

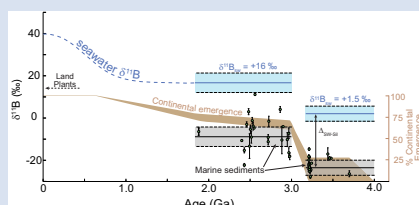
Boron isotopes in Archean-Proterozoic marine deposits trace continental emergence

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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.

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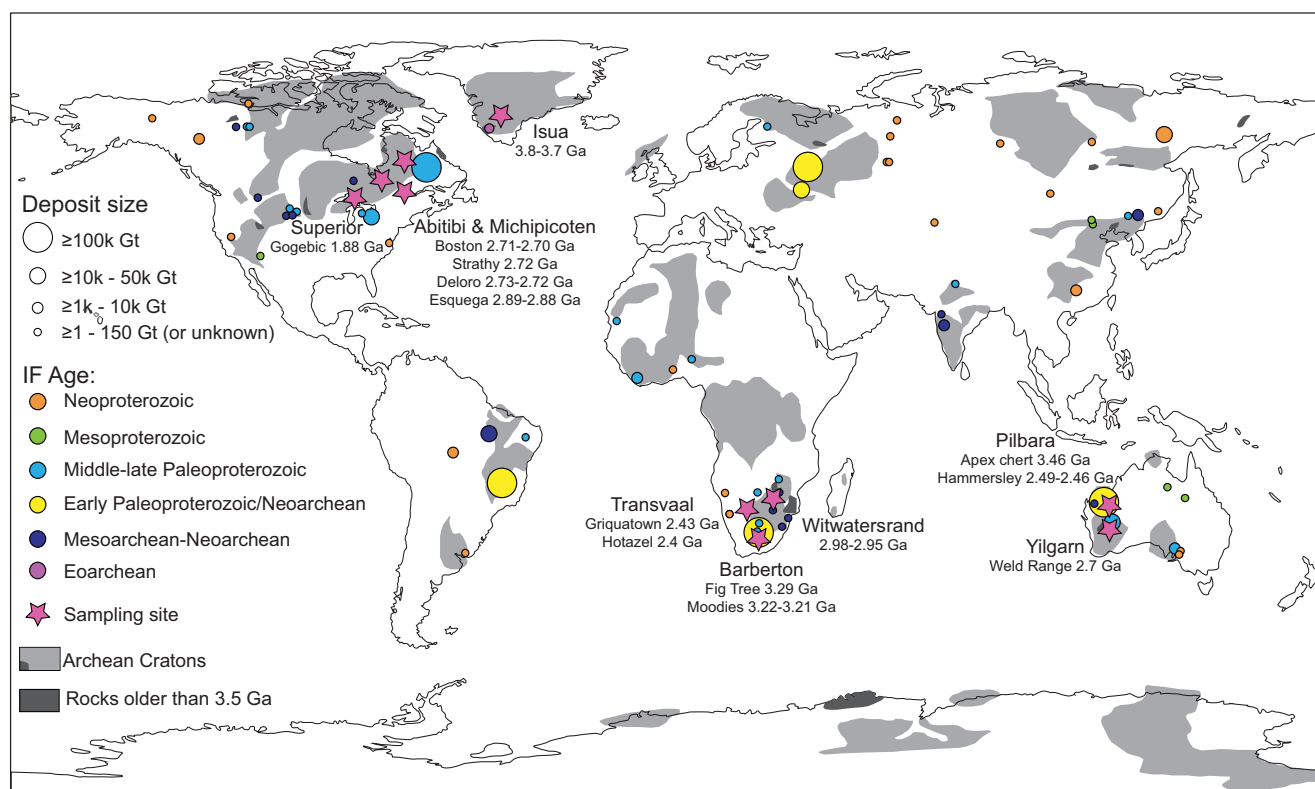


Figure 1 Global distribution of Iron Formations (after Konhauser *et al.*, 2017). Stars indicate sample locations (Table S-1). Also shown are Archean cratons and rocks >3.5 Ga.

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

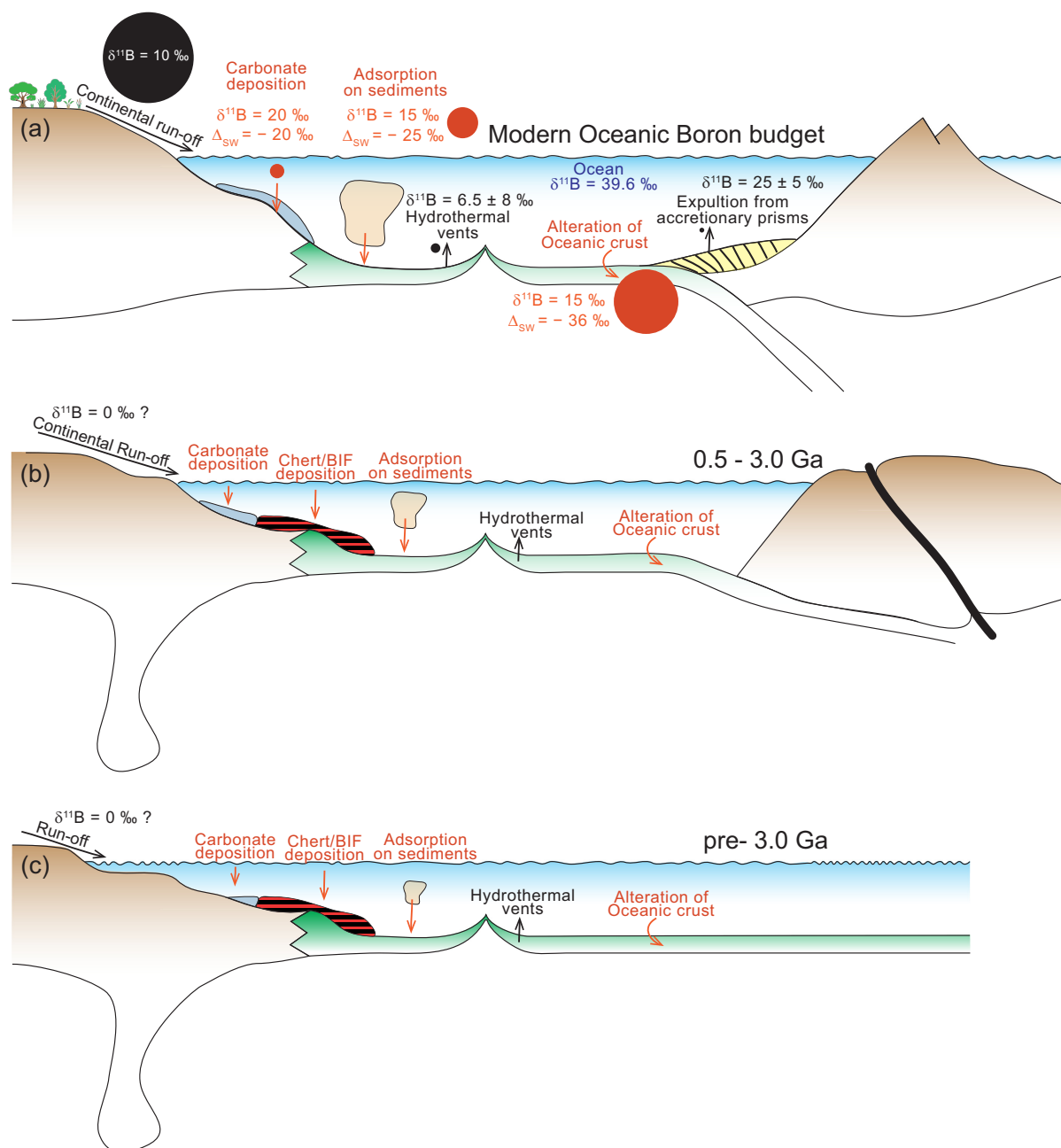


Figure 2 (a) Modern oceanic boron budget showing fluxes in/out of the ocean with $\delta^{11}\text{B}$ composition and fractionation factors (Δ). Circle sizes are proportional to modern flux magnitudes (after Lemarchand *et al.*, 2002). (b) Proposed oceanic boron budget for 3.0–0.5 Ga showing main fluxes 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

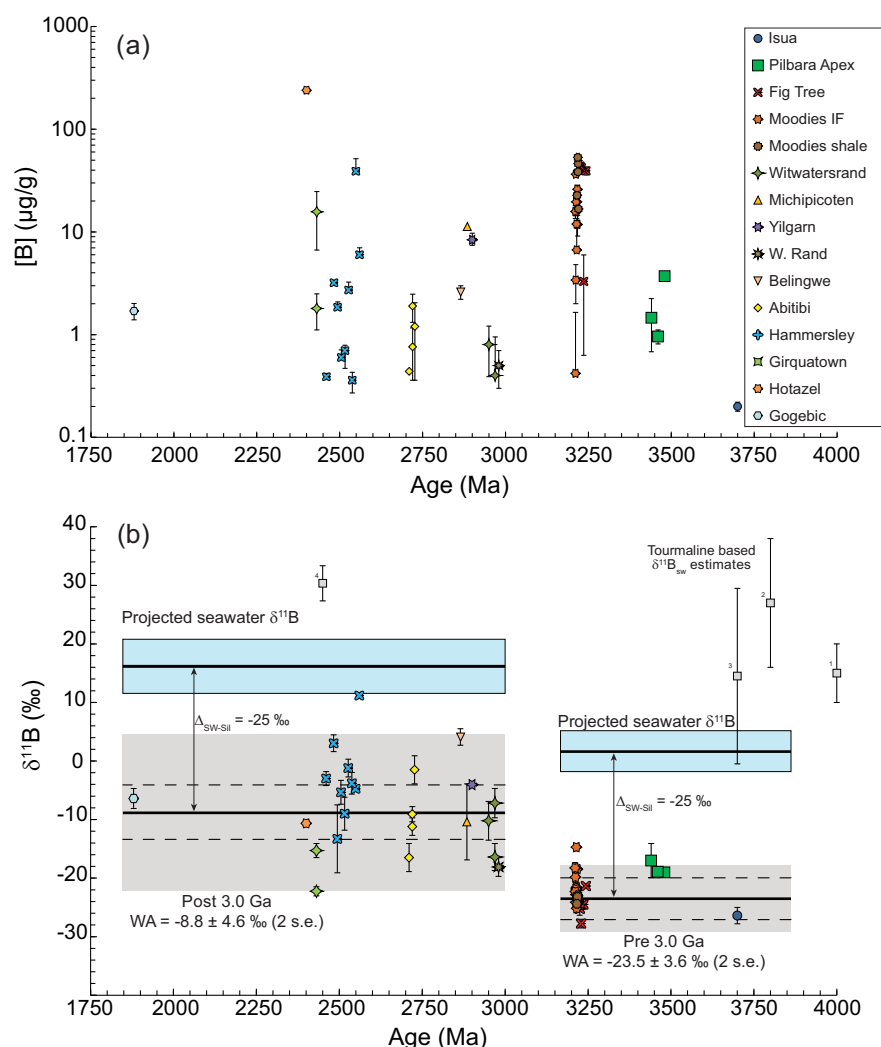


Figure 3 (a) Boron concentrations vs. age for all samples (Table S-1). (b) Boron isotopic composition vs. age for all samples (Table S-1). Values shown are of silica in IF, chert or shale (see Table S-1). Also shown are Archean-Proterozoic oceanic B estimates (¹Chaussidon and Albarède, 1992; ²Chaussidon 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

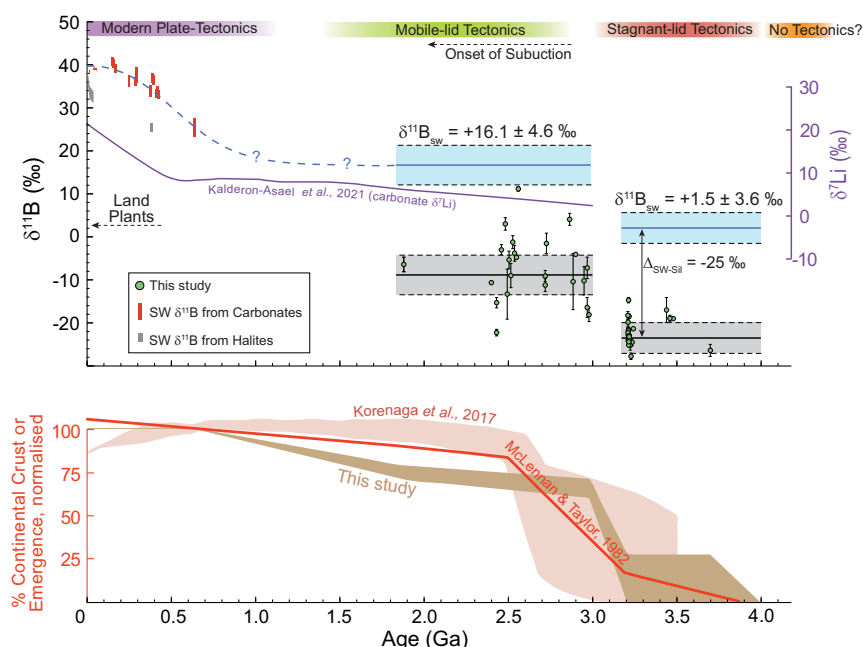


Figure 4 $\delta^{11}\text{B}$ and projected seawater composition from marine sediments (this study). Also shown: Phanerozoic carbonate/halite records (Lemarchand *et al.*, 2002; Joachimski *et al.*, 2005; Kasemann *et al.*, 2010; Paris *et al.*, 2010; Foster *et al.*, 2012; Clarkson *et al.*, 2015; 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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References

- ALBAREDE, F., THIBON, F., Blichert-Toft, J., Tsikos, H. (2020) Chemical archaeoceanography. *Chemical Geology* 548, 119625–119625. <https://doi.org/10.1016/j.chemgeo.2020.119625>
- ANAGNOSTOU, E., JOHN, E.H., EDGAR, K.M., FOSTER, G.L., RIDGWELL, A., *et al* (2016) Changing atmospheric CO₂ concentration was the primary driver of early Cenozoic climate. *Nature* 533, 380–384. <https://doi.org/10.1038/nature17423>
- ANDERSEN, T., ELBURG, M.A., MAGWAZA, B.N. (2019) Sources of bias in detrital zircon geochronology: Discordance, concealed lead loss and common lead correction. *Earth-Science Reviews* 197, 102899–102899. <https://doi.org/10.1016/j.earscirev.2019.102899>
- BEKKER, A., PLANAVSKY, N.J., KRAPEZ, B., RASMUSSEN, B., HOFMANN, A., SLACK, J.F., ROUXEL, O.J., KONHAUSER, K.O. (2014) 9.18 - Iron Formations: Their Origins and Implications for Ancient Seawater Chemistry. In: HOLLAND, H.D., TUREKIAN, K.K. (Eds.) *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford, 561–628. <https://doi.org/10.1016/B978-0-08-095975-7.00719-1>
- BHUYAN, N., HAZARIKA, P., UPADHYAY, D. (2023) Continental evaporites as brine sources for formation of SEDEX and MVT deposits: Implications from boron isotope compositions of tourmaline. *Geochimica et Cosmochimica Acta* 361, 82–100. <https://doi.org/10.1016/j.gca.2023.10.014>
- BINDEMAN, I.N., ZAKHAROV, D.O., PALANDRI, J., GREBER, N.D., DAUPHAS, N., RETALLACK, G.J., HOFMANN, A., LACKEY, J.S., BEKKER, A. (2018) Rapid emergence of subaerial landmasses and onset of a modern hydrologic cycle 2.5 billion years ago. *Nature* 557, 545–548. <https://doi.org/10.1038/s41586-018-0131-1>
- BRASIER, M.D. (2012) *Secret chambers: the inside story of cells and complex life*. Oxford University Press.
- BYERLY, G.R., PALMER, M.R. (1991) Tourmaline mineralization in the Barberton greenstone belt, South Africa: early Archean metasomatism by evaporite-derived boron. *Contributions to Mineralogy and Petrology* 107, 387–402. <https://doi.org/10.1007/BF00325106>
- CHAUSSIDON, M., ALBAREDE, F. (1992) Secular boron isotope variations in the continental crust: an ion microprobe study. *Earth and Planetary Science Letters* 108, 229–241. [https://doi.org/10.1016/0012-821X\(92\)90025-Q](https://doi.org/10.1016/0012-821X(92)90025-Q)
- CHAUSSIDON, M., APPEL, P.W.U. (1997) Boron isotopic composition of tourmalines from the 3.8-Ga-old Isua supracrustals, West Greenland: Implications on the $\delta^{11}\text{B}$ value of early Archean seawater. *Chemical Geology* 136, 171–180. [https://doi.org/10.1016/S0009-2541\(96\)00140-4](https://doi.org/10.1016/S0009-2541(96)00140-4)

- CLARKSON, M.O., KASEMANN, S.A., WOOD, R.A., LENTON, T.M., DAINES, S.J., *et al* (2015) Ocean acidification and the Permo-Triassic mass extinction. *Science* 348, 229–232. <https://doi.org/10.1126/science.aaa0193>
- DHUIE, B., HAWKESWORTH, C.J., DELAVALT, H., CAWOOD, P.A. (2018) Rates of generation and destruction of the continental crust: Implications for continental growth. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 376, 20170403. <https://doi.org/10.1098/rsta.2017.0403>
- FOSTER, G.L., LEAR, C.H., RAE, J.W.B. (2012) The evolution of pCO₂, ice volume and climate during the middle Miocene. *Earth and Planetary Science Letters* 341–344, 243–254.
- FRINGS, P.J., CLYMANS, W., FONTORBE, G., DE LA ROCHA, C.L., CONLEY, D.J. (2016) The continental Si cycle and its impact on the ocean Si isotope budget. *Chemical Geology* 425, 12–36. <https://doi.org/10.1016/j.chemgeo.2016.01.020>
- GAILLARDET, J., LEMARCHAND, D. (2018) Boron in the Weathering Environment. In: MARSCHALL, H., FOSTER, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, Cham, 163–188. https://doi.org/10.1007/978-3-319-64666-4_7
- GREW, E.S., DYMEK, R.F., DE HOOG, J.C.M., HARLEY, S.L., BOAK, J., HAZEN, R.M., YATES, M.G. (2015) Boron isotopes in tourmaline from the ca. 3.7–3.8Ga Isua supracrustal belt, Greenland: Sources for boron in Eoarchean continental crust and seawater. *Geochimica et Cosmochimica Acta* 163, 156–177. <https://doi.org/10.1016/j.gca.2015.04.045>
- ISHIKAWA, T., NAKAMURA, E. (1993) Boron isotope systematics of marine sediments. *Earth and Planetary Science Letters* 117, 567–580. [https://doi.org/10.1016/0012-821X\(93\)90103-G](https://doi.org/10.1016/0012-821X(93)90103-G)
- JOACHIMSKI, M.M., SIMON, L., VAN GELDERN, R., LÉCUYER, C. (2005) Boron isotope geochemistry of Paleozoic brachiopod calcite: Implications for a secular change in the boron isotope geochemistry of seawater over the Phanerozoic. *Geochimica et Cosmochimica Acta* 69, 4035–4044. <https://doi.org/10.1016/j.gca.2004.11.017>
- JURIKOVA, H. *et al.* (2025) Rapid rise in atmospheric CO₂ marked the end of the Late Palaeozoic Ice Age. *Nature Geoscience* 18, 91–97. <https://doi.org/10.1038/s41561-024-01610-2>
- KALDERON-ASAEI, B., KATCHINOFF, J.A.R., PLANAVSKY, N.J., HOOD, A.V.S., DELLINGER, M., *et al.* (2021) A lithium-isotope perspective on the evolution of carbon and silicon cycles. *Nature* 595, 394–398. <https://doi.org/10.1038/s41586-021-03612-1>
- KASEMANN, S.A., PRAVE, A.R., FALICK, A.E., HAWKESWORTH, C.J., HOFFMANN, K.H. (2010) Neoproterozoic ice ages, boron isotopes, and ocean acidification: Implications for a snowball Earth. *Geology* 38, 775–778. <https://doi.org/10.1130/G30851.1>
- KONHAUSER, K.O., PLANAVSKY, N.J., HARDISTY, D.S., ROBBINS, L.J., WARCHOLA, T.J., *et al.* (2017) Iron formations: A global record of Neoarchean to Palaeoproterozoic environmental history. *Earth-Science Reviews* 172, 140–177. <https://doi.org/10.1016/j.earscirev.2017.06.012>
- KORENAGA, J., PLANAVSKY, N.J., EVANS, D.A.D. (2017) Global water cycle and the coevolution of the Earth's interior and surface environment. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences* 375, 20150393. <https://doi.org/10.1098/rsta.2015.0393>
- KRISSANSEN-TOTTON, J., ARNEY, G.N., CATLING, D.C. (2018) Constraining the climate and ocean pH of the early Earth with a geological carbon cycle model. *Proceedings of the National Academy of Sciences of the United States of America* 115, 4105–4110. <https://doi.org/10.1073/pnas.1721296115>
- LEGETT, S.A., RASBURY, E.T., GROSSMAN, E.L., HEMMING, N.G., PENMAN, D.E. (2020) The Brachiopod $\delta^{11}\text{B}$ Record Across the Carboniferous-Permian Climate Transition. *Paleoceanography and Paleoclimatology* 35, 1–13. <https://doi.org/10.1029/2019PA003838>
- LEMARCHAND, D., GAILLARDET, J., LEWIN, É., ALLÈGRE, C.J. (2002) Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chemical Geology* 190, 123–140. [https://doi.org/10.1016/S0009-2541\(02\)00114-6](https://doi.org/10.1016/S0009-2541(02)00114-6)
- MARSCHALL, H.R., WANLESS, V.D., SHIMIZU, N., POGGE VON STRANDMANN, P.A.E., ELLIOTT, T., MONTELEONE, B.D. (2017) The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle. *Geochimica et Cosmochimica Acta* 207, 102–138. <https://doi.org/10.1016/j.gca.2017.03.028>
- MARSCHALL, H.R. (2018) Boron Isotopes in the Ocean Floor Realm and the Mantle. In: MARSCHALL, H., FOSTER, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, Cham, 189–215.
- McLENNAN, S.M., TAYLOR, S.R. (1982) Geochemical constraints on the growth of the continental crust. *The Journal of Geology* 90, 347–361. <https://doi.org/10.1086/628690>
- MINEART, D., DUNCANSON, S., NACHLAS, W., JOHNSON, B.W. (2025) Continental crust had fully emerged by the end of the Paleoproterozoic. *Geochemical Perspectives Letters* 38, 23–28. <https://doi.org/10.7185/geochemlet.2551>
- PALIN, R.M., SANTOSH, M., CAO, W., LI, S.S., HERNÁNDEZ-URIBE, D., PARSONS, A. (2020) Secular change and the onset of plate tectonics on Earth. *Earth-Science Reviews* 207, 103172–103172. <https://doi.org/10.1016/j.earscirev.2020.103172>
- PARIS, G., GAILLARDET, J., LOUVAT, P. (2010) Geological evolution of seawater boron isotopic composition recorded in evaporites. *Geology* 38, 1035–1038.
- RASMUSSEN, B., MUHLING, J.R., KRAPEŽ, B. (2021) Greenalite and its role in the genesis of early Precambrian iron formations – A review. *Earth-Science Reviews* 217, 103613. <https://doi.org/10.1016/j.earscirev.2021.103613>
- REIMINK, J.R., DAVIES, J.H.F.L., MOYEN, J.F., PEARSON, D.G. (2023) A whole-lithosphere view of continental growth. *Geochemical Perspectives Letters* 26, 45–49. <https://doi.org/10.7185/geochemlet.2324>
- ROERDINK, D.L., RONEN, Y., STRAUSS, H., MASON, P.R.D. (2022) Emergence of felsic crust and subaerial weathering recorded in Palaeoarchean barite. *Nature Geoscience* 15, 227–232. <https://doi.org/10.1038/s41561-022-00902-9>
- SALDI, G.D., LOUVAT, P., SCHOTT, J., GAILLARDET, J. (2021) The pH dependence of the isotopic composition of boron adsorbed on amorphous silica. *Geochimica et Cosmochimica Acta* 308, 1–20. <https://doi.org/10.1016/j.gca.2021.05.052>
- SPENCER, C.J., ROBERTS, N.M.W., SANTOSH, M. (2017) Growth, destruction, and preservation of Earth's continental crust. *Earth-Science Reviews* 172, 87–106. <https://doi.org/10.1016/j.earscirev.2017.07.013>
- SPIVACK, A.J., PALMER, M.R., EDMOND, J.M. (1987) The sedimentary cycle of the boron isotopes. *Geochimica et Cosmochimica Acta* 51, 1939–1949. [https://doi.org/10.1016/0016-7037\(87\)90183-9](https://doi.org/10.1016/0016-7037(87)90183-9)
- STERN, R.J., GERYA, T.V. (2024) The importance of continents, oceans and plate tectonics for the evolution of complex life: implications for finding extraterrestrial civilizations. *Scientific Reports* 14, 8552–8552. <https://doi.org/10.1038/s41598-024-54700-x>



Boron isotopes in Archean–Proterozoic marine deposits trace continental emergence

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Supplementary Information

The Supplementary Information includes:

- Rationale, Sampling and methods
- Tables S-1 to S-5
- Figures S-1 to S-5
- Supplementary Information References

1. Rationale, sampling and methods

1.1 Research concept:

Boron isotopes are a powerful tracer of a large variety of geological processes (e.g. Foster *et al.*, 2018; Marschall and Foster, 2018 and references therein). As an incompatible lithophile element, boron is readily concentrated in the continental crust and depleted in the mantle (Marschall *et al.*, 2017). Processes of erosion, dissolution and deposition in the terrestrial and the marine environment fractionate boron isotopes and consequently drive modern seawater towards a high $\delta^{11}\text{B}$ value over time (modern seawater $\delta^{11}\text{B} = +39.6\text{‰}$; Foster *et al.*, 2010). Yet, the B isotopic composition of the ocean varied over geologic time (Joachimski *et al.*, 2005; Kasemann *et al.*, 2005, 2009; Lemarchand *et al.*, 2000; Legett *et al.*, 2020; Jurikova *et al.*, 2025). These long-term changes in oceanic B concentration and $\delta^{11}\text{B}_{\text{sw}}$ are controlled by the balance between input and output fluxes of boron to and from the ocean, which are relatively well characterized for the modern Earth (Marschall, 2018; Lemarchand *et al.*, 2002; Joachimski *et al.*, 2005; Simon *et al.*, 2006; Legett *et al.*, 2020). The largest in-flux of boron into the modern ocean is through continental erosion, together with smaller fluxes of hydrothermal venting and fluid expelled from accretionary prisms at convergent margins (Lemarchand *et al.*, 2002). The most dominant boron sink from the ocean is low-temperature alteration of oceanic crust (AOC), with additional

sinks of boron adsorption on oceanic clastic sediments and clays, as well as coprecipitation of boron in carbonate rocks (Fig. 2a; Lemarchand *et al.*, 2000; Simon *et al.*, 2006). For the modern setting, the isotopic composition, isotopic offset values (Δ ; see below), and flux magnitude of each of the boron sources and sinks to and from the ocean are relatively well constrained (Fig. 2a).

On the Archean Earth, in the absence of emerged continents, many of the boron fluxes to and from the oceans were not operating, and available constraints on the fluxes that likely operated are either poor or absent (Fig. 2b). The only large reservoir which certainly interacted with the ocean water at that time was the oceanic crust. Thus, the only major operating flux of boron in the absence of emerged continents is the removal of boron from the ocean by AOC. Therefore, prior to the emergence of continents, the Archean ocean likely reached an equilibrium with the oceanic crust (or mantle rocks exposed to the seafloor) and was low in its boron concentration, as the sources of boron were small to negligible. From this starting point, the emergence of continental crust will have ensued the operation of additional fluxes of B into and out of the ocean through the development of terrestrial erosion systems and rivers. Over time, the enrichment of ocean water with nutrients from terrestrial erosion also enabled the evolution and flourishing of biomineralizing marine microorganisms and the development of boron sinks out of the ocean through co-precipitation during carbonate deposition. Terrestrial erosion is also responsible for the introduction of clay material into the ocean by riverine and aeolian transport. These clay particles remove boron from the ocean water via adsorption as they sink through the water column. Thus, the emergence of continental crust above sea-level, together with the ensuing development of Earth's tectonic and physical and geochemical mechanisms, eventually drove the oceanic B cycle closer to its modern state. Chemical marine deposits, such as cherts, IFs and shales preserved from ages across the suggested continental emergence transition (3.5–2.5 Ga; Fig. S-1) will record this change in $\delta^{11}\text{B}_{\text{sw}}$, in the same way they record Archean oceanic chemistry (Bekker *et al.*, 2010, 2014; Konhauser *et al.*, 2017); accordingly, we targeted such rock units in the present study.

For the evaluation of the oceanic composition, any measured $\delta^{11}\text{B}$ value from a given marine deposit needs to be translated to the contemporaneous oceanic value ($\delta^{11}\text{B}_{\text{sw}}$) by the application of a fractionation factor (α ; expressed in equilibrium as $1000\ln\alpha \approx \Delta^{11}\text{B}_{\text{a-b}} = \delta^{11}\text{B}_{\text{phase a}} - \delta^{11}\text{B}_{\text{phase b}}$). Boron isotope fractionation between seawater and silica and/or clays have been constrained both empirically (Spivack *et al.*, 1987; Kolodny and Chaussidon, 2004) as well as by experimental work (Saldi *et al.*, 2021; Ring *et al.*, 2025), usually testing the effects of pH on fractionation. The effect of variation in temperature on boron isotope fractionation is also relatively well understood from experiments and ab-initio modelling (Kowalski and Wunder, 2018). The major ion composition and ionic strength of the seawater solution also have the potential to affect fractionation. While it may seem that all these variables, as well as the possible post depositional alteration of the boron signal (see below) pose difficulty for the reconstruction of $\delta^{11}\text{B}_{\text{sw}}$ from marine deposits, a critical evaluation of each of these elements can allow us to assign fractionation factors and evaluate past $\delta^{11}\text{B}_{\text{sw}}$ with meaningful confidence, given the available constraints on the pH and T of Archean–Proterozoic seawater (Krissansen-Totton *et al.*, 2018).

In silicate materials, the magnitude of boron isotope fractionation increases at lower temperatures (Kowalski and Wunder, 2018), and while an increase in SW temperature may reduce the fractionation factor, a 10 ‰ shift in $\Delta^{11}\text{B}$ would require a temperature increase of ca. 100 °C. Modelling envelopes of Archean seawater temperature range between 0–45 °C (Krissansen-Totton *et al.*, 2018), while empirical proxies suggest a range between 32–65 °C (Hren *et al.*, 2009). The suggested model mean predicts fluctuations of no more than 10 °C in seawater temperatures across all of Earth history (Krissansen-Totton *et al.*, 2018). These considerations render the plausibility that large variations in reconstructed $\delta^{11}\text{B}_{\text{sw}}$ come from temperature fluctuations very low, as these would realistically result in relatively minor changes.

The effect of pH on fractionation is the one best tested experimentally and well evaluated both for SW–silica (Saldi *et al.*, 2021) and SW–clay (Spivack *et al.*, 1987; Ring *et al.*, 2025). Both materials show a large deviation and pH dependence of the fractionation factor between pH = 7.5–8.5, at which boron speciation is approximately equally divided between boric acid ($\text{B}(\text{OH})_3$) and borate ion ($\text{B}(\text{OH})_4^-$) and mineral–seawater fractionation is considered as a combination of boric acid/mineral and borate/mineral fractionations. In contrast, under acidic to circumneutral conditions, boron speciation is vastly dominated by boric acid and there is thus little to no variation of the fractionation factor with pH. Hence at low pH, boron isotope fractionation can be expressed through a single mineral/bulk seawater isotope fractionation factor. Considering the modelled pH of Archean–Proterozoic seawater is not predicted to reach 7.5 until the Phanerozoic (Krissansen-Totton *et al.*, 2018), changes in the recorded $\delta^{11}\text{B}_{\text{sw}}$ due to pH fluctuations are unlikely, and the fractionation factor is expected to remain constant. Moreover and importantly, the SW–clay fractionation factor (Spivack *et al.*, 1987) and the SW–silica fractionation factor (Saldi *et al.*, 2021), evaluated at pH values modelled for Archean seawater (Krissansen-Totton *et al.*, 2018), converge to the same value of $\Delta^{11}\text{B} = -25$ ‰. This allows us to use a single value for the reconstruction of $\delta^{11}\text{B}_{\text{sw}}$ from both archives.

The ion composition and salinity of Archean seawater are less firmly constrained (Albarede *et al.*, 2020). It has been shown though that the strong variation in the SW–clay fractionation factor between pH = 7.5–8.5 is largely removed in experiments conducted with pure water, and that B fractionation and adsorption on clay surfaces is mostly modulated by fluid composition (Ring *et al.*, 2025). Therefore, if Archean seawater was less saline than today due to reduced continental weathering fluxes, this would reduce rather than amplify departures from the experimentally determined fractionation factors we assigned for the purpose of $\delta^{11}\text{B}_{\text{sw}}$ reconstruction.

While we acknowledge the inherent uncertainties when aiming to reconstruct seawater isotopic compositions from periods in Earth history for which little constraints exist, available theoretic and experimental data allow us to assign and implement the aforementioned fractionation factors to our data with reasonable confidence. Moreover, the magnitude of variation we observe in $\delta^{11}\text{B}_{\text{sw}}$ is such that is robust to any plausible variation in these parameters (T , pH, salinity), given the magnitude of the observed signal (see main text).

1.2 Sampling and analytical methods:

Rock samples of IFs, chert and marine shales, with constrained ages between 3.70–1.88 Ga were selected for analysis in the present study (Fig. 1; Table S-1). Sample material for analysis was carefully selected preferably from previously well characterized localities known for their IFs, and which their available age constrains place them in the period of interest for the present study. We attempted to include in our sample suite material that i) comes from multiple Archean cratons, ii) covers the time interval of interest as densely as possible, and iii) comprises units which experienced no metamorphic overprint or conditions of greenschist facies or below in order to minimize the possibility of post depositional and/or diagenetic alteration of its boron inventory. Where available, drill core material was preferred over surface samples to minimize the effects of surface and post-depositional alteration. We also benefited from the possibility to directly collect sample material from ICDP drill core projects BARB and BASE.

The assembled suite of IFs as well as cherts and marine shales associated with them includes material from the Isua belt in Greenland (Frei *et al.*, 1999; Polat and Frei, 2005; Nutman and Friend, 2009; Czaja *et al.*, 2013), the Pilbara and Yilgarn cratons in Australia (Chen *et al.*, 2003; Czaja *et al.*, 2018; Duuring *et al.*, 2020; Angerer *et al.*, 2022), the Abitibi Greenstone Belt in NE North America (Delvigne, 2012; Delvigne *et al.*, 2012), the Barberton Greenstone Belt (Hofmann, 2005; Bontognali *et al.*, 2013; Heubeck *et al.*, 2013; Satkoski *et al.*, 2015; Ledevin *et al.*, 2019;) and other localities within the Kaapvaal craton in Southern Africa (Hofmann *et al.*, 2003; Smith *et al.*, 2013; Smith and Beukes, 2023), as well as one sample from the Gogebic Range in the Superior province (Eyster *et al.*, 2021). Sample origins, locations, geological formations and age constraints are given in Table S-1 and Fig. 1.

Given that boron is a fluid-mobile element and that the response of its isotopic signal to post depositional alteration in IFs is not well constrained, the possibility of alteration hampering the original seawater signal exists, especially in Archean-Proterozoic rocks. As IFs are typically comprised of alternations of siliceous and Fe-oxide phases, we measured $\delta^{11}\text{B}$ in both mineral domains in the examined samples to test whether the two phases do indeed preserve an original signal manifested by distinct isotopic values. Such a sedimentary signal results from the different fractionation factors of the two phases relative to seawater. Only samples preserving such distinct values were considered for the reconstruction of the seawater B composition from the $\delta^{11}\text{B}$ value of the siliceous phase. Our data below shows that this approach was constructive, as we can show that IF samples exhibit a pronounced alternation between two distinct B isotopic values depending on the mineral phase (Fig. S-2). Additional support comes from the fact that shale samples from the Moodies group align in their B isotopic composition with silica in IF and chert from the same section (Fig. 3). This serves as independent evidence for the legibility of using a single value for the fractionation factor of both SW–silica and SW–clay during the Archean, as the measured values of both mineral phases precipitated from the same seawater in the same locality at the same time converge to the same $\delta^{11}\text{B}$. This also provides evidence for the lack of matrix effects on our measurements.

From each sample a thin section was cut for petrographic examination, as well as a matching 100 μm (or thicker) thick section for the purpose of in situ $\delta^{11}\text{B}$ analysis by Laser-Ablation Multi-Collector Inductively-Coupled-Plasma Mass-Spectrometry (LA-MC-ICPMS). Prior to analysis, samples were cleaned and then desiccated overnight under inert Ar in order to minimize background caused by degassing into the analytical system. For B concentration and isotopic measurement, samples were ablated using a RESolution LR 193 nm ArF laser ablation system equipped with a large, two-volume Laurin Technic S155 ablation cell. Ablation was performed in a He atmosphere while admixing Ar and N_2 sample gasses into the upper funnel of the ablation cell. Depending on the B concentration in the different samples and the size of target mineral phases, we used laser spot sizes between 60 μm and 235 μm diameter, repetition rates of 8–12 Hz, and laser fluences of ca. 2.0–3.5 J/cm^2 . Ablated material was then directed to the Neptune Plus MC-ICPMS. A primary reference material of NIST-SRM612 glass or GSC-1G basaltic glass was used for tuning the machines for maximum B signal and low background, as well as low oxide formation and low Ar^{4+} production, and later to correct for drift over the analytical sequence. This was achieved by optimizing the MS lenses, as well as the flow of N_2 , Ar sample gas and RF power. All analyses were run in automatic mode in sequences of up to 500 analyses following a standard-sample-standard bracketing procedure, involving duplicate measurements of reference materials following fifty unknown analyses. Secondary standards used for matrix match correction were BIR, BHVO, and BCR basaltic glasses, as well as two in-house hematite reference materials (HEM, Elba; See Table S-4, Fig. S-3). Each spot analysis took 45 s, with 0.25 s integration time, 25 s of ablation, and 20 s of gas blank analysis. Pre-ablation (2 s) followed by 20 s wash out was conducted to minimize potential surface boron contamination. B isotopic measurement on the MC-ICP-MS was performed either using two Faraday cups (equipped with $10^{13} \Omega$ amplifiers) for the m/z 11 and 10 in material with high B concentration, two ion counters in low B concentration, or a combined method where ^{11}B was measured using a Faraday cup and ^{10}B was measured using an ion counter. Due to observed elevated background in the m/z range between 9.7 and 11 (Coenen *et al.*, 2024; “bulge effect”; Standish *et al.*, 2019; Evans *et al.*, 2021; Fietzke and Anagnostou, 2023; Xu *et al.*, 2024), we monitored the intermediary mass range between $m/z = 9.9$ – 10.9 in order to quantify and correct for it. Detailed elaboration on the method developed at FIERCE for measurement of B isotopes in low concentration silicate materials, as well as for the possible causes and means of correction for the ‘bulge effect’ are detailed in Xu *et al.*, (2024). Data processing was performed using an in-house spreadsheet developed by Axel Gerdes. Processing steps include resolving signal from the background, rejection of outliers from the analysis, correction for the bulge interference effect on the ^{10}B and ^{11}B masses (see Standish *et al.*, 2019; Evans *et al.*, 2021; Fietzke and Anagnostou, 2023; Xu *et al.*, 2024), correction for instrumental drift and matrix matching using primary and secondary reference materials respectively, and evaluating boron concentration from the total signal based on post analytical examination of the laser pit volume. Consequently, we are able to attain a $<1\%$ uncertainty (2SE) on replicate analysis ($n > 10$) in samples with $<1 \mu\text{g/g}$ [B].

On individual analyses, the reported uncertainties on the $\delta^{11}\text{B}$ value are quoted at the 2-sigma level and are quadratic additions of the internal measurement uncertainty, the excess scatter of the primary reference material and the excess

scatter of the secondary reference material. Reported values of each of the measured samples are the product of replicate analysis ($n = 30\text{--}100$) of a mineral phase within a thin section or slab. To produce these, we calculate a weighted average which considers both the measured value as well as the associated analytical error of each considered datapoint. We then report the weighted mean $\pm 2\text{SE}$, as the standard error quantifies well the confidence in the mean value, despite the possibility of natural internal scatter. For sample populations (like pre- and post-3.0 Ga, see main text), a simple mean with 2SD and 2SE are reported, as well as the results of standard Welch's t-test, to quantify the distinction of the two populations. All data reduction calculations, including error propagations and statistical analysis were performed by using code-supported Microsoft Excel®-based spreadsheets developed by Axel Gerdes.

1.2.1 Post hoc processing of sample data:

The majority of measured samples (43 out of 48) does exhibit rather homogeneous compositions of boron concentration as well as $\delta^{11}\text{B}$ values (Fig. S-4). Some of the samples do show the expected B partitioning and isotope fractionation between points measured in silica and Fe-oxide zones. However, it is also expected that due to either detrital contamination or inhomogeneity of silica and Fe-oxide zones (e.g. small fragments of Fe-oxides within silica bands and vice versa), measured values will show some spread between the pure silica endmember and the detrital and Fe-oxide endmembers. In order to control these effects, we examined our results in Fig. S-4, and identified samples which required further screening to make sure the quoted values indeed represent silica endmember from which we can reliably reconstruct the seawater composition. A prime example of such treatment is seen in sample P7.3f (Fig. S-4), in which the pure Fe-oxide endmember is evident, but also values from the measured silica points that show a large spread between a group of low-B, high- $\delta^{11}\text{B}$ spots and the high-[B], low- $\delta^{11}\text{B}$ of the Fe oxide. This spread between points of low concentration with heavy isotopic composition and points of high boron concentration with light isotopic composition represent mixing of a Fe oxide (and possibly a detrital component) within the silica. As continent-derived detrital material would consist mostly of clay, it would also contain high boron concentration and show an isotopically light composition (Ishikawa and Nakamura, 1993). In samples showing a trend like this we applied a filter to consider only the silica endmember for seawater reconstruction. We selected a subset of spot from within each such sample which show low boron concentration and high $\delta^{11}\text{B}$. Such a filter was applied to 5 samples in total (Fig. S-4).

1.3 Reconstruction of crustal emergence from seawater $\delta^{11}\text{B}$:

The reconstruction of crustal emergence is based on a number of assumptions. These include: (1) a near-equilibrium state between seawater and its boron sources and sinks; (2) uniform erosion of the continents that is, on the timescale of tens of millions of years, independent of topography and exposed rock types; (3) that other fluxes, such as seafloor-alteration and adsorption to sediments remained constant.

Elevated activity of oceanic spreading centres at 3.5–2.9 Ga relative to modern Earth, as predicted by higher mantle potential temperatures and estimates of elevated degassing (Herzberg *et al.*, 2010; Aulbach and Arndt, 2019) would have removed increased amounts of boron from the ocean. However, increased boron removal by oceanic crust alteration drives seawater towards heavier $\delta^{11}\text{B}$ (due to the large negative fractionation factor; Fig. 2a in main text). To balance

this effect and keep seawater $\delta^{11}\text{B}$ at a lighter value, more continental crust would need to emerge and erode. This renders our estimates of continental exposure a minimum one. Our calculation assumes boron is spread and erodes uniformly within and from the continental crust. Rapid buildup of orogens in a condensed period causing enhanced emergence, the complex behavior of boron in the continental weathering environment (Gaillardet and Lemarchand, 2018), rapid eruption and erosion of flood basalts with near mantle $\delta^{11}\text{B}$ composition, the difference in boron concentration between dominantly mafic and felsic crust – all these may introduce complexities to this estimate, and are expected to guide future models building on our data. Nevertheless, it is unlikely that a process other than continental erosion could introduce large quantities of boron into the ocean and drive the oceanic composition towards a heavier value over extended periods of Earth history to change the first-order results of our model.

The model is further based on a number of fix points that are reasonable to assume or were established in this study:

- 1) In the Hadean (i.e. at 4 Ga), there was no continental crust emerged above sea level
- 2) In the late Neoproterozoic (i.e. at 635 Ma) 100 % emergence was reached (relative to the modern amount; but in a world without land plants)
- 3) The $\delta^{11}\text{B}$ of seawater at 3.70–3.21 Ga was +1.9 ‰
- 4) The $\delta^{11}\text{B}$ of seawater at 2.98–2.40 Ga was +16.1 ‰
- 5) The $\delta^{11}\text{B}$ of seawater at 1.88 Ga was +18.6 ‰
- 6) The $\delta^{11}\text{B}$ of seawater at 635 Ma was +25.5 ‰

Continental emergence in the Archean and throughout most of the Proterozoic (3.70–0.64 Ga) is unknown and its first-order reconstruction is the goal of this study. There may have been some emergence prior to the deposition of our oldest sample (3.7 Ga); hence, the model can at this stage only provide brackets for a possible evolution instead of an accurate solution. For this, we choose the following solution:

We first assume that seawater $\delta^{11}\text{B}$ can never be lower than the $\delta^{11}\text{B}$ of the primitive mantle (-7.1 ‰), because the differentiation of the silicate Earth and the hydrosphere started with the mantle and there is no mechanism that would fractionate the lighter isotope into water. Hence, the lowest possible $\delta^{11}\text{B}$ value of seawater in the Hadean in a world free of any (emerged) continents is -7.1 ‰. The highest possible value is +1.9 ‰, assuming that our reconstruction of Eoarchean and Paleoarchean (3.70–3.21 Ga) seawater reflects a world that still had no (or only negligible) emerged continents and thus seawater $\delta^{11}\text{B}$ had not changed at all until the end of the Paleoarchean.

In the first case, with the lowermost possible Hadean seawater $\delta^{11}\text{B}$ value (-7.1 ‰), seawater would have already risen by 9 ‰ (from -7.1 to +1.9) between the Hadean and the deposition of our oldest sample (3.7 Ga). Continental emergence would have driven seawater from -7.1 ‰ at 4 Ga to +1.9 ‰ at 3.7 Ga to eventually +25.5 ‰ in the Neoproterozoic. Hence, in this model, 100 % emergence is equivalent to a 32.6 ‰ rise in seawater $\delta^{11}\text{B}$, and a change of 1 ‰ is equivalent to 3.1 % increase in crustal emergence (hence, 1 % of crustal emergence causes a shift of 0.33 ‰ in seawater $\delta^{11}\text{B}$). The 9 ‰ increase to +1.9 ‰ by 3.7 Ga thus means 27.6 % crustal emergence in the earliest Archean, and the total of 23.2 ‰ increase to +16.1 ‰ by 2.98 Ga means 71.2 % emergence at that time.

The upper-boundary model (second case), which suggests that no continental crust had emerged prior to the deposition of our oldest sample, means that Hadean seawater already had a $\delta^{11}\text{B}$ of +1.9 ‰, and this value represents an ocean without (significant) emerged continental crust. In this case, 100 % emergence led to a total change in seawater $\delta^{11}\text{B}$ from +1.9 to +25.5 ‰ (a change of 23.6 ‰) between 3.21 Ga and the Neoproterozoic. Hence, a change of 1 ‰ would be equivalent to 4.2 % increase in crustal emergence (or 1 % of crustal emergence causes a shift of 0.24 ‰ in seawater $\delta^{11}\text{B}$). At 3.21 Ga with a seawater $\delta^{11}\text{B}$ of +1.9 ‰ there was 0 % crustal emergence, and at 2.98 Ga with seawater $\delta^{11}\text{B}$ = +16.1 ‰ (a 14.2 ‰ increase) there was 60.2 % emergence.

Based on the currently available data, the amount of emerged continental crust in the Eo-/Paleoarchean is bracketed to between zero and approximately 1/4 of the amount of crust emerged that we see today (0–27.6 %). The value of emergence in the late Archean to early Proterozoic (2.98–2.40 Ga) is not very sensitive to the choice of model: it only changes from 60.2 % continental emergence for one extreme to 71.2 % for the other extreme.

Supplementary Tables

Tables S-1 to S-5 (.xlsx) are available for downloading from the online version of this article at <https://doi.org/10.7185/geochemlet.2635>

Table S-1	list of samples and their origins used in the present study
Table S-2	LA-MC-ICP-MS B isotope data from all samples measured in this study:
Table S-3	LA-MC-ICP-MS B isotope data from all standards measured in this study:
Table S-4	LA-MC-ICP-MS B isotope data report
Table S-5	Crustal emergence model calculation table

Supplementary Figures

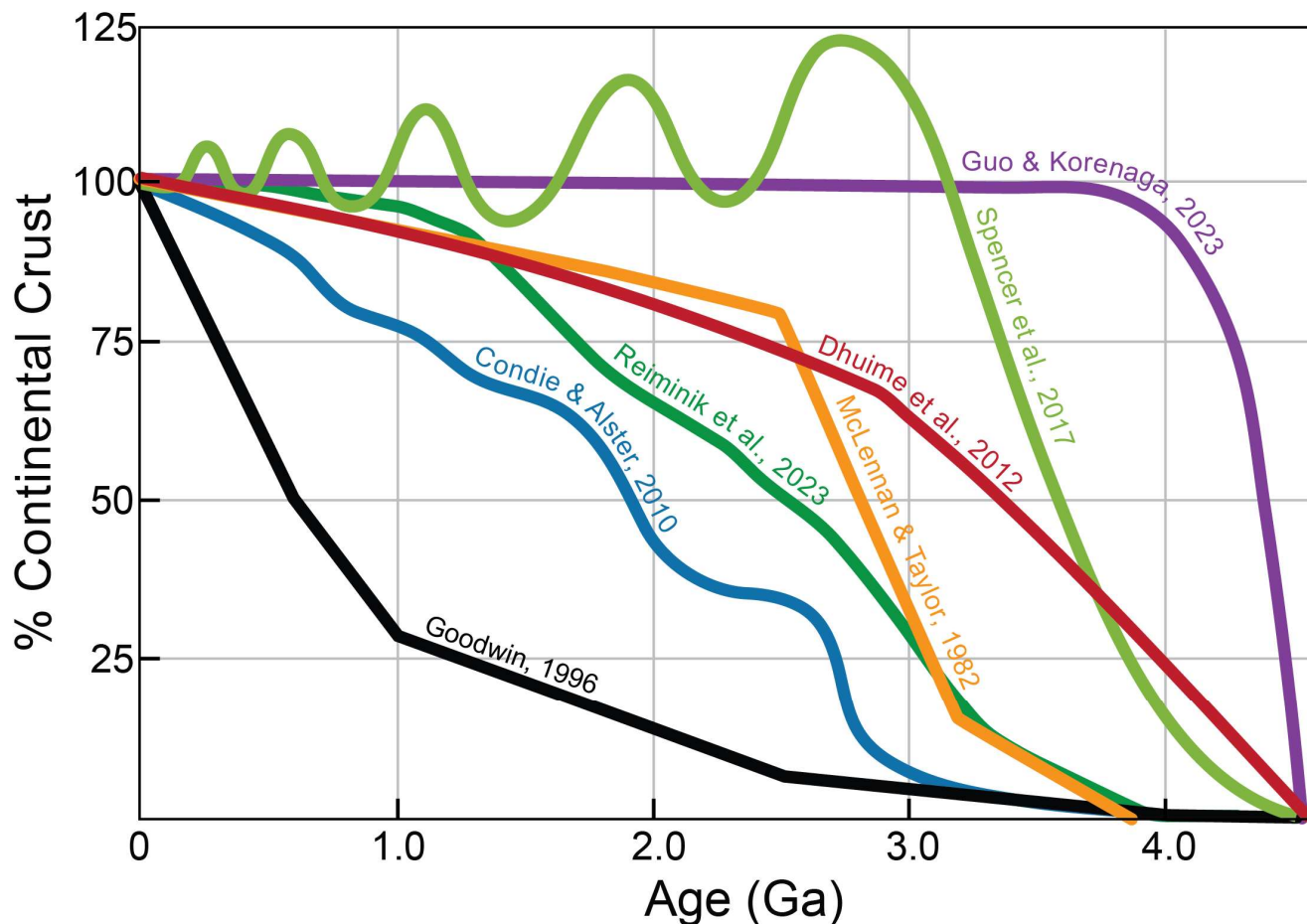


Figure S-1 Selected crustal growth models showing different modes of continental crust accumulation throughout geologic time, founded in different considerations: ^{142}Nd anomalies in Archean Mantle rocks (Guo and Korenaga, 2023), O and Hf isotopes in igneous and detrital zircons (Dhuime *et al.*, 2012), adjustment of growth curves to account for biased preservation (Spencer *et al.*, 2017), Eu anomalies and Nd- T_{DM} ages in sediments (McLennan and Taylor, 1982), major element indexes identifying reworked crustal rocks (Reimink *et al.*, 2023), present day distribution of juvenile continental crust (Condie and Aster, 2010), and present day distribution of all exposed continental crust (Goodwin, 1996).

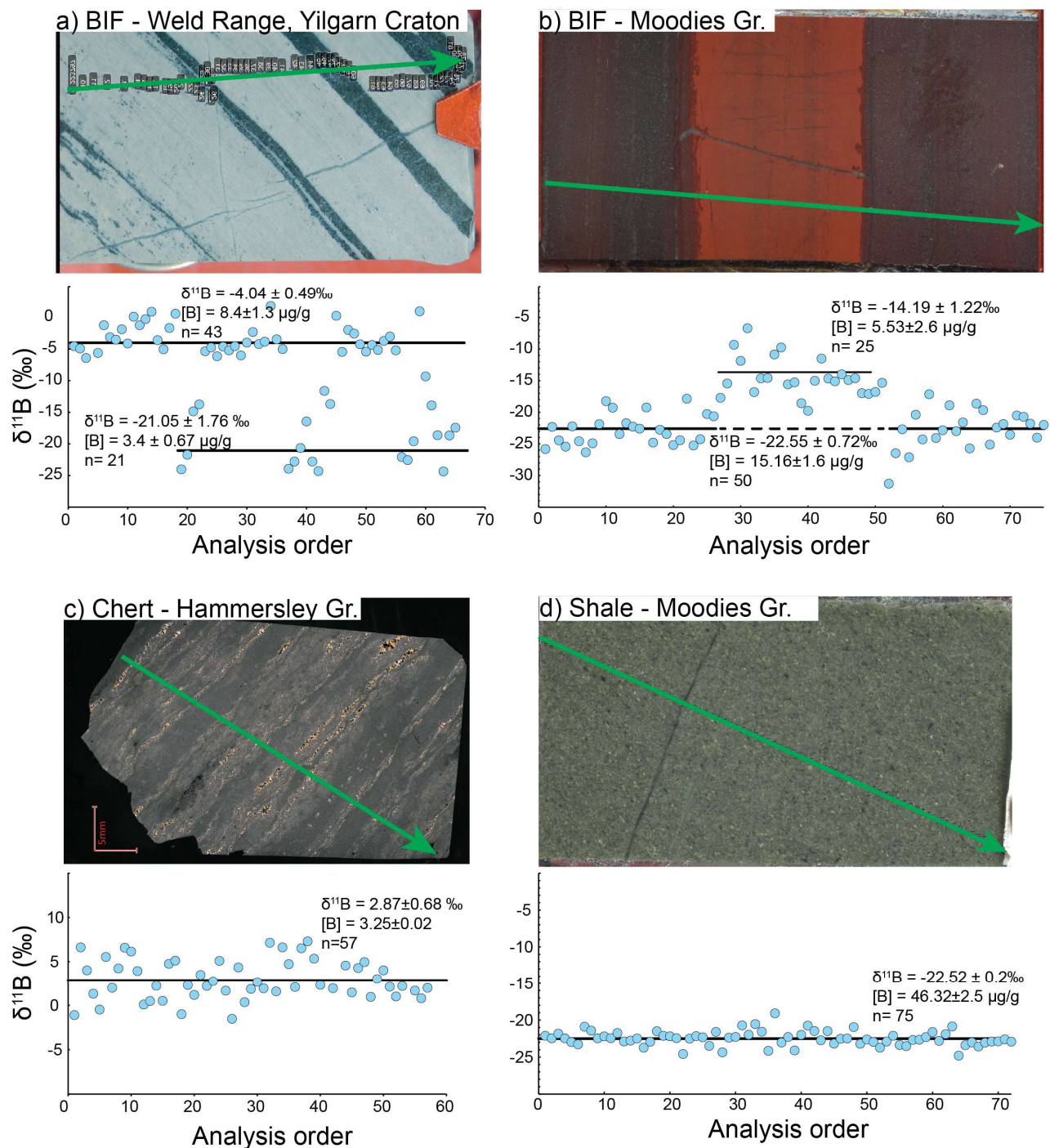


Figure S-2 Representative images of analyzed samples showing bi-modal variability of $\delta^{11}\text{B}$ in Iron Formations, or lack thereof in single phase samples like chert and shale. Green arrow denotes the direction of spot analysis order across the thin-section or slab in each sample.

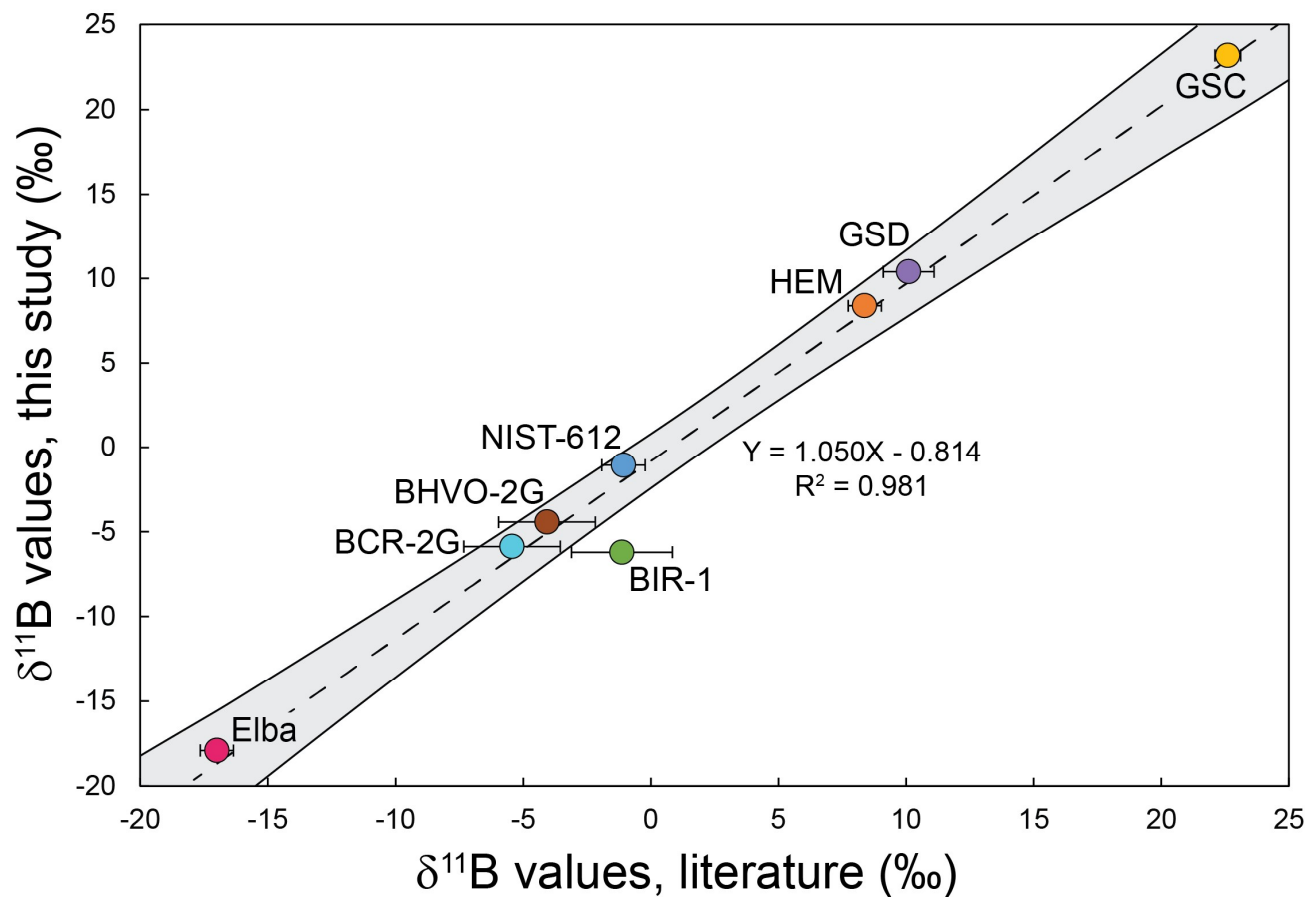


Figure S-3 Comparison of $\delta^{11}\text{B}$ values of standard reference materials determined in this study with weighted mean value of literature values (He *et al.*, 2020; Jochum *et al.*, 2011; Kasemann *et al.*, 2010; Xu *et al.*, 2024). Horizontal bars represent 2SE of the compiled literature values, depicting the variability of published data. Vertical bars are 2SE of values measured in this study, most of which are smaller than the symbol size (Table S-3). Dashed line shows a linear regression of the data, with the shaded area depicting 95% confidence level around it.

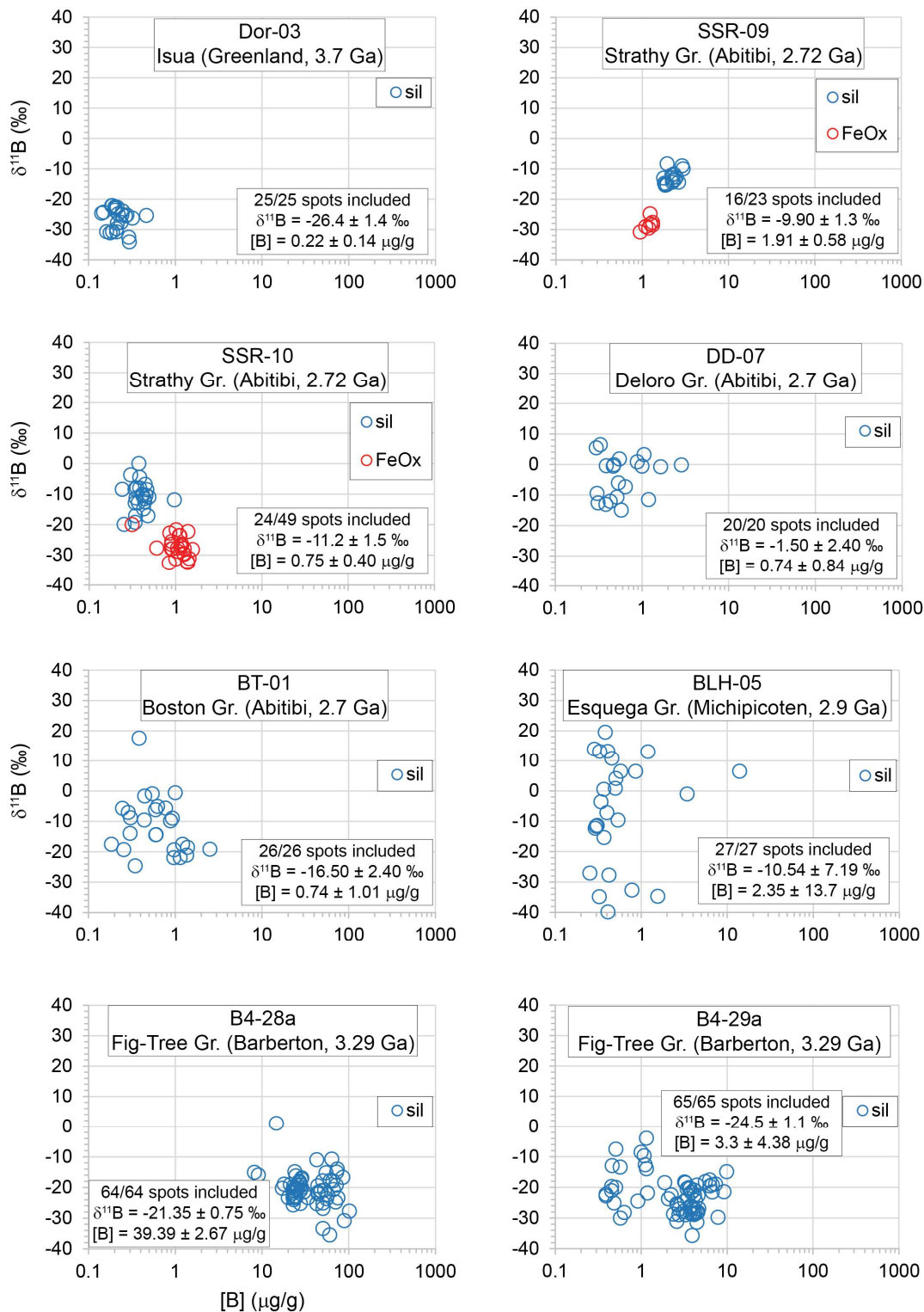


Figure S-4 Measured $\delta^{11}\text{B}$ vs. [B] values of every analytical point within each sample, from both silica and Fe-oxide phases. Samples showing a trend of mixing between silica and Fe-oxide or a detrital component were further filtered and their silica value was evaluated from a subset of points of the silica end-member. See text for explanation.

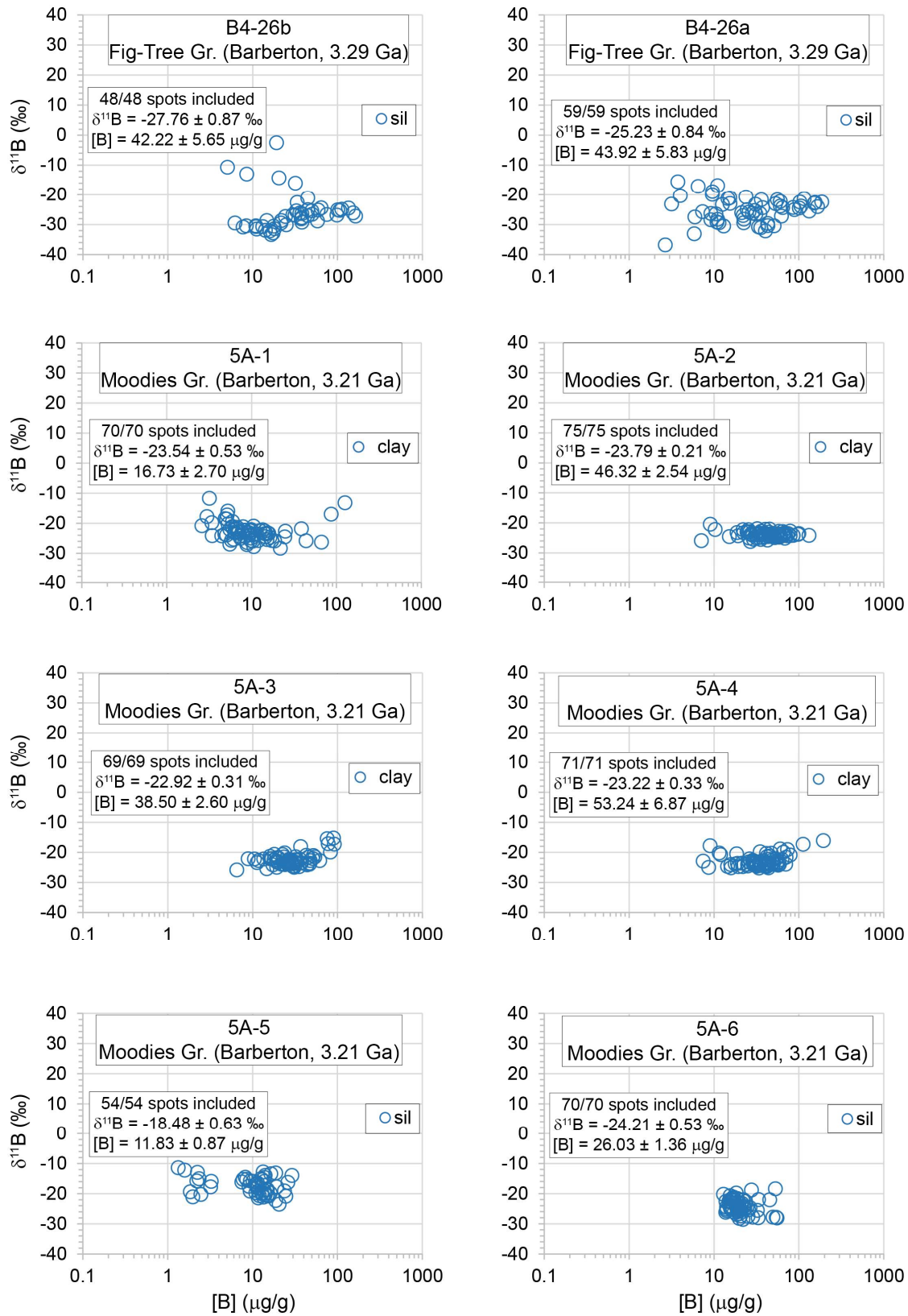


Figure S-4 cont.

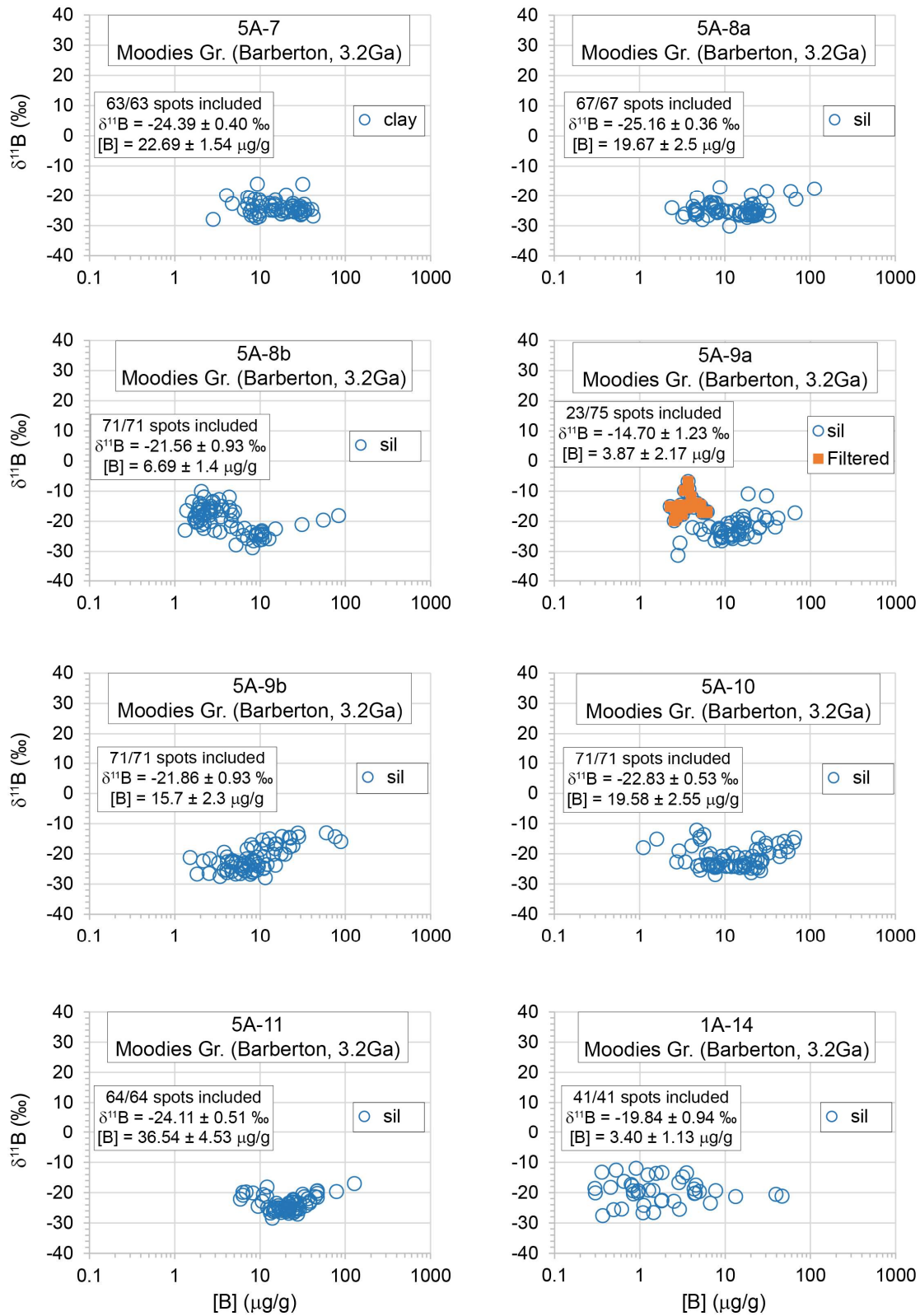


Figure S-4 cont.

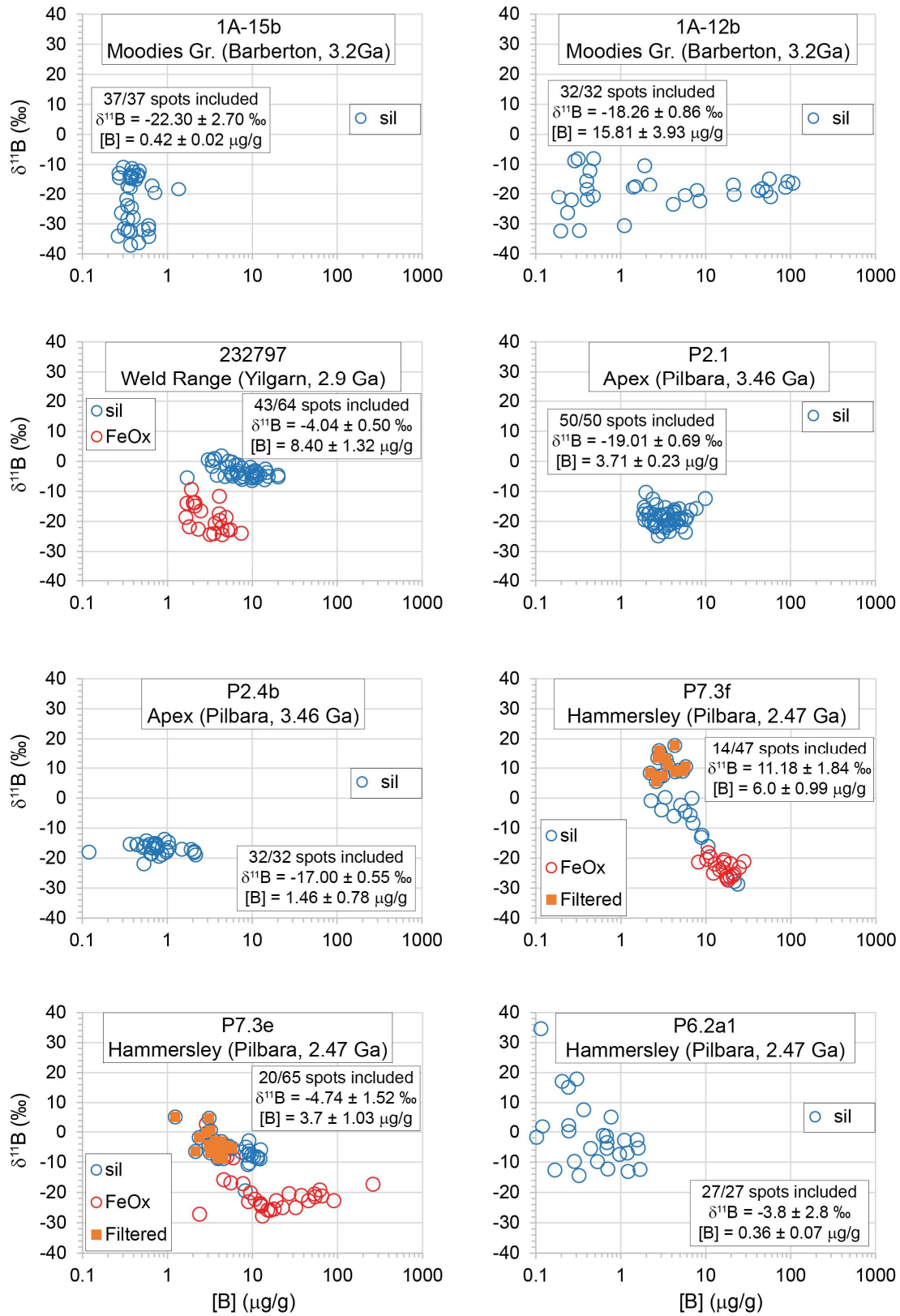


Figure S-4 cont.

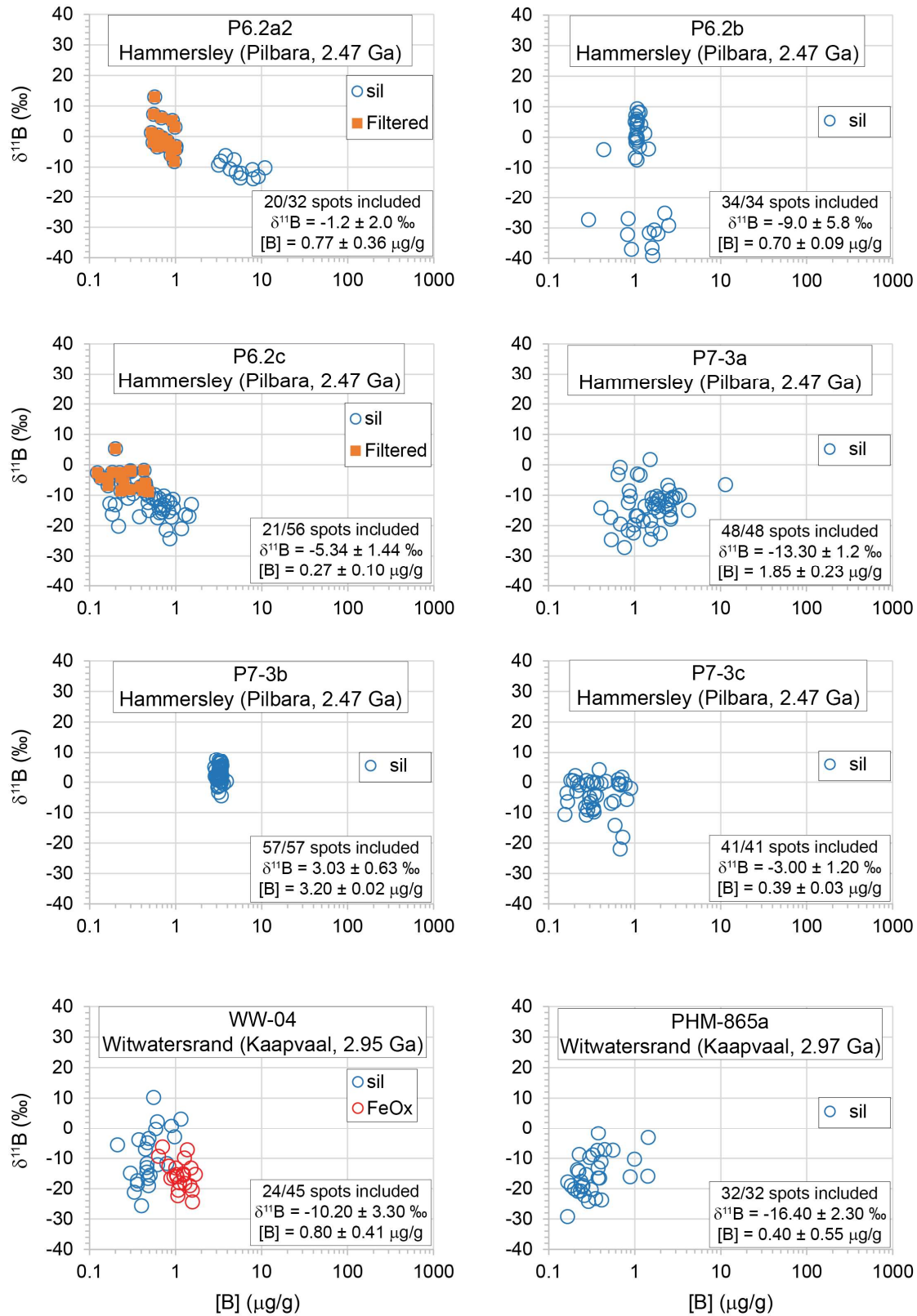


Figure S-4 cont.

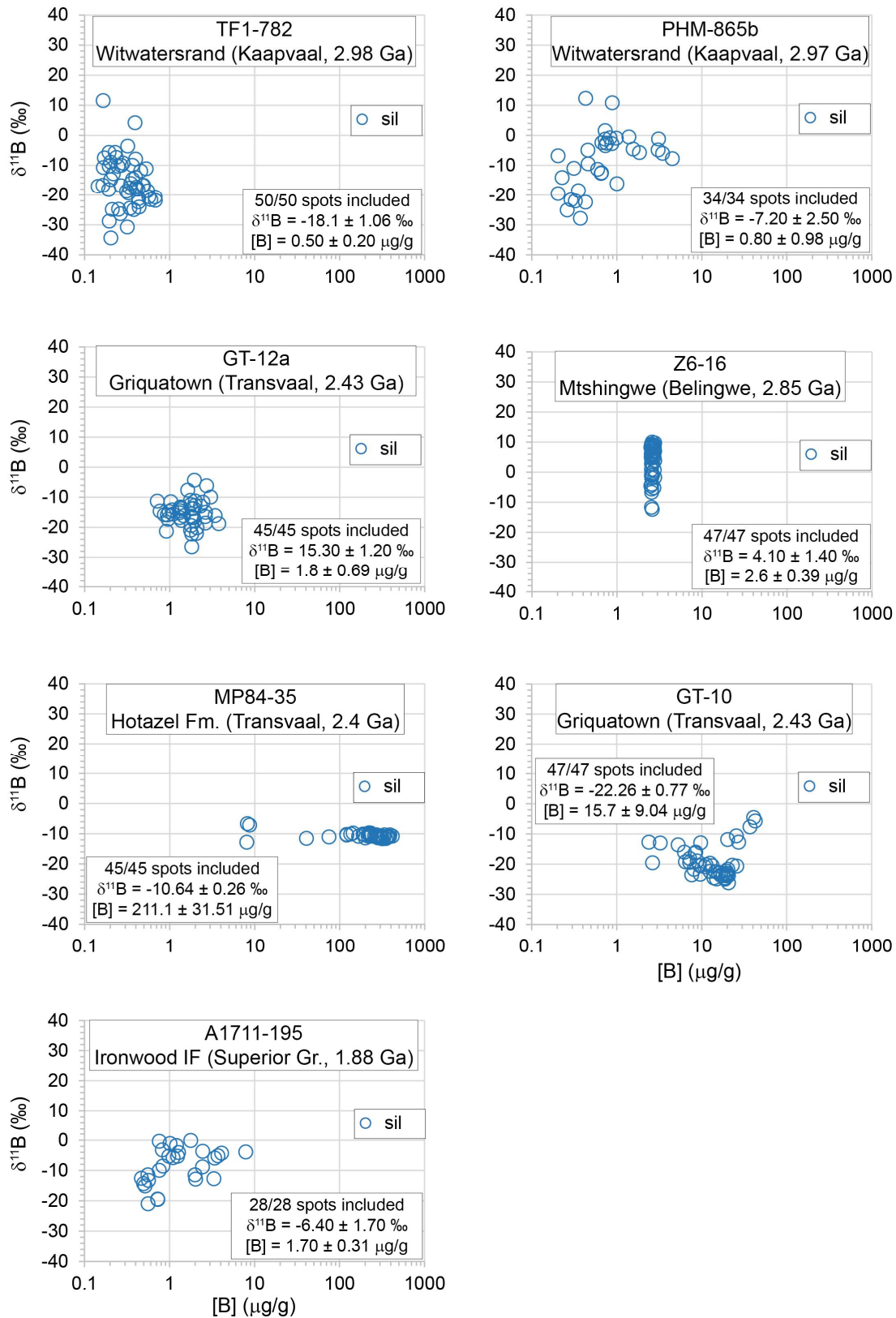


Figure S-4 cont.

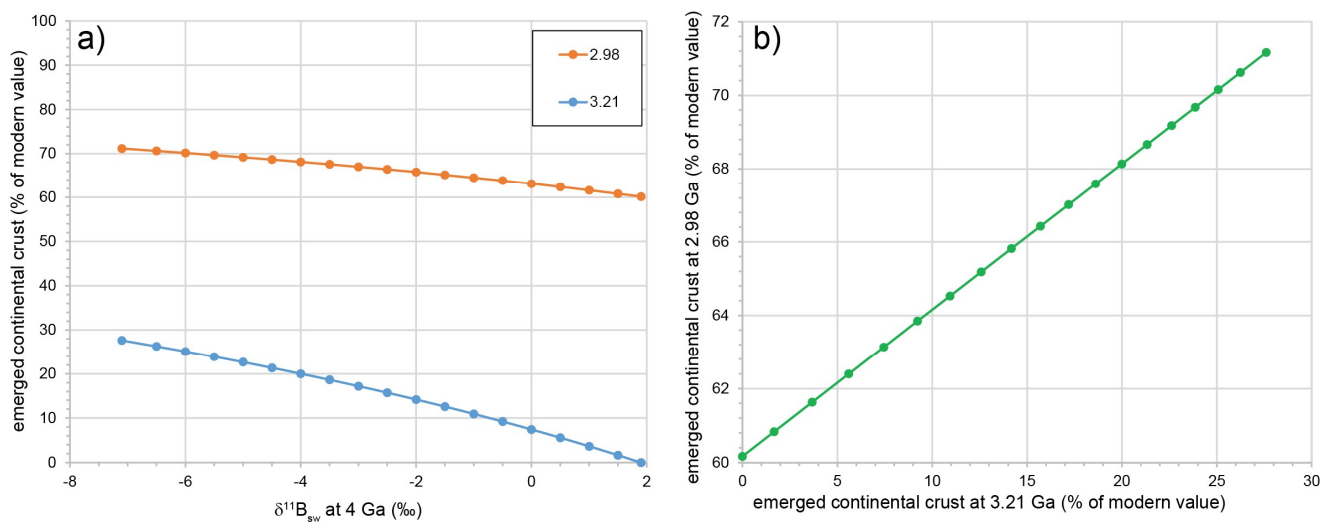


Figure S-5 Results of the mass balance model calculation. a) Comparison of emerged continental crust (expressed as % of the modern value) as a function of $\delta^{11}\text{B}_{\text{sw}}$. b) The variation of emerged continental crust at 2.98 Ga as a function of the amount of emerged crust at 3.21 Ga. See text and supplementary data for discussion.

Supplementary Information References

- Albarede, F., Thibon, F., Blichert-Toft, J., Tsikos, H. (2020) Chemical archeoceanography. *Chemical Geology* 548, 119625–119625. <https://doi.org/10.1016/j.chemgeo.2020.119625>
- Angerer, T., Thorne, W., Hagemann, S.G., Tribus, M., Evans, N.J., Savard, D. (2022) Iron oxide chemistry supports a multistage hydrothermal genesis of BIF-hosted hematite ore in the Mt. Tom Price and Mt. Whaleback deposits. *Ore Geology Reviews* 144, 104840–104840. <https://doi.org/10.1016/j.oregeorev.2022.104840>
- Aulbach, S., Arndt, N.T. (2019) Eclogites as palaeodynamic archives: Evidence for warm (not hot) and depleted (but heterogeneous) Archaean ambient mantle. *Earth and Planetary Science Letters* 505, 162–172. <https://doi.org/10.1016/j.epsl.2018.10.025>
- Bekker, A., Planavsky, N.J., Krapež, B., Rasmussen, B., Hofmann, A., Slack, J.F., Rouxel, O.J., Konhauser, K.O. (2014) 9.18 - Iron Formations: Their Origins and Implications for Ancient Seawater Chemistry. In: Holland, H.D., Turekian, K.K. (Eds.) *Treatise on Geochemistry (Second Edition)*. Elsevier, Oxford, 561–628. <https://doi.org/10.1016/B978-0-08-095975-7.00719-1>
- Bekker, A., Slack, J.F., Planavsky, N., Krapež, B., Hofmann, A., Konhauser, K.O., Rouxel, O.J. (2010) Iron Formation: The Sedimentary Product of a Complex Interplay among Mantle, Tectonic, Oceanic, and Biospheric Processes. *Economic Geology* 105, 467–508. <https://doi.org/10.2113/gsecongeo.105.3.467>
- Bontognali, T.R.R., Fischer, W.W., Föllmi, K.B. (2013) Siliciclastic associated banded iron formation from the 3.2Ga Moodies Group, Barberton Greenstone Belt, South Africa. *Precambrian Research* 226, 116–124. <https://doi.org/10.1016/j.precamres.2012.12.003>
- Chen, S.F., Riganti, A., Wyche, S., Greenfield, J.E., Nelson, D.R. (2003) Lithostratigraphy and tectonic evolution of contrasting greenstone successions in the central Yilgarn Craton, Western Australia. *Precambrian Research* 127, 249–266. [https://doi.org/10.1016/S0301-9268\(03\)00190-6](https://doi.org/10.1016/S0301-9268(03)00190-6)
- Coenen, D., Evans, D., Jurikova, H., Dumont, M., Rae, J., Muller, W. (2024) Determining the sources of (sub)permil-level inaccuracy during laser ablation-MC-ICPMS boron isotope measurements of carbonates. *Journal of Analytical Atomic Spectrometry* 39, 2409–2420. <https://doi.org/10.1039/D4JA00154K>
- Condie, K.C., Aster, R.C. (2010) Episodic zircon age spectra of orogenic granitoids: The supercontinent connection and continental growth. *Precambrian Research* 180, 227–236. <https://doi.org/10.1016/j.precamres.2010.03.008>
- Czaja, A.D., Johnson, C.M., Beard, B.L., Roden, E.E., Li, W., Moorbath, S. (2013) Biological Fe oxidation controlled deposition of banded iron formation in the ca. 3770Ma Isua Supracrustal Belt (West Greenland). *Earth and Planetary Science Letters* 363, 192–203. <https://doi.org/10.1016/j.epsl.2012.12.025>
- Czaja, A.D., Van Kranendonk, M.J., Beard, B.L., Johnson, C.M. (2018) A multistage origin for Neoarchean layered hematite-magnetite iron formation from the Weld Range, Yilgarn Craton, Western Australia. *Chemical Geology* 488, 125–137. <https://doi.org/10.1016/j.chemgeo.2018.04.019>
- Delvigne, C. (2012) The Archaean silicon cycle insights from silicon isotopes and Ge/Si ratios in banded iron formations, palaeosols and shales. PhD thesis, Free University of Brussels, 183pp.

- Delvigne, C., Cardinal, D., Hofmann, A., André, L. (2012) Stratigraphic changes of Ge/Si, REE+Y and silicon isotopes as insights into the deposition of a Mesoarchaeon banded iron formation. *Earth and Planetary Science Letters* 355–356, 109–118. <https://doi.org/10.1016/j.epsl.2012.07.035>
- Dhuime, B., Hawkesworth, C.J., Cawood, P.A., Storey, C.D. (2012) A Change in the Geodynamics of Continental Growth 3 Billion Years Ago. *Science* 335, 1334–1337. <https://doi.org/10.1126/science.1216066>
- Duuring, P., Santos, J.O.S., Fielding, I.O.H., Ivanic, T.J., Hagemann, S.G., Angerer, T., Lu, Y.J., Roberts, M., Choi, J. (2020) Dating hypogene iron mineralization events in Archean BIF at Weld Range, Western Australia: insights into the tectonomagmatic history of the northern margin of the Yilgarn Craton. *Mineralium Deposita*. *Mineralium Deposita* 55, 1307–1332. <https://doi.org/10.1007/s00126-019-00930-3>
- Evans, D., Gerdes, A., Coenen, D., Marschall, H.R., Müller, W. (2021) Accurate correction for the matrix interference on laser ablation MC-ICPMS boron isotope measurements in CaCO₃ and silicate matrices. *Journal of Analytical Atomic Spectrometry* 36, 1607–1617. <https://doi.org/10.1039/D1JA00073J>
- Eyster, A., Brengman, L.A., Nichols, C.I.O., Levitt, Z., Wilcots, J., Bergmann, K.D. (2021) A New Depositional Framework for Massive Iron Formations After the Great Oxidation Event. *Geochemistry, Geophysics, Geosystems* 22, e2020GC009113. <https://doi.org/10.1029/2020GC009113>
- Fietzke, J., Anagnostou, E. (2023) Sources of Inaccuracy in Boron Isotope Measurement Using LA-MC-ICP-MS. *Geostandards and Geoanalytical Research* 47, 481–492. <https://doi.org/10.1111/ggr.12511>
- Foster, G.L., Marschall, H.R., Palmer, M.R. (2018) Boron Isotope Analysis of Geological Materials. In: Marschall, H., Foster, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, 13–31. https://doi.org/10.1007/978-3-319-64666-4_2
- Foster, G.L., Pogge Von Strandmann, P.A.E., Rae, J.W.B. (2010) Boron and magnesium isotopic composition of seawater. *Geochemistry, Geophysics, Geosystems* 11, 1–10. <https://doi.org/10.1029/2010GC003201>
- Frei, R., Bridgwater, D., Rosing, M., Stecher, O. (1999) Controversial Pb-Pb and Sm-Nd isotope results in the early Archean Isua (West Greenland) oxide iron formation: Preservation of primary signatures versus secondary disturbances. *Geochimica et Cosmochimica Acta* 63, 473–488. [https://doi.org/10.1016/S0016-7037\(98\)00290-7](https://doi.org/10.1016/S0016-7037(98)00290-7)
- Gaillardet, J., Lemarchand, D. (2018) Boron in the Weathering Environment. In: Marschall, H., Foster, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, 163–188. https://doi.org/10.1007/978-3-319-64666-4_7
- Goodwin, A.M. (1996) *Principles of Precambrian geology*. Elsevier.
- Guo, M., Korenaga, J. (2023) The combined Hf and Nd isotope evolution of the depleted mantle requires Hadean continental formation. *Science Advance* 9, eade2711. <https://doi.org/10.1126/sciadv.ade2711>
- He, M. *et al.* (2020) Rapid determination of the original boron isotopic composition from altered basaltic glass by in situ secondary ion mass spectrometry. *Journal of Analytical Atomic Spectrometry* 35, 238–245. <https://doi.org/10.1039/C9JA00374F>

- Herzberg, C., Condie, K., Korenaga, J. (2010) Thermal history of the Earth and its petrological expression. *Earth and Planetary Science Letters* 292, 79–88. <https://doi.org/10.1016/j.epsl.2010.01.022>
- Heubeck, C., Engelhardt, J., Byerly, G.R., Zeh, A., Sell, B., Lubert, T., Lowe, D.R. (2013) Timing of deposition and deformation of the Moodies Group (Barberton Greenstone Belt, South Africa): Very-high-resolution of Archaean surface processes. *Precambrian Research* 231, 236–262. <https://doi.org/10.1016/j.precamres.2013.03.021>
- Hofmann, A. (2005) The geochemistry of sedimentary rocks from the Fig Tree Group, Barberton greenstone belt: Implications for tectonic, hydrothermal and surface processes during mid-Archaean times. *Precambrian Research* 143, 23–49. <https://doi.org/10.1016/j.precamres.2005.09.005>
- Hofmann, A., Dirks, P.H.G.M., Jelsma, H.A., Matura, N. (2003) A tectonic origin for ironstone horizons in the Zimbabwe craton and their significance for greenstone belt geology. *Journal of the Geological Society* 160, 83–97. <https://doi.org/10.1144/0016-764901-172>
- Hren, M.T., Tice, M.M., Chamberlain, C.P. (2009) Oxygen and hydrogen isotope evidence for a temperate climate 3.42 billion years ago. *Nature* 462, 205–208. <https://doi.org/10.1038/nature08518>
- Ishikawa, T., Nakamura, E. (1993) Boron isotope systematics of marine sediments. *Earth and Planetary Science Letters* 117, 567–580. [https://doi.org/10.1016/0012-821X\(93\)90103-G](https://doi.org/10.1016/0012-821X(93)90103-G)
- Joachimski, M.M., Simon, L., van Geldern, R., Lécuyer, C. (2005) Boron isotope geochemistry of Paleozoic brachiopod calcite: Implications for a secular change in the boron isotope geochemistry of seawater over the Phanerozoic. *Geochimica et Cosmochimica Acta* 69, 4035–4044. <https://doi.org/10.1016/j.gca.2004.11.017>
- Jochum, K.P. *et al.* (2011) GSD-1G and MPI-DING Reference Glasses for In Situ and Bulk Isotopic Determination. *Geostandards and Geoanalytical Research* 35, 193–226. <https://doi.org/10.1111/j.1751-908X.2010.00114.x>
- Jurikova, H. *et al.* (2025) Rapid rise in atmospheric CO₂ marked the end of the Late Palaeozoic Ice Age. *Nature Geoscience* 18, 91–97. <https://doi.org/10.1038/s41561-024-01610-2>
- Kasemann, S.A., Hawkesworth, C.J., Prave, A.R., Fallick, A.E., Pearson, P.N. (2005) Boron and calcium isotope composition in Neoproterozoic carbonate rocks from Namibia: Evidence for extreme environmental change. *Earth and Planetary Science Letters* 231, 73–86. <https://doi.org/10.1016/j.epsl.2004.12.006>
- Kasemann, S.A., Schmidt, D.N., Bijma, J., Foster, G.L. (2009) In situ boron isotope analysis in marine carbonates and its application for foraminifera and palaeo-pH. *Chemical Geology* 260, 138–147. <https://doi.org/10.1016/j.chemgeo.2008.12.015>
- Kasemann, S.A., Prave, A.R., Fallick, A.E., Hawkesworth, C.J., Hoffmann, K.H. (2010) Neoproterozoic ice ages, boron isotopes, and ocean acidification: Implications for a snowball Earth. *Geology* 38, 775–778. <https://doi.org/10.1130/G30851.1>
- Kolodny, Y., Chaussidon, M. (2004) Boron isotopes in DSDP cherts: Fractionation and diagenesis. In: Hill, R.J., Leventhal, J., Aizenshtat, Z., Baedeker, M.J., Claypool, G., Eganhouse, R., Goldhaber, M., Peters, K. (Eds.) *The Geochemical Society Special Publications* 9, 1–14. [https://doi.org/10.1016/S1873-9881\(04\)80003-8](https://doi.org/10.1016/S1873-9881(04)80003-8)

- Konhauser, K.O. *et al.* (2017) Iron formations: A global record of Neoarchaeon to Palaeoproterozoic environmental history. *Earth-Science Reviews* 172, 140–177. <https://doi.org/10.1016/j.earscirev.2017.06.012>
- Kowalski, P.M., Wunder, B. (2018) Boron Isotope Fractionation Among Vapor--Liquids--Solids--Melts: Experiments and Atomistic Modeling. In: Marschall, H., Foster, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, 33–69. https://doi.org/10.1007/978-3-319-64666-4_3
- Krissansen-Totton, J., Arney, G.N., Catling, D.C. (2018) Constraining the climate and ocean pH of the early Earth with a geological carbon cycle model. *Proceedings of the National Academy of Sciences of the United States of America* 115, 4105–4110. <https://doi.org/10.1073/pnas.1721296115>
- Ledevin, M., Arndt, N., Chauvel, C., Jaillard, E., Simionovici, A. (2019) The sedimentary origin of black and white banded cherts of the Buck Reef, Barberton, South Africa. *Geosciences* 9, 424. <https://doi.org/10.3390/geosciences9100424>
- Legett, S.A., Rasbury, E.T., Grossman, E.L., Hemming, N.G., Penman, D.E. (2020) The Brachiopod $\delta^{11}\text{B}$ Record Across the Carboniferous-Permian Climate Transition. *Paleoceanography and Paleoclimatology* 35, 1–13. <https://doi.org/10.1029/2019PA003838>
- Lemarchand, D., Gaillardet, J., Lewin, É., Allègre, C.J. (2000) The influence of rivers on marine boron isotopes and implications for reconstructing past ocean pH. *Nature* 408, 951–954. <https://doi.org/10.1038/35050058>
- Lemarchand, D., Gaillardet, J., Lewin, É., Allègre, C.J. (2002) Boron isotope systematics in large rivers: implications for the marine boron budget and paleo-pH reconstruction over the Cenozoic. *Chemical Geology* 190, 123–140. [https://doi.org/10.1016/S0009-2541\(02\)00114-6](https://doi.org/10.1016/S0009-2541(02)00114-6)
- Marschall, H.R. (2018) Boron Isotopes in the Ocean Floor Realm and the Mantle. In: Marschall, H., Foster, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, Cham, 189–215. https://doi.org/10.1007/978-3-319-64666-4_8
- Marschall, H.R., Foster, G.L. (2018) Boron Isotopes in the Earth and Planetary Sciences---A Short History and Introduction. In: Marschall, H., Foster, G. (Eds.) *Boron Isotopes: The Fifth Element*. Springer International Publishing, Cham, 1–11. https://doi.org/10.1007/978-3-319-64666-4_1
- Marschall, H.R., Wanless, V.D., Shimizu, N., Pogge von Strandmann, P.A.E., Elliott, T., Monteleone, B.D. (2017) The boron and lithium isotopic composition of mid-ocean ridge basalts and the mantle. *Geochimica et Cosmochimica Acta* 207, 102–138. <https://doi.org/10.1016/j.gca.2017.03.028>
- McLennan, S.M., Taylor, S.R. (1982) Geochemical constraints on the growth of the continental crust. *The Journal of Geology* 90, 347–361. <https://doi.org/10.1086/628690>
- Nutman, A.P., Friend, C.R.L. (2009) New 1:20,000 scale geological maps, synthesis and history of investigation of the Isua supracrustal belt and adjacent orthogneisses, southern West Greenland: A glimpse of Eoarchean crust formation and orogeny. *Precambrian Research* 172, 189–211. <https://doi.org/10.1016/j.precamres.2009.03.017>
- Polat, A., Frei, R. (2005) The origin of early Archean banded iron formations and of continental crust, Isua, southern West Greenland. *Precambrian Research* 138, 151–175. <https://doi.org/10.1016/j.precamres.2005.04.003>

- Reimink, J.R., Davies, J.H.F.L., Moyen, J.F., Pearson, D.G. (2023) A whole-lithosphere view of continental growth. *Geochemical Perspectives Letters* 26, 45–49. <https://doi.org/10.7185/geochemlet.2324>
- Ring, S.J., Henehan, M.J., Blukis, R., von Blanckenburg, F. (2025) Adsorption pathways of boron on clay and their implications for boron cycling on land and in the ocean. *Geochimica et Cosmochimica Acta* 389, 74–83. <https://doi.org/10.1016/j.gca.2024.08.014>
- Saldi, G.D., Louvat, P., Schott, J., Gaillardet, J. (2021) The pH dependence of the isotopic composition of boron adsorbed on amorphous silica. *Geochimica et Cosmochimica Acta* 308, 1–20. <https://doi.org/10.1016/j.gca.2021.05.052>
- Satkoski, A.M., Beukes, N.J., Li, W., Beard, B.L., Johnson, C.M. (2015) A redox-stratified ocean 3.2 billion years ago. *Earth and Planetary Science Letters* 430, 43–53. <https://doi.org/10.1016/j.epsl.2015.08.007>
- Simon, L., Lécuyer, C., Maréchal, C., Coltice, N. (2006) Modelling the geochemical cycle of boron: Implications for the long-term $\delta^{11}\text{B}$ evolution of seawater and oceanic crust. *Chemical Geology* 225, 61–76. <https://doi.org/10.1016/j.chemgeo.2005.08.011>
- Spencer, C.J., Roberts, N.M.W., Santosh, M. (2017) Growth, destruction, and preservation of Earth's continental crust. *Earth-Science Reviews* 172, 87–106. <https://doi.org/10.1016/j.earscirev.2017.07.013>
- Smith, A.J.B., Beukes, N.J. (2023) The paleoenvironmental implications of pre-Great Oxidation Event manganese deposition in the Mesoarchean Ijzermijn Iron Formation Bed, Mozaan Group, Pongola Supergroup, South Africa. *Precambrian Research* 384, 106922–106922. <https://doi.org/10.1016/j.precamres.2022.106922>
- Smith, A.J.B., Beukes, N.J., Gutzmer, J. (2013) The composition and depositional environments of Mesoarchean iron formations of the West Rand Group of the Witwatersrand Supergroup, South Africa. *Economic Geology* 108, 111–134. <https://doi.org/10.2113/econgeo.108.1.111>
- Spivack, A.J., Palmer, M.R., Edmond, J.M. (1987) The sedimentary cycle of the boron isotopes. *Geochimica et Cosmochimica Acta* 51, 1939–1949. [https://doi.org/10.1016/0016-7037\(87\)90183-9](https://doi.org/10.1016/0016-7037(87)90183-9)
- Standish, C.D., Chalk, T.B., Babila, T.L., Milton, J.A., Palmer, M.R., Foster, G.L. (2019) The effect of matrix interferences on in situ boron isotope analysis by laser ablation multi-collector inductively coupled plasma mass spectrometry. *Rapid Communications in Mass Spectrometry* 33, 959–968. <https://doi.org/10.1002/rcm.8432>
- Xu, J.D., Gerdes, A., Schmidt, A., Hezel, D.C., Marschall, H.R. (2024) Simultaneous Bulk-Rock Elemental and Boron Isotope Ratio Measurement Using LA-ICP-MS on Silicate Micro-Particulate Pellets. *Geostandards and Geoanalytical Research* 48, 807–822. <https://doi.org/10.1111/ggr.12574>