Geochemical Perspectives Letters

Neoarchean marine chemical sediments as archives of Hadean silicate differentiation

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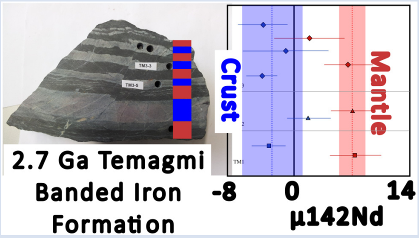

Planetary differentiation had a profound influence on the geochemical signature of the Earth's silicate reservoirs. Some of the early created complementary reservoirs dissipated with time (*e.g.*, Bennett *et al.*, 2007) and only remnants can be observed. Here, we apply the short lived isotopic system ^{146}Sm-^{142}Nd to an alternative archive —marine chemical sediments—and show that alternating Fe- and Si-rich bands from the 2.7 billion-year-old Temagami banded iron formation (BIF), Canada, display significantly different ^{142}Nd isotopic compositions. The Fe-rich bands yield a depleted signature (expressed as deviation from the standard in µ notation) with an average µ^{142}Nd of $+7.02 \pm 0.71$, while the Si-rich bands display modern mantle-like signatures (average µ^{142}Nd -2.83 ± 2.32) likely being the results of mixing between different sources. These complementary signatures reflect the dominant, locally derived source of Nd in the seawater at the time of deposition. Our results promote that layering in BIFs is a syn-depositional feature, and that BIFs are unique geochemical archives capable of recording silicate reservoirs that formed during the Hadean but were still extant during the Neoarchean.

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Introduction

The ^{146}Sm-^{142}Nd radiogenic isotope system is the primary tool for tracing early Earth silicate differentiation due to the systems short half-life and decoupling of the parent and daughter elements during silicate differentiation. The parent isotope, ^{146}Sm, was only present during the first ~500 Ma of the solar system, and as such records silicate differentiation during the Hadean. To date, a wide number of (meta)igneous rock samples have been analysed which record µ^{142}Nd anomalies (where $\mu^{142}Nd = \left(\frac{\frac{^{142}Nd}{^{144}Nd_{sample}}}{\frac{^{142}Nd}{^{144}Nd_{standard}}} - 1\right) \times 10^6$), positive if related to the Hadean depleted mantle and negative if derived from a trace element enriched reservoir (Caro *et al.*, 2006, 2017; Bennett *et al.*, 2007; O'Neil *et al.*, 2012, 2016; Rizo *et al.*, 2012, 2013; Debaille *et al.*, 2013; Morino *et al.*, 2017; Schneider *et al.*, 2018; Garcia *et al.*, 2023).

The Superior Craton contains many well preserved and largely unmodified greenstone belts, including the Abitibi and Temagami. The Abitibi Greenstone Belt contains the youngest Archean rock to show a positive ^{142}Nd anomaly, in 2.7 Ga tholeiite lavas (Debaille *et al.*, 2013). The Temagami region has suffered only minor metamorphism (lower greenschist facies; Jolly, 1982) and hosts sedimentary deposits, including banded iron formations (BIF) that give internal Sm-Nd and Lu-Hf isochron ages of 2.7 Ga and for which the ^{143}Nd isotope compositions have been shown to derive from local Abitibi seawater (Viehmann *et al.*, 2014). The banded iron formation at Temagami is a layered marine chemical sediment with alternating bands of Fe-rich magnetite and Si-rich metachert, showing evidence that both high temperature hydrothermal fluids and subaerial terrestrial weathering affected 2.7 Ga Temagami seawater chemistry (Bau and Alexander, 2009; Viehmann *et al.*, 2014; Bau *et al.*, 2022; Mundl-Petermeier *et al.*, 2022). Previous work has shown that the Temagami BIF has unaltered rare earth element (Bau and Alexander, 2009; Supplementary Information), ^{143}Nd and ^{176}Hf isotope compositions (Viehmann *et al.*, 2014). Recently, a multi-proxy approach on the Temagami BIF, using Ge/Si and Th/U ratios as well as Cr isotopes, indicated that the magnetite layers precipitated from ambient seawater with chemistry dominated by hydrothermal fluids, while the (meta)chert layers formed during periods when the ambient seawater chemistry was dominated by continental sources (Bau *et al.*, 2022). As the BIF's trace element composition derives directly from the sources contributing to local seawater, they provide a unique opportunity to investigate the ^{142}Nd composition of these source lithologies at 2.7 Ga. Besides the importance of Nd as the daughter product in both a short lived and long lived chronometer, Nd is also particularly relevant when studying seawater-derived sediments, as its residence time in modern seawater (<700 years; Tachikawa *et al.*, 1999) is significantly shorter than the global mixing time of the oceans (1500 years; Broecker and Peng, 1982). Although the Nd residence time might be somewhat longer in Archean seawater under more reducing atmospheric and hydrospheric conditions and the resulting lack of abundant Fe and Mn (oxyhydr)oxide particles to scavenge REE, Nd and its isotopes are prime geochemical proxies in Archean marine chemical sediments (Viehmann *et al.*, 2015). Hence, they trace the source of components affecting local seawater composition (*e.g.*, Viehmann *et al.*, 2015). This is in marked

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contrast to the ^{182}W systematics in the Temagami BIF investigated by Mundl-Petermeier *et al.* (2022), where positive $\mu^{182}W$ anomalies were observed. While $\mu^{182}W$ tracks metal–silicate partitioning and earlier differentiation events than $\mu^{142}Nd$, generally they should show similar trends. The difference in the Temagami BIF can be explained due to tungsten's long residence time in seawater, that exceeds the global mixing time of the oceans. As such, the positive anomalies reported by Mundl-Petermeier *et al.* (2022) represent more global sources, while the $\mu^{142}Nd$ discussed here rather represents the local source flux into the seawater.

Methods and Results

Three spatially separate sections of BIF from the Temagami Greenstone Belt were sampled, and homogeneous powders of individual magnetite and metachert layers of each section analysed for high-precision ^{142}Nd. Samples were processed through ion exchange chemistry adapted from the procedures of Debaille *et al.* (2013), prior to 3-lines multi-static analysis by Thermal Ionisation Mass Spectrometer (see Supplementary Information for further details). The raw measurements are corrected for mass fractionation using an exponential law that will account for mass-dependent isotope fractionation. Any possible induced mass-independent fractionation due to nuclear field shift effect during chemical purification is unlikely due to the high Nd yield (>99 %). Sample TM1 shows the largest dissimilarity between the metachert and magnetite layers, with a difference of 10.4 μ units. The two different layers from TM2 are just outside of analytical uncertainty (~4 μ unit) of each other, but the metachert layer is 4.3 μ units lower than the magnetite layer, exceeding the analytical uncertainty. Section TM3 shows the widest variability, with two of the three metachert layers giving an average composition of −3.7 ± 0.19 (2 s.d., error on the average, not analytical error), and one magnetite layer giving +6.6 ± 2.9 (2 s.d.). The two layers TM3-3 and TM3-4 share a similar composition of −0.9 ± 5.1 (2 s.d.) and +1.9 ± 4.1 (2 s.d.) and overlap within uncertainty, despite one being Fe-rich and the other Si-rich (Fig. 1). Due to the similarity of these two adjacent layers, we assume they do not represent a pure end member composition, potentially due to mixing during the resampling process. Therefore, they will not be considered in the following discussion. The Si- and Fe-rich samples of the Temagami BIF define two distinct end member compositions: the metachert bands typically have a lower (negative and close to the present day average) $\mu^{142}Nd$ weighted average of −2.5 ± 3.8 (95 % confidence), whereas the magnetite bands are systematically positive with a weighted average of +7.0 ± 1.6 (95 % confidence, Table S-1). However, the ^{142}Nd and ^{143}Nd systematics are decoupled and the samples do not provide any hint on respective source's model age in a two-stage evolution diagram (see Supplementary Information). As observed by Viehmann *et al.* (2014), the ^{143}Nd systematics is below the expected evolution of the depleted MORB mantle (DMM) at 2.7 Ga. With the BIF giving ~+0.2 ± 1.7 ε-unit in the present study (not considering TM1-2), compared to ~+4 for the DMM at 2.7 Ga, this corroborates previous conclusions that both volcanic and more felsic sources affected ancient Temagami seawater. Such decoupling is also to be expected, considering that the ^{142}Nd value of the mantle has stopped growing at 4 Ga, while ^{143}Nd has continued to grow and mix after 4 Ga.

Discussion

We suggest here that the significant difference in ^{142}Nd isotopic compositions between the Fe-rich and Si-rich BIF end members reflects ^{142}Nd input from distinctly different sources that cannot be resolved by the long lived system ^{143}Nd. As such, the short

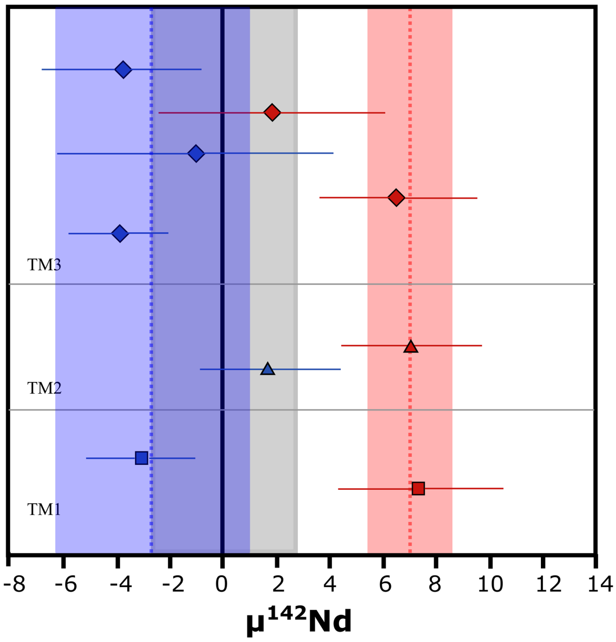

Figure 1 $\mu^{142}Nd$ of the Temagami BIF. Blue symbols are Si-rich layers, red symbols are Fe-rich bands. Samples are reproduced in stratigraphic order. All uncertainties are 2 s.d. Light grey band is the 2σ error on the terrestrial standard JNdi, light blue box is the weighted average and error on the chert samples and the light red box is the weighted average and error on the magnetite layer. See text for details.

residence time of Nd in seawater allows us to detect this disparate source of the Nd, with the preservation and continued tapping of both, an early depleted reservoir, mostly represented by Fe-rich layers, and a modern-like reservoir, represented by Si layers, at 2.7 Ga. The distinct ^{142}Nd compositions seen in the adjacent BIF bands also strongly support interpretations that the prominent banding in BIFs is a primary depositional feature (for a recent discussion see, *e.g.*, Bau *et al.*, 2022). The ^{182}W results (Mundl-Petermeier *et al.*, 2022) also support the banding as a depositional feature, as the metachert and magnetite layers have distinctly different ^{182}W compositions. Interestingly, the ^{182}W results have excesses in both the metachert and the magnetite layers, with the former showing a stronger excess in ^{182}W. Due to the significantly longer marine residence time of W than Nd (*e.g.*, Sohrin *et al.*, 1987), it is not surprising that the ^{142}Nd and ^{182}W results seem to disagree as they are tracing different mixing scales, with ^{182}W tracing the rather *global* seawater composition and the ^{142}Nd rather tracing *local* input into Temagami seawater.

Remarkably, the ^{142}Nd composition of the depleted end member, with a consistent positive $\mu^{142}Nd$ anomaly and a weighted average of +7.0 ± 1.6, perfectly matches the composition of the depleted mantle at 2.7 Ga observed in tholeiites from Theo's Flow, located 200 km north of Temagami (Figs. 1, S-1; Debaille *et al.*, 2013). This provides a highly constrained value for the ^{142}Nd composition of the mantle beneath the Abitibi province at 2.7 Ga. Indeed, this mantle reservoir was not fully homogenised after its formation during the Hadean. It was still an active component during the Neoarchean and contributed positive ^{142}Nd signatures to the seawater from which the Fe-rich bands precipitated, via high temperature hydrothermal fluids that leached submarine volcanics. Interestingly, the 2.7 Ga Boston Creek komatiite flow lies between Theo's Flow and Temagami and has distinctly different $\mu^{142}Nd$ of −3.8 ± 2.8 (Puchtel *et al.*, 2018). This flow is unique amongst the Archean komatiites with a deficit in highly siderophile elements compared to the modern mantle, chondritic $^{187}Os/^{188}Os$ coupled with a positive ^{182}W anomaly. Puchtel *et al.* (2018) concluded that the Boston Creek flow was sourced from a mantle that formed early in Earth's history and was then isolated from the convecting mantle for ≥1.8 billion years. While this would require there to be several heterogeneous mantle domains beneath the Abitibi Greenstone Belt, it supports the conclusion of this study, that the local mantle was not well homogenised and pockets of Hadean-formed mantle remained well into the Neoarchean.

In contrast, the weighted average for the metachert bands is not fully resolvable from the modern homogenised value of 0 ± 3 μ-units, even though it tends towards negative values (Fig. 1). We emphasise, however, that these metachert bands (like most BIF-hosted metacherts) also carry an Fe oxide component which, for example, even dominates the Ga-Al systematics of the metchert bands of the Temagami BIF (Ernst *et al.*, 2023). Hence, the $\mu^{142}Nd$ of -2.5 ± 3.8 for the metachert bands represents a mixture between (i) Nd provided by continental run-off derived from enriched crust and (ii) hydrothermal Nd input from vent fluids that had leached seafloor basalts (*i.e.* depleted mantle), resulting in a 'modern' ^{142}Nd signature.

A negative $\mu^{142}Nd$ value is expected for crust that differentiated from the mantle within the first 500 Myr of the Earth. The extent of this anomaly would depend on both the Sm/Nd ratio of the crust and the age of differentiation, both parameters not being accessible. In addition, erosion results in the mixing of different crustal sources of widely varying age and composition or it could represent the actual composition of the locally derived continental crust, which also contained Eoarchean rocks in the Superior craton (*e.g.*, Böhm *et al.*, 2003). Within seawater, a number of different factors are at play, such as continued input of chemically weathered crustal material mixing with a weakened, but still present, mantle component due to ongoing, but reduced, hydrothermal activity. Regardless, knowing the local mantle was characterised by a $\mu^{142}Nd$ value of +7, obtaining an Archean $\mu^{142}Nd$ value close to 0 requires that locally some crust with negative $\mu^{142}Nd$ was involved in the mixing, and as such was derived from sources that formed while ^{146}Sm was extant, that is, during the Hadean. Intriguingly, the ^{143}Nd systematics of the BIF measured in the present study clearly indicate a mixture between the DMM and an enriched end member (see Supplementary Information) that cannot be identified, while the ^{142}Nd systematics retains a larger spread, with the magnetite bands matching the composition of the DMM at 2.7 Ga. However, modelling of this mixing cannot be performed in absence of Nd concentrations of the respective end members, especially in seawater. Following the approach (Fig. 2) of O'Neil and Carlson (2017), and considering that ^{142}Nd can directly identify the enriched end member, its minimum differentiation age from a mafic precursor should be late (~4.1 Ga). This suggests a time span of at least 1.4 Ga for the longevity of the Hadean crust, implying a low recycling rate.

Implications of Archean mantle geodynamics

The Neoarchean is considered by some to be a transitional period from a stagnant lid to a plate tectonic-like global regime (Debaille *et al.*, 2013; Cawood *et al.*, 2018), with evidence of this seen in parts of the Superior Craton where there are cyclic subduction episodes and periods of stagnant lid quiescence (Wyman, 2018). It is also the time of amalgamation of the Superior Craton, which happened during the formation of the Temagami BIF (Wyman, 2018). Nevertheless, there has been much debate about how the Abitibi Greenstone Belt formed,

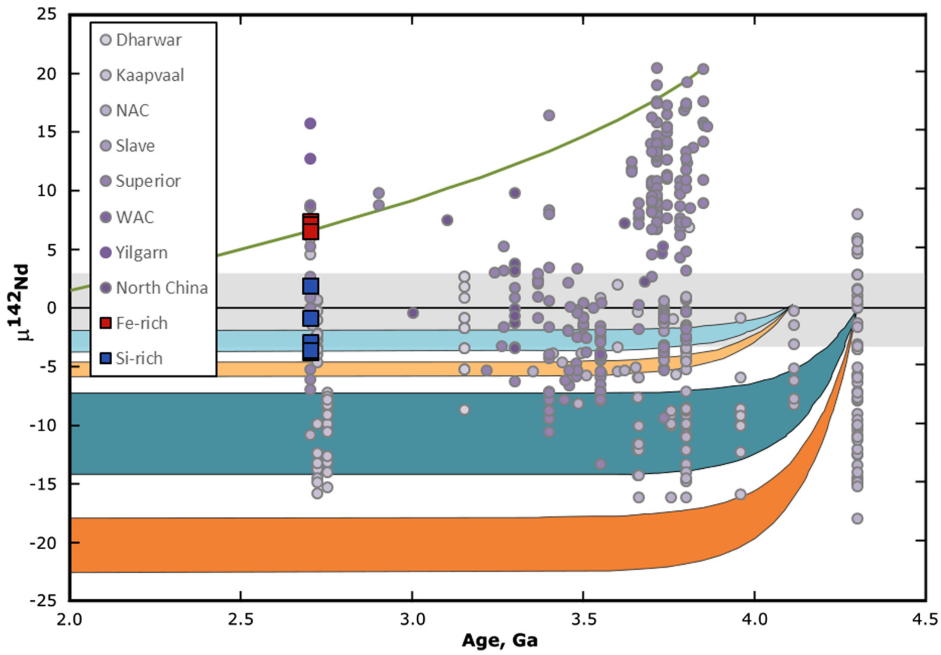

Figure 2 Model showing the evolution of $\mu^{142}Nd$ through time, based on extraction of a Tonalite-Trondhjemite-Granodiorite (TTG) from a mafic (blue) or felsic (orange shaded area) source at 4.3 and 4.1 Ga (from O'Neil and Carlson, 2017). Model was calculated using the approach of Morino *et al.* (2017), using a modern-like terrestrial ^{142}Nd composition as the bulk Earth, with a $\mu^{142}Nd$ of 0. Squares are data from this work, circles are the available ^{142}Nd literature data (Caro *et al.*, 2006, 2017, Bennett *et al.*, 2007; O'Neil *et al.*, 2008, 2012, 2016; Rizo *et al.*, 2012, 2013; Debaille *et al.*, 2013; Puchtel *et al.*, 2013, 2016; Roth *et al.*, 2013, 2014; Li *et al.*, 2017; Maya *et al.*, 2017; Morino *et al.*, 2017; O'Neil and Carlson, 2017; Schneider *et al.*, 2018; Wainwright *et al.*, 2019). The green line is the model from Debaille *et al.* (2013) showing trend of mixing in the mantle required to progress from the most positive values at 3.8 Ga to the +7 found in Abitibi at 2.7 Ga.

with two competing theories involving cyclic subduction or a mantle plume (van Hunen and Moyen, 2012; Wyman, 2018). While the data obtained in this study cannot exclude either of these hypotheses, it suggests that any subduction that could have occurred, should have only been short lived as it was unable to destroy all early crust (*e.g.*, by erosion of uplifted continental margins) and to homogenise the depleted mantle reservoir—at least until 2.7 Ga. As such, the preservation of a depleted mantle reservoir and an enriched continental crust at 2.7 Ga in the Abitibi is of great significance. It reveals that, in spite of intense mantle convection (Debaille *et al.*, 2013, and references therein) and magmatic activity, any global homogenisation process in the Archean was slow, and that BIF and potentially other chemical sediments that are derived from seawater are important archives able to trace early formed Hadean silicate reservoirs even during the Archean.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2421.

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