

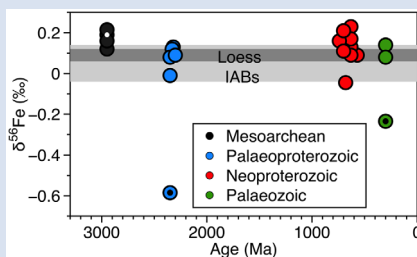
# Constant iron isotope composition of the upper continental crust over the past 3 Gyr

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## Abstract



The Fe isotopic composition of twenty four glacial diamictite composites with depositional ages ranging from the Mesoarchean to the Palaeozoic serve as proxies of the average upper continental crust (UCC) and can be used to track how  $\delta^{56}\text{Fe}$  may have changed in the continental crust through time. The diamictites have elevated chemical index of alteration (CIA) values and other characteristics of weathered regoliths (*e.g.*, strong depletion in soluble elements such as Sr), which they inherited from their upper crustal source regions. The  $\delta^{56}\text{Fe}$  values in the diamictite composites range from  $-0.59\text{‰}$  to  $+0.23\text{‰}$ . Excluding three samples impacted by the incorporation of materials from Fe formations, the diamictites have an average  $\delta^{56}\text{Fe}$  of  $0.12 \pm 0.13\text{‰}$  ( $2\sigma$ ), overlapping the recent estimated average  $\delta^{56}\text{Fe}$  of  $0.09 \pm 0.03\text{‰}$

(2 s.d.) in the upper continental crust (Dauphas *et al.*, 2017, and references therein). There is no obvious correlation between  $\delta^{56}\text{Fe}$  of the glacial diamictites and the CIA. Our data suggest that the Fe isotope composition of the upper continental crust has been relatively constant throughout Earth history and that chemical weathering is not important in producing Fe isotope variations in the upper continental crust. Pre-Great Oxidation Event (GOE) anoxic weathering, when iron was soluble in its divalent state, did not generate different Fe isotopic signatures from the post-GOE oxidative weathering environment in the upper continental crust. Therefore, the large Fe isotopic fractionations observed in various marine sedimentary records are likely due to processes occurring in the oceans (*e.g.*, biological activity) rather than abiotic redox reactions on the continents.

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## Introduction

Iron is the fourth most abundant element in the continental crust (Rudnick and Gao, 2003) and it influences global climate and biogeochemical cycles in the ocean (Martin, 1990). Continental inputs, including riverine inputs and atmospheric dust, are dominant sources (>95 %) of iron in the modern ocean (Fantle and DePaolo, 2004). Thus, understanding how continental inputs may have changed through time is important in understanding the secular evolution of the marine iron cycle. Continental weathering in the modern oxidising environment transports the majority of iron as detrital phases and little iron in Fe (III) colloidal form, leading to a very low dissolved iron concentration in modern seawater (Fantle and DePaolo, 2004; Johnson *et al.*, 2020). However, the mechanism(s) of iron transportation in the geological past, especially before the Great Oxidation Event (GOE), was different due to very low oxygen levels in the atmosphere and oceans. Then, iron was transported in dissolved divalent form and deposited on the ocean floor in the form of marine sedimentary rocks such as iron formations (Holland, 2006). Overall, it is important to understand the secular evolution of the  $\delta^{56}\text{Fe}$  composition of the continental crust and potential effects of varying oxidation levels on chemical weathering signatures.

Iron isotopes in the upper continental crust (UCC) were first determined in the pioneering work of Beard *et al.* (1999) and summarised in Beard and Johnson (2004), where they estimated the average  $\delta^{56}\text{Fe}$  of UCC as  $0.11 \pm 0.1\text{‰}$ , based on the Fe isotopic compositions of clastic sedimentary rocks and suspended loads from rivers. More recently, Gong *et al.* (2017) measured Fe isotopic compositions in loess-paleosols horizons, which have relatively homogeneous Fe isotopic compositions with  $\delta^{56}\text{Fe}$  ranging from  $0.06\text{‰}$  to  $0.12\text{‰}$ , overlapping the previously determined UCC values. The UCC  $\delta^{56}\text{Fe}$  values are on the higher end but mostly within the range observed for mantle/primitive basalts, as constrained by island arc basalts (IABs) (Dauphas *et al.*, 2009).

Potential weathering influences on continental crustal Fe isotope compositions have been investigated through case studies of weathering profiles and soils in modern oxic environments (*e.g.*, Wiederhold *et al.*, 2007; Kiczka *et al.*, 2011; Yesavage *et al.*, 2012). Although the exact mechanisms of Fe isotope fractionation in the upper continental crust may vary from case to case, the general direction is that weathering produces isotopically light dissolved Fe, leaving behind a slightly heavy regolith (Fantle and DePaolo, 2004). By contrast, weathering under anoxic conditions may have been very different from modern

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environments and changes of weathering patterns on the continents from pre-GOE to the present may be recorded by the weathered upper continental crust. However, few studies of the effects of weathering on Fe isotopes in pre-GOE anoxic environments exist. For example, previous paleosol studies all show that chemical weathering preferentially removed isotopically light iron and left a heavy isotopic composition in regolith/paleosol. Overall, the reported magnitudes of isotopic fractionation are larger during oxidative weathering ( $\delta^{56}\text{Fe} = -0.8\text{‰}$  to  $+1.2\text{‰}$ ) compared to anoxic weathering ( $\delta^{56}\text{Fe} = -0.06\text{‰}$  to  $+0.51\text{‰}$ ), while the direction remains the same (e.g., [Wiederhold et al., 2007](#); [Yamaguchi et al., 2007](#); [Babechuk et al., 2019](#); [Heard et al., 2021](#)). Nonetheless, there is no systematic study on how different chemical weathering conditions before and after the GOE may have influenced the Fe isotopic composition of the upper continental crust. Glacial diamictites may be useful proxies of the exposed upper continental crust because they derive from physical erosion of large continental areas with little associated (syn-depositional) chemical weathering or post-depositional weathering, though they do carry a weathering signature derived from the exposed upper continental crust ([Li et al., 2016](#)).

The objective of this study is to understand how Fe isotope compositions in the upper continental crust may have changed through time and whether changes in chemical weathering conditions on the continents influenced Fe isotope compositions of the upper continental crust. Here, we report Fe isotope compositions for twenty four glacial diamictite composites (including 143 individual diamictite samples, [Table S-1](#); [Gaschnig et al., 2016](#)) with depositional ages ranging from Mesoarchean to the Palaeozoic eras, which serve as proxies of the upper continental crust to track how  $\delta^{56}\text{Fe}$  may have changed in the continental crust through time.

## Samples and Methods

The well-characterised glacial diamictite composites ([Gaschnig et al., 2016](#)) are composed of material derived from the abrasion and erosion of soil and bedrock that was transported by glaciers and sea ice. Glacial diamictites are poorly sorted and were deposited either on the continent or in a shallow marine environment. Because glacial sediments derive from physical erosion of large continental areas by glaciers with little syn/post-depositional weathering, [Goldschmidt \(1933\)](#) first suggested that they could be robust proxies to estimate the average upper continental crust composition.

Glacial deposits occur in five broad geological periods: the Mesoarchean (ca. 2900 Ma), Palaeoproterozoic (2400–2200 Ma), Neoproterozoic (750–550 Ma), Palaeozoic (a short glacial event at 450 Ma and a longer one at 330–300 Ma), and Cenozoic (2.58–0.01 Ma) ([Gaschnig et al., 2014, 2016](#); and references therein). The glacial diamictites investigated in this study come from four main geological intervals, including the Mesoarchean, Palaeoproterozoic, Neoproterozoic, and Palaeozoic eras. Individual diamictite samples ( $n = 143$ ) were crushed in a ceramic jaw crusher, where the resulting chips were handpicked to concentrate the fine grained matrix and exclude clasts larger than 1 mm in diameter at the University of Maryland ([Gaschnig et al., 2014](#)). These chips were then ground into powders in a ceramic mill. All twenty four diamictite composites were made by weighing out equal weight aliquots ( $\pm 0.1$  grams) of powders from each individual stratigraphic formation listed in [Gaschnig et al. \(2016\)](#), as well as in [Supplementary Information \(Table S-1\)](#).

Iron isotope analyses were performed at the Carnegie Institution for Science. A brief description of sample dissolution, column chemistry, and instrumental analysis is provided in the

**Supplementary Information.** Purified Fe solutions ( $\sim 4$  ppm Fe in 0.4 M  $\text{HNO}_3$ ) were analysed using a Nu Plasma II Multi-Collector Inductively Coupled Plasma Mass Spectrometer (MC-ICP-MS). Standard bracketing, using IRMM524a (made from IRMM® certified Reference iron foil), was performed for all analyses. The Fe isotope composition of IRMM524a is identical to that of previously used international standard, IRMM-014. Therefore, the Fe isotope composition is reported as  $\delta^{56}\text{Fe}$ , where  $\delta^{56}\text{Fe}_{\text{sample}} = [({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{sample}}/({}^{56}\text{Fe}/{}^{54}\text{Fe})_{\text{IRMM-014}} - 1] \times 1000$ . The external precision and accuracy of the measurements were evaluated by repeatedly running two USGS rock standards, BIR-1 (Icelandic basalt) and MAG-1 (marine mud), respectively ([Table S-2](#)). BIR-1 yielded  $\delta^{56}\text{Fe} = 0.05 \pm 0.03\text{‰}$  ( $2\sigma$ ,  $n = 5$ ; cf. 0.03–0.06 ‰ in the literature; GeoReM database, <http://georem.mpch-mainz.gwdg.de/>), and MAG-1 yielded  $\delta^{56}\text{Fe} = 0.11 \pm 0.04\text{‰}$  ( $2\sigma$ ,  $n = 5$ ; cf. 0.09–0.13 ‰ in the GeoReM database).

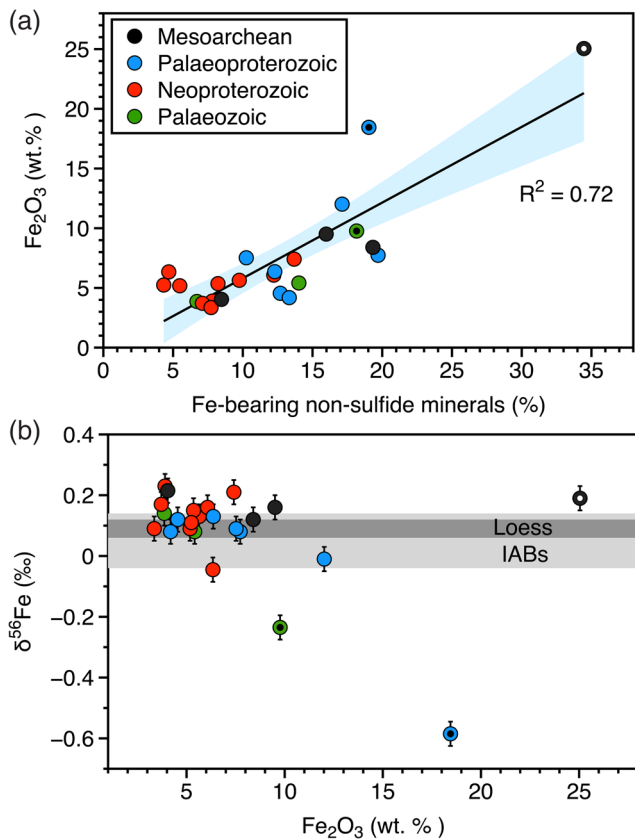
## Secular Evolution of Fe Isotope Composition of the Upper Continental Crust

Iron contents and isotopic compositions of the diamictite composites are reported in [Table S-1](#). Total Fe concentrations ( $\text{Fe}_2\text{O}_3$ ) in the composites vary considerably, from 3 wt. % to 25 wt. % and correlate with the proportions of Fe-bearing minerals ([Fig. 1a](#)), where Fe-containing non-sulfide minerals are defined using the sum of the following Fe-bearing silicates and oxides: chlorite, biotite, amphibole, hematite, and magnetite ([Table S-3](#)). By contrast, the diamictites show a limited spread in their Fe isotope compositions ( $-0.59\text{‰}$  to  $+0.23\text{‰}$ ; average,  $0.08 \pm 0.34\text{‰}$  [ $2\sigma$ ]), with no correlation between  $\delta^{56}\text{Fe}$  values and total iron concentrations ([Fig. 1b](#)). This range overlaps with the values of juvenile continental crustal material: IABs and the present day upper continental crust (UCC) both show narrow ranges in  $\delta^{56}\text{Fe}$  from  $-0.04\text{‰}$  to  $+0.14\text{‰}$  ([Dauphas et al., 2009](#)) and from  $+0.06\text{‰}$  to  $+0.12\text{‰}$  ([Gong et al., 2017](#)), respectively.

Major element data ([Gaschnig et al., 2016](#)) and new Si isotope data ([Murphy et al., 2022](#)) show that banded iron formation (BIF) influenced some composites, including the Archean/Palaeoproterozoic Mozaan and Makganyene diamictites, which have distinctly lower  $\delta^{30}\text{Si}$  and higher  $\text{Fe}_2\text{O}_3$ . The Palaeozoic Dwyka West sample, which derives from an ancient provenance ([Gaschnig et al., 2022](#)), contains clasts of BIF and moderately high  $\text{Fe}_2\text{O}_3$  (9.8 wt. %) and has slightly lower  $\delta^{30}\text{Si}$ . BIF shows great variability in  $\delta^{56}\text{Fe}$  ([Heard and Dauphas, 2020](#)), and two of the samples that show evidence for BIF based on low  $\delta^{30}\text{Si}$  and high  $\text{Fe}_2\text{O}_3$  also show low  $\delta^{56}\text{Fe}$  (i.e. Makganyene and Dwyka West). By contrast, the Mozaan composite, which has the highest  $\text{Fe}_2\text{O}_3$  and lowest  $\delta^{30}\text{Si}$  has 'normal'  $\delta^{56}\text{Fe}$ . These observations explain the lowest two  $\delta^{56}\text{Fe}$  values in the Makganyene and Dwyka West composites. We exclude these three samples (Mozaan, Makganyene, and Dwyka West) when calculating the average UCC Fe isotope compositions.

The data show that the Fe isotope composition of the upper continental crust has not varied significantly since 2.9 Ga ([Fig. 2](#)). The  $\delta^{56}\text{Fe}$  values in the Archean diamictite composites appear higher ( $\delta^{56}\text{Fe}_{\text{ave}} = 0.17\text{‰}$ ) compared to those of the Palaeoproterozoic composites ( $\delta^{56}\text{Fe}_{\text{ave}} = 0.11\text{‰}$ ) ([Fig. 2](#)) (excluding the Makganyene sample with known BIF influence). However, a Student's  $t$ -test yields a  $p$  value greater than 0.05, demonstrating that there is no difference between the means of the two groups.



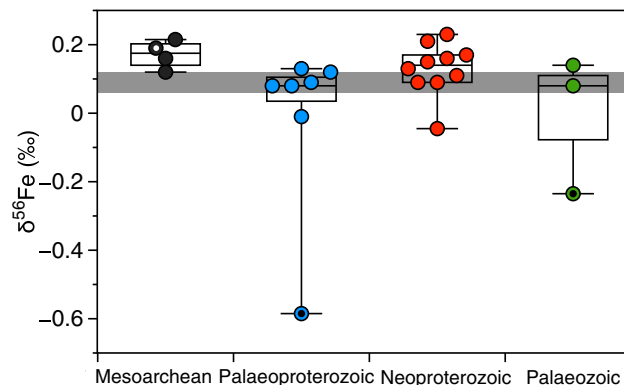


**Figure 1** (a) Total iron content (Fe<sub>2</sub>O<sub>3</sub>, wt. %) vs. Fe-bearing non-sulfide minerals (%) in all glacial diamictite composites. (b) Plot of δ<sup>56</sup>Fe vs. total iron content (Fe<sub>2</sub>O<sub>3</sub>, wt. %) in all diamictites. Error bars represent two standard deviations. Black lines denote linear fit with light blue fields indicating 95 % confidence interval of fitting. The horizontal gray bars indicate the UCC values (dark gray, 2σ) calculated from loess (Gong et al., 2017) and the juvenile bulk crust values (light gray, 2σ) from IABs (Dauphas et al., 2009), respectively. Two outliers with distinctive Fe isotope compositions are shown with a black dot in the centre of symbols, whereas the Mozaan sample is marked with a white dot.

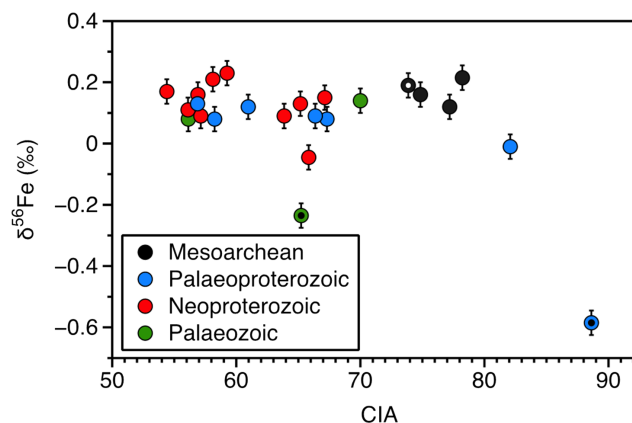
## Weathering Signatures and Their Influence on the Secular Evolution of Fe Isotopes in UCC

Using the diamictite’s Fe isotope compositions and excluding the three samples having a BIF influence, we calculate an average upper continental crust δ<sup>56</sup>Fe value of 0.12 ± 0.13 ‰ (2σ), which represents the UCC over Earth history. This new estimate is within the uncertainty of the recently estimated average δ<sup>56</sup>Fe of 0.09 ± 0.03‰ (2σ) for the present day upper continental crust based on loess (Gong et al., 2017). IABs with δ<sup>56</sup>Fe = 0.06 ± 0.08 ‰ (2σ), which are possible analogues of the juvenile continental crust, have near-chondritic iron isotope compositions (δ<sup>56</sup>Fe = -0.005 ± 0.006 ‰) (Dauphas et al., 2009, 2017). Student’s *t*-test results show that the UCC δ<sup>56</sup>Fe from these diamictites (δ<sup>56</sup>Fe<sub>ave</sub> = 0.12 ‰) are statistically different (*p* < 0.05) from juvenile crust as sampled by IABs (δ<sup>56</sup>Fe<sub>ave</sub> = 0.06 ‰). These slightly heavier upper continental crustal values may reflect the influence of chemical weathering, which produces heavier Fe isotope compositions in the regolith compared to that of the juvenile crust (Fantle and DePaolo, 2004).

As demonstrated earlier, total Fe concentrations correlate well with Fe-containing silicate minerals and oxides (Fig. 1a), and do not correlate with total sulfur content (Fig. S-1). Thus, in contrast to the isotopes of elements controlled by sulfide



**Figure 2** Box and whiskers plot of δ<sup>56</sup>Fe in diamictite composites of four age groups: the Mesoarchean, Palaeoproterozoic, Neoproterozoic, and Palaeozoic groups. Each individual box includes 50 % of samples and whiskers mark the maximum and minimum of the bin population. The horizontal gray bar indicates the UCC values (2σ) calculated from loess (Gong et al., 2017).



**Figure 3** Plot of δ<sup>56</sup>Fe vs. CIA (chemical index of alteration) in diamictites. CIA is calculated as defined in molar ratio as [Al<sub>2</sub>O<sub>3</sub> / (Al<sub>2</sub>O<sub>3</sub> + CaO\* + Na<sub>2</sub>O + K<sub>2</sub>O)] × 100, where CaO\* is corrected to remove the contribution from carbonate and apatite (Nesbitt and Young, 1982). CIA data for diamictite plotted here are from Gaschnig et al. (2016).

weathering such as Ni (Wang et al., 2019), sulfide weathering did not significantly affect the Fe isotopic compositions in the pre-GOE samples. Therefore, anoxic weathering appears to generate similar Fe isotope signatures as the post-GOE oxidative weathering environment in the upper continental crust.

There is no correlation between δ<sup>56</sup>Fe and CIA in the diamictites (Fig. 3). While chemical weathering produces an isotopically heavier regolith, as seen by the slightly higher δ<sup>56</sup>Fe values in the diamictites and other UCC materials compared to the juvenile crust represented by IABs, this has only resulted in a 0.06 ‰ difference between average UCC and juvenile crust δ<sup>56</sup>Fe. Therefore, we conclude that chemical weathering has only a minor influence on the Fe isotope composition of the upper continental crust.

## Conclusions

Glacial diamictites are faithful recorders of the upper continental crust composition, which has been through chemical weathering compared to the juvenile crust. Their δ<sup>56</sup>Fe values do not vary with depositional age (from ~3 Ga onwards), indicating that changes in the oxidation state have no bearing on Fe isotopic fractionation during chemical weathering. Thus, the large Fe isotopic





fractionation in marine sedimentary records (Heard and Dauphas, 2020) is likely due to authigenic processes occurring in the oceans and not changes in the continental input to the oceans.

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## Additional Information

Supplementary Information accompanies this letter at <https://www.geochemicalperspectivesletters.org/article2221>.



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