethe-University Frankfurt, D-60438 Frankfurt am Main, Germany

2. Frankfurt Isotope and Element Research Center (FIERCE), Goethe-University Frankfurt, Germany

* Corresponding author (email: abbo@geo.uni-frankfurt.de)

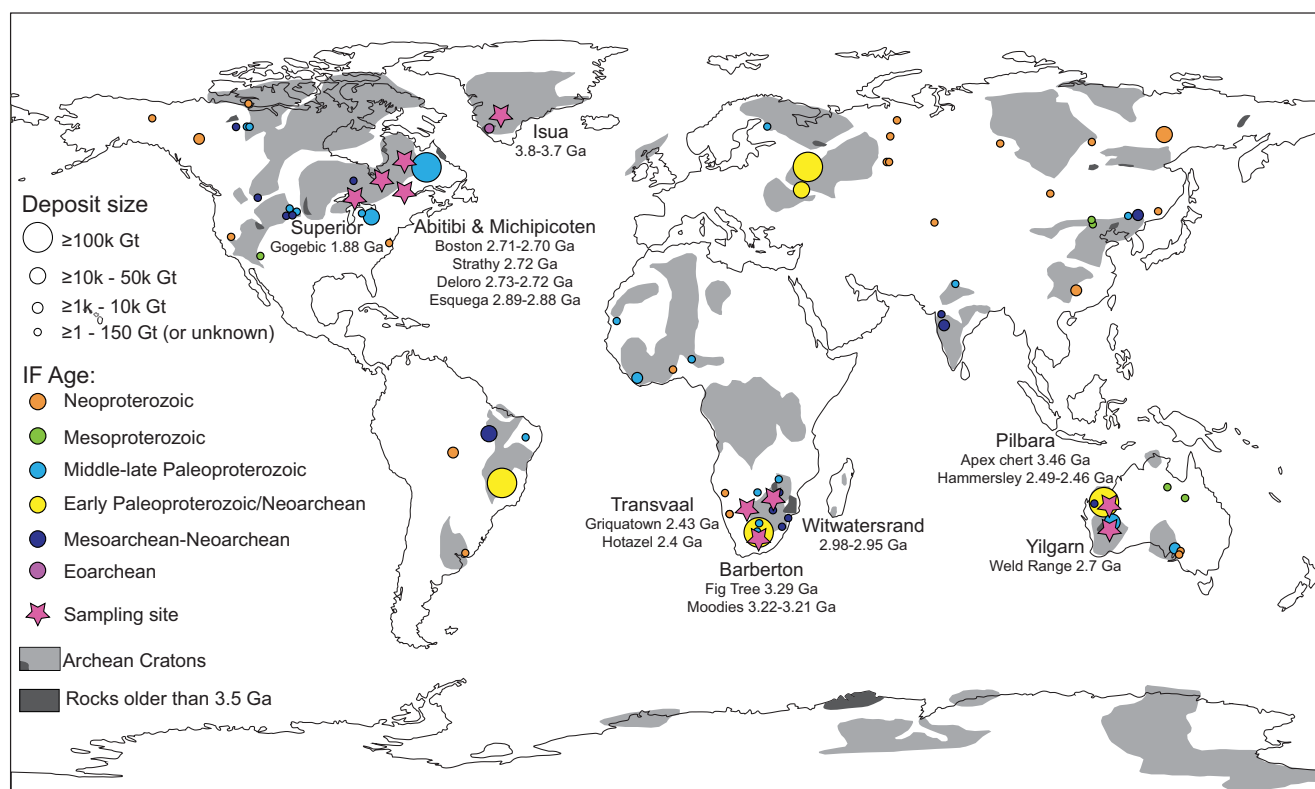


Figure 1 Global distribution of Iron Formations (after Konhauser *et al.*, 2017). Stars indicate sample locations (Table S-1). Also shown are Archean cratons and rocks >3.5 Ga.

Unlike continental rocks, the ocean is a well mixed global reservoir, greatly affected geochemically by changes in the adjacent emerged landmass exposed to subaerial erosion. Marine sediments record the geochemical composition of ocean water, which is in part controlled by the global continental runoff. Marine sediments thus allow tracing of continental processes on Earth (Frings *et al.*, 2016). Modern oceans are oxygenated, slightly alkaline and host a variety of biomineralising microorganisms that account for most marine sedimentation – carbonate and silica. Properties of the Archean ocean are less firmly constrained (Bekker *et al.*, 2014; Albarede *et al.*, 2020). Archean oceans were probably deficient of oxygen, more acidic than their modern counterparts and for the most part devoid of biomineralising agents (Krissansen-Totton *et al.*, 2018; Albarede *et al.*, 2020). Archean marine chemical sediments (such that precipitated directly from the ocean water) mostly consist of chert and/or Iron Formations (IFs) alongside subordinate carbonate rocks and marine shales. The mechanisms responsible for IFs and chert deposition are still debated (Bekker *et al.*, 2014; Konhauser *et al.*, 2017; Rasmussen *et al.*, 2021), yet they are considered to represent chemical precipitation from seawater, probably assisted by Fe oxidising bacteria (Konhauser *et al.*, 2017). Archean cherts and IFs are chemical marine deposits, which precipitated hydrothermally sourced Fe and Si directly from seawater (assisted by microbial and/or photochemical Fe oxidation). Therefore, these deposits serve as an archive of the chemical composition of Archean seawater (Bekker *et al.*, 2014; Konhauser *et al.*, 2017) and record the effects continental emergence had upon it.

The long-term variation in oceanic B isotopic composition ($\delta^{11}\text{B}_{\text{sw}}$) is controlled by the balance of input and output fluxes, which are affected in composition and magnitude by the global tectonic regime (Fig. 2; see discussion in the Supplementary Information). Emergence of continental crust above sea level

and its erosion significantly affected the chemical composition of global seawater, $\delta^{11}\text{B}_{\text{sw}}$ included. The geochemical signal preserved in Archean-Proterozoic marine deposits such as IFs, cherts and marine shales is expected to record that change. In this study we utilise the analysis of B isotopes in Archean-Proterozoic marine deposits to reconstruct the ancient seawater composition and its secular variation, and to infer the influence of continental erosion (and emergence) on this compositional change.

Results

Samples of IFs, chert and shale, with age constraints spanning between 3.7–1.88 Ga (Table S-1), were prepared, examined by optical and electron microscopy, and measured for boron concentrations and isotope composition using Laser Ablation-Multi-Collector-Inductively Coupled Plasma Mass Spectrometry (LA-MC-ICPMS). Obtained $\delta^{11}\text{B}$ results were translated to the contemporaneous seawater composition ($\delta^{11}\text{B}_{\text{sw}}$) by applying a fractionation factor (see Supplementary Information for details; Figs. 3,4), while accounting for the measured mineral phase and evaluated pH for Archean-Proterozoic seawater (Spivack *et al.*, 1987; Krissansen-Totton *et al.*, 2018; Saldi *et al.*, 2021). Multiple analytical spots on mineralogically different sediment layers (if present) were measured within each sample. Seawater composition was reconstructed from values measured in silica and clay phases. We accounted for possible detrital contamination and mixing (co-ablation) with Fe oxides by examining results in $\delta^{11}\text{B}$ vs. [B] space and isolating the silica end member. This was apparent in 5 of the 48 samples, whereas the remaining 43 samples showed a homogenous composition (see Supplementary Information; Fig. S-4). A detailed discussion of the boron fractionation factors between bulk acidic seawater

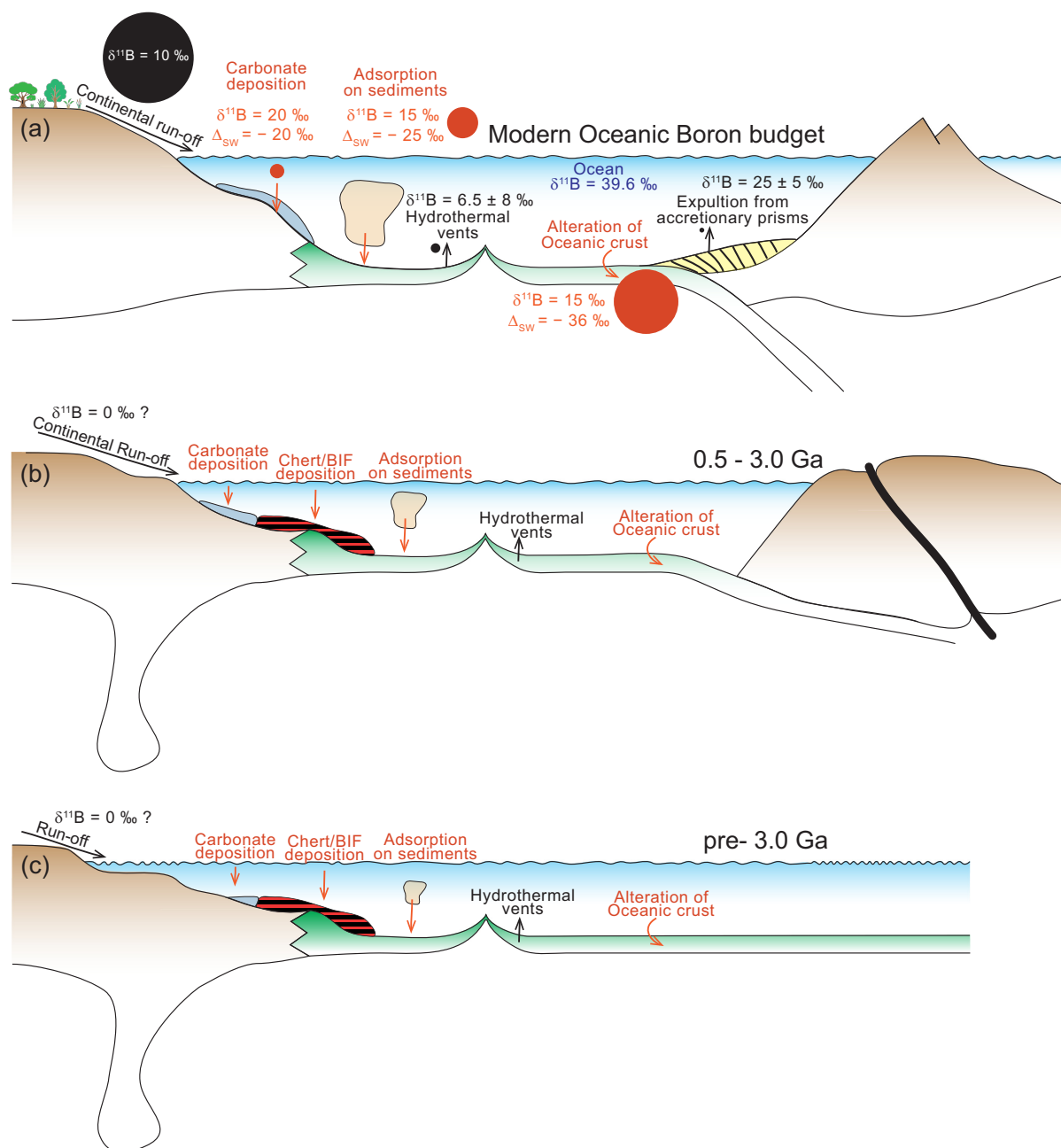


Figure 2 (a) Modern oceanic boron budget showing fluxes in/out of the ocean with $\delta^{11}\text{B}$ composition and fractionation factors (Δ). Circle sizes are proportional to modern flux magnitudes (after Lemarchand *et al.*, 2002). (b) Proposed oceanic boron budget for 3.0–0.5 Ga showing main fluxes including IF deposition and growing continental crust. (c) Proposed oceanic boron budget for pre-3.0 Ga Earth (see text). While fractionation factors remain mostly unchanged, past magnitudes and $\delta^{11}\text{B}$ values of the different fluxes are mostly unconstrained.

and the precipitated solids, sample selection criteria including a detailed discussion on the determination of $\delta^{11}\text{B}_{\text{sw}}$ from marine sediments, description of our analytical setup including data processing and statistical considerations, and the determination of $\delta^{11}\text{B}_{\text{sw}}$ from marine sediments are given in the [Supplementary Information](#).

Most IFs, especially older than 3.0 Ga, show boron concentrations below 10 $\mu\text{g/g}$ (Fig. 3a). Higher B concentrations of up to 30 $\mu\text{g/g}$ were found in IFs and cherts of the Fig Tree group in the Barberton Greenstone Belt (BGB). Marine shale samples from overlying the Moodies group also show high [B], akin to modern shales (50–150 $\mu\text{g/g}$; Spivack *et al.*, 1987; Ishikawa and Nakamura, 1993;). In addition, samples from

the Moodies group include subordinate IFs with variably lower [B]. Overall IFs, cherts and shales show boron concentrations between 0.1–60 $\mu\text{g/g}$, and an increased variability of [B] set in at *ca.* 3.2 Ga (Fig. 3a). Out of all measured samples, 57 % show [B] < 10 $\mu\text{g/g}$. Hammersley group samples show some variability in boron concentration, however only one sample has [B] > 10 $\mu\text{g/g}$.

It is evident from measured $\delta^{11}\text{B}$ of silica in IFs and shales that the seawater boron isotopic composition shifted prominently in the Mesoarchean. Samples older than 3 Ga from Isua, the BGB and the Pilbara craton all cluster between $\delta^{11}\text{B}$ of -28 and -17 ‰ with a weighted mean of $-23.5 \pm 3.6 \text{ ‰}$ (2 s.e.; Figs. 3b, 4), translating to seawater composition of

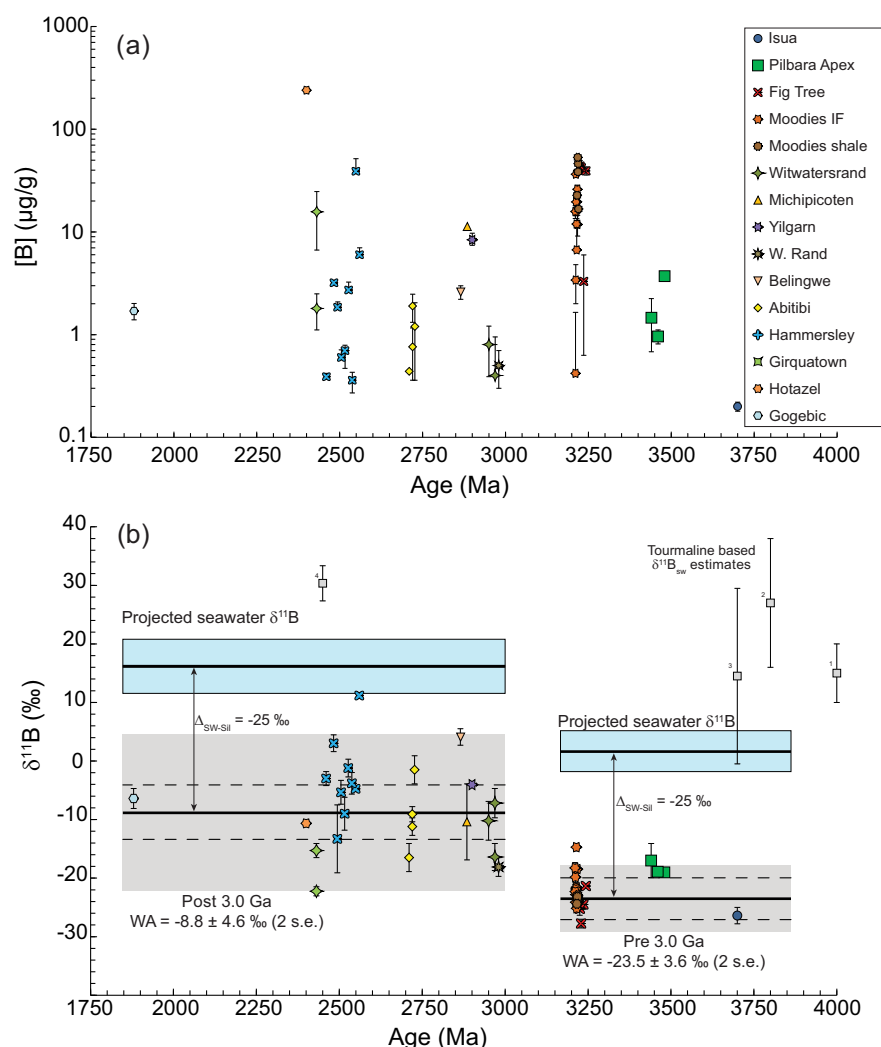


Figure 3 (a) Boron concentrations vs. age for all samples (Table S-1). (b) Boron isotopic composition vs. age for all samples (Table S-1). Values shown are of silica in IF, chert or shale (see Table S-1). Also shown are Archean-Proterozoic oceanic B estimates (¹Chaussidon and Albarède, 1992; ²Chaussidon and Appel, 1997; ³Grew *et al.*, 2015; ⁴Bhuyan *et al.*, 2023). Grey shaded areas and dashed lines represent 2 s.d. and 2 s.e. respectively about the weighted mean of each sample group (see text).

$\delta^{11}\text{B}_{\text{SW}} = +1.5 \pm 3.6 \text{ ‰}$, which is isotopically much lighter than modern seawater (+39.6 ‰). The post-2.9 Ga Mesoarchean and the Neoarchean samples show a noticeably heavier $\delta^{11}\text{B}$ compositions, with values as high as $\delta^{11}\text{B} = +4.1 \text{ ‰}$, as well as an increased scatter in $\delta^{11}\text{B}$ compared to pre-3.0 Ga. Post-3.0 Ga material represents a mean seawater value of $+16.1 \pm 4.6 \text{ ‰}$ (Figs. 3, 4). This is a well pronounced shift from the pre-3 Ga signal notwithstanding the spread and uncertainties in our data set. The pre- and post-3.0 Ga sample populations are statistically different (Welch's t test: $t = 8.60$, $p = 1.16 \times 10^{-9}$), demonstrating they remain distinct well beyond the 99.9 % confidence level, despite internal variability within each group. The youngest Paleoproterozoic samples, represented by the Hammersley group of the Pilbara craton and the Griquatown IF from the Transvaal Supergroup show a large variation in $\delta^{11}\text{B}$ spanning almost 25 ‰ (Fig. 3b). Such variation over less than 150 Myr raises questions whether it reflects global changes in seawater composition or rather local or regional effects. We also noted the effect of admixing of Fe oxide and possibly detrital components to the silica phase in some of the Hammersley samples. We took care to isolate the effects of such mixing as much as possible (Fig. S-4; see above and [Supplementary Information](#) for elaboration).

Discussion

The notion that variation of the seawater isotopic composition reflects changes in the continental regime and was impacted by the extent of emerged continental crust was previously demonstrated based on traditional isotope systems (Frings *et al.*, 2016). Boron has a long residence time in the modern ocean and large shifts of the boron isotopic composition in global seawater reflect changes in the dominant fluxes of boron to and from the ocean (Lemarchand *et al.*, 2002; Joachimski *et al.*, 2005). While the Phanerozoic record of $\delta^{11}\text{B}_{\text{sw}}$ shows an increase of similar magnitude (*ca.* 10 ‰) to our recorded shift across the 3.0 Ga boundary (where it occurred over a time interval of less than 300 Myr; Fig. 4), we should highlight the fundamental difference in the boron cycle between the Archean and Phanerozoic. Without terrestrial vegetation covering the continents, boron fractionation is limited to processes of continental crust formation producing an average composition very close to the mantle and Bulk Silicate Earth (BSE). Terrestrial vegetation and soils were shown to enrich ^{11}B in the weathering environment, in a mechanism also described for ^7Li (Gaillardet and Lemarchand, 2018; Kalderon-Asael *et al.*, 2021). Therefore, influx of B from continental weathering into the Archean ocean

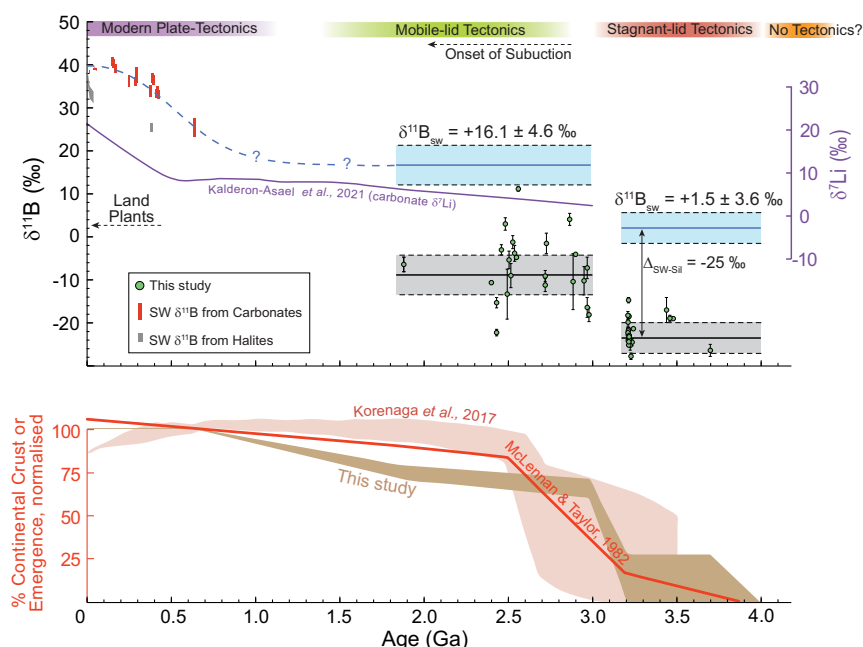


Figure 4 $\delta^{11}\text{B}$ and projected seawater composition from marine sediments (this study). Also shown: Phanerozoic carbonate/halite records (Lemarchand *et al.*, 2002; Joachimski *et al.*, 2005; Kasemann *et al.*, 2010; Paris *et al.*, 2010; Foster *et al.*, 2012; Clarkson *et al.*, 2015; Anagnostou *et al.*, 2016; Marschall, 2018); carbonate $\delta^7\text{Li}$ (Kalderon-Asael *et al.*, 2021); tectonic regimes (Palin *et al.*, 2020). Bottom panel shows continental emergence model envelope based on $\delta^{11}\text{B}_{\text{SW}}$ (see text) alongside crustal growth and emergence curves normalised to 100 % crust or emergence at 0.64 Ga (McLennan and Taylor, 1982; Korenaga *et al.*, 2017; see text).

was significantly lighter than the modern equivalent (Fig. 2). The observed shift in $\delta^{11}\text{B}_{\text{SW}}$ of more than 10 ‰ in the time interval between 3.2 and 2.9 Ga in absence of vegetation, requires major changes in the boron flux to the ocean. The most plausible candidate that can explain such a change is the emergence of continental landmass of a significant extent above sea level followed by subaerial weathering, transporting boron into the ocean, and the isotopic fractionation these processes entail.

Using a mass balance model, we reconstruct the history of continental emergence from the boron isotopic evolution of the reconstructed seawater curve, which evolves from $\delta^{11}\text{B}_{\text{SW}} = +1.9$ ‰ between 3.70–3.21 Ga to +16.2 ‰ at 2.98–2.40 Ga to +25.5 ‰ in the Neoproterozoic (Kasemann *et al.*, 2010). The Neoproterozoic $\delta^{11}\text{B}_{\text{SW}}$ value (Kasemann *et al.*, 2010) is taken to represent 100 % continental emergence (relative to the modern state), but still in the absence of terrestrial vegetation (Fig. 4), and assuming continental emergence is the sole component contributing to changes in $\delta^{11}\text{B}_{\text{SW}}$. Continental emergence is then computed from its proportionality with the shift in $\delta^{11}\text{B}_{\text{SW}}$, which is 3.1–4.2 ‰ per percent of emerged crust relative to the present, or 0.24–0.33 % emerged crust for each per mille elevation in $\delta^{11}\text{B}_{\text{SW}}$ (see Supplementary Information; Table S-5). Our model suggests that the amount of emerged continental crust in the Eo-/Paleoarchean is bracketed to between zero and approximately one quarter (0–27.6 %) of the amount of crust emerged today (depending on the degree to which the shift from the $\delta^{11}\text{B} = -7.1$ ‰ of the mantle to +1.9 ‰ recorded by the oldest marine sediments was caused by continental emergence). The value of continental emergence in the late Archean to early Proterozoic (2.98–2.40 Ga) is not very sensitive to the choice of this parameter and is bracketed between 60.2 % and 71.2 % (Fig. 4; see Table S-5).

It is noteworthy that our results align with published continental growth curves (McLennan and Taylor, 1982; Korenaga *et al.*, 2017; Reimink *et al.*, 2023; Figs. 4, S-1), portraying rapid growth and emergence of continents in the

Mesoarchean. Our results also show that continental growth and emergence produced an isotopic signal that is globally evident and is sensitive to the amount of exposed crust above sea level.

Previous reconstructions of Archean-Proterozoic $\delta^{11}\text{B}_{\text{SW}}$ have relied on multi-step calculations from $\delta^{11}\text{B}$ analyses of tourmaline (Chaussidon and Albarède, 1992; Chaussidon and Appel, 1997; Grew *et al.*, 2015; Bhuyan *et al.*, 2023). Because tourmaline does not form on the ocean floor, such reconstructions are indirect: they require estimates of mineral-fluid fractionation and assumptions about the protolith of the schists in which the tourmaline is found, and it has been argued that they may not constrain ancient seawater composition (Byerly and Palmer, 1991). Full propagation of the uncertainties related to the various fractionation steps yields a precision of ± 15 ‰ (Grew *et al.*, 2015); hence, although tourmaline based values are nominally 10–15 ‰ heavier than ours (Fig. 3b), some overlap within error. Our approach, *in situ* analysis of marine deposits combined with the established seawater-silica fractionation (Saldi *et al.*, 2021), rests on fewer assumptions and accumulates less uncertainty.

Our data suggest an evolution of $\delta^{11}\text{B}_{\text{SW}}$ from an initially low value (closer to the mantle value of -7.1 ± 0.9 ‰; Marschall *et al.*, 2017) toward its present level, not through a continuous secular increase, but in a stepped increase across 3.0 Ga (Figs. 2, 4). Evolution across the Mesoproterozoic, however, calls for further exploration.

Phanerozoic $\delta^{11}\text{B}_{\text{SW}}$ evolution is constrained by a denser set of estimates from analysed marine sediments, as well as box model reconstructions (Lemarchand *et al.*, 2002; Joachimski *et al.*, 2005; Legett *et al.*, 2020; Jurikova *et al.*, 2025). Seawater boron isotopic reconstructions from Neoproterozoic carbonates provide $\delta^{11}\text{B}_{\text{SW}} = +25$ ‰ (Kasemann *et al.*, 2010), which are only 11 ‰ heavier than the mean of our estimate from early Paleoproterozoic IFs (Fig. 4). This suggests that change in the extent of emerged continents was not insignificant (21–29 %

of the modern extent) over the gap of 1.25 billion years between 1.88 and 0.64 Ga, *i.e.* the so called 'boring billion' (Brasier, 2012).

The first major observable shift in $\delta^{11}\text{B}_{\text{sw}}$ precedes the formation of the first supercontinent at *ca.* 2.7 Ga (Ur). Some crustal growth models predict the formation of large swaths of continental crust already at that time (Figs. 4, S-1). The post-3 Ga major rise in $\delta^{11}\text{B}_{\text{sw}}$ documented here likely represents the response of the oceans to accumulation and emergence of continental crust after 3.2 Ga, due to the onset of boron input into the ocean *via* erosion and the resultant additional fluxes (*e.g.*, adsorption) that began to operate. A second stage of increase in $\delta^{11}\text{B}_{\text{sw}}$ occurred in the Neoproterozoic and Phanerozoic towards the modern value (Fig. 4). Interestingly, oceanic $\delta^7\text{Li}$ values estimated from carbonate rocks also show a similar increase towards the modern value starting in the early Phanerozoic, attributed to the evolution of terrestrial plants (Kalderon-Asael *et al.*, 2021). To date, the seawater Li isotope record does not extend far enough back to allow for an evaluation of the critical period around 3 Ga identified here in the B isotope record (Kalderon-Asael *et al.*, 2021). Overall, we demonstrated that the record of $\delta^{11}\text{B}_{\text{sw}}$ may be used as a proxy for the buildup and emergence of continental crust and its erosion. This new tool of boron isotopic analysis of Precambrian marine deposits may shed light on early Earth and Archean-Proterozoic processes and can complement existing isotopic tracers of continental evolution.

Implications for seawater and crustal evolution:

We present the first comprehensive record of Archean-Proterozoic $\delta^{11}\text{B}_{\text{sw}}$ traced from marine deposits including IFs, chert, and shales, utilising a protocol capable of measuring boron isotopes in low concentration samples ($\geq 0.2 \mu\text{g/g}$) with meaningful precision and accuracy. Our data spanning 3.7 to 1.88 Ga across multiple cratons reveal a significant compositional shift in silica $\delta^{11}\text{B}$ from a mean of $-23.5 \pm 3.6 \text{‰}$ pre-3.0 Ga to a mean of $-8.8 \pm 4.6 \text{‰}$ post-3.0 Ga, corresponding to projected $\delta^{11}\text{B}_{\text{sw}}$ values of $+1.5 \pm 3.6 \text{‰}$ and $+16.1 \pm 4.6 \text{‰}$ respectively. We suggest this shift reflects enhanced continental crustal emergence and associated subaerial weathering driving increased boron transport into the ocean that outpaced boron removal by seafloor alteration. Our results support independent crustal growth models that indicate rapid continental crust accumulation by 3.0 Ga. Our simple model based on the evolution of $\delta^{11}\text{B}_{\text{sw}}$ suggests that continental emergence had reached 0–27 % of the modern value by 3.7 Ga, evolved further to 60–71 % continental emergence between 3.2 and 3.0 Ga and further emergence throughout the Proterozoic, particularly the Mesoproterozoic. A second phase of apparent increase in $\delta^{11}\text{B}_{\text{sw}}$ throughout the Phanerozoic (parallel to the increase in seawater $\delta^7\text{Li}$) was likely related to the appearance and radiation of terrestrial plants, developing incongruent weathering regimes that led to the enhanced formation of terrestrial clays.

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Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2635>.



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