



The Hf-Nd isotope record of Archean seawater: potential and pitfalls

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Banded Iron Formations (BIFs) are Precambrian marine chemical sediments that may be used as archives of the trace element and isotope compositions of ancient seawater. Comparable to hydrogenetic FeMn crusts which are archives of modern seawater, a recent study [1] successfully used the Neoproterozoic Temagami BIF to study the (de)coupled Hf-Nd systematics of Late Archean seawater. Here, we evaluate the best approach to discriminate effects of syn- or postdepositional processes (e.g. detrital contamination, metamorphic or hydrothermal overprint) of the pristine seawater signature. To step further back in time we report Hf-Nd isotope and trace element data of pure Si- and Fe-rich layers from the Eoarchean ~ 3.75 Ga Isua BIF (Greenland) and the Mesoproterozoic ~ 3.25 Ga Fig Tree BIF (Barberton Greenstone Belt, South Africa) and compare them to data for the Neoproterozoic ~ 2.70 Ga Temagami BIF (Canada).

To evaluate the effect of syn- or postdepositional processes on the Nd isotopic budget, shale-normalised REY (rare earths and yttrium) patterns of each particular sample should be compared with those of modern seawater and other Archean marine precipitates. Positive La, Gd and Y anomalies (i.e. super-chondritic Y/Ho ratios) and enrichments of HREE over LREE indicate a pristine seawater-derived REY (including Sm and Nd) composition in a BIF sample.

Zr/Hf ratios serve as a perfect tool to distinguish seawater Hf from detrital Hf, because both particle-reactive, geochemical twins behave similarly during igneous processes, but show a strong decoupling in aqueous solutions, leading to non-chondritic Zr/Hf [2].

Information about open system behaviour of the Hf-Nd systems during metamorphic events can be evaluated by an isochron approach. In contrast to the lower greenschist facies Temagami BIF with its well-defined Nd and Hf isochrons yielding an accurate depositional age [1], errorochrons derived from the data from the Isua and Barberton BIFs, respectively, yield unrealistically young ages. This strongly suggests open system behaviour of both isotope systems during (amphibolite facies) metamorphic events. Strong post-depositional disturbance of Hf-Nd isotopic systems is also shown by initial isotope compositions: Isua BIFs yield $\epsilon_{\text{Nd}}(3.75\text{Ga})$ from -299.5 to $+39.7$ and $\epsilon_{\text{Hf}}(3.75\text{Ga})$ values from -1242.3 to $+1093.9$ and Fig Tree BIFs exhibit $\epsilon_{\text{Nd}}(3.25\text{Ga})$ from -6.7 to $+4.8$ and $\epsilon_{\text{Hf}}(3.25\text{Ga})$ from -313.0 to $+105.6$. Therefore, the Isua and Barberton BIFs studied and probably many other high grade metamorphic units are poor archives of the Hf-Nd isotopic composition of ambient seawater, despite their pristine trace element signatures. Only BIFs that show the combination of ultrapurity (i.e. absence of any aluminosilicate detritus), with seawater-like REY patterns, non-chondritic Zr/Hf ratios and accurate isochron ages, may provide reliable information about the Hf-Nd isotopic distribution in Archean seawater.

References:

- [1] Viehmann et al. (2014) *Geology*. doi: 10.1130/G35014.1
- [2] Bau (1996) *Contrib. Mineral. Petrol.* 123, pp. 323-333.