

## Iron isotope fractionation in stromatolitic oncolidal iron formation, Mesoarchean Witwatersrand-Mozaan Basin, South Africa

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Iron isotope fractionation in an Archean marine basin through biological and abiological processes is well illustrated in an iron rich unit in the Mesoarchean (2.96-2.92 Ga) Witwatersrand-Mozaan Succession [1] of South Africa and Swaziland. The unit comprises the oldest known shallow water oncolidal granular iron formation interbedded with magnetite- and stilpnomelane-rich mudstone and mixed mineralogical facies banded iron formation. The banded iron formation marks the most distal and the oncolidal iron formation the most proximal depositional settings. The oncolidal iron formation shows domal and columnar micro-stromatolite rims composed of magnetite around chert and calcite grains in a matrix of chert and minor iron-rich silicate. The more distal banded iron formations and iron-rich mudstones have  $\delta^{56}\text{Fe}$  values ranging from slightly positive to strongly negative depending on the dominant iron-rich phase. The stromatolitic oncolidal iron formation has  $\delta^{56}\text{Fe}$  values from zero to strongly positive. Moreover, the  $\delta^{13}\text{C}$  values of the calcite in the latter are strongly negative, suggesting the carbonates formed through the oxidation of organic carbon.

The geochemical evidence along with the depositional facies reconstruction show that the mode of iron deposition varied from the distal to proximal depositional settings, and is the most dominant control on iron isotope fractionation. The limited iron source that reached the proximal setting of the stromatolitic oncolidal iron formation had zero to positive  $\delta^{56}\text{Fe}$  values. Textural and geochemical evidence suggest that iron oxidizing microbes [2] living on the rims of reworked chert grains used the limited ferrous iron in the shallower part of the basin in their metabolism to precipitate ferrihydrite, which would concentrate heavy iron isotopes [3]. The ferrihydrite underwent a redox reaction with organic carbon during diagenesis to form magnetite that retains the heavy iron isotopic signature and isotopically light calcite. The lighter iron isotopes remaining in solution were incorporated into iron-rich silicates in the matrix.

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## The pyroxene sponge: amphibole signatures and controls on water in arc magmas

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Many arc magmas show evidence of amphibole fractionation, in the form of characteristic REE profiles and exhumed amphibole cumulates. However, amphibole is not always a major modal phase in the erupted suites: thus, fractionation is cryptic [1]. In water-rich (>4 wt% H<sub>2</sub>O) magmas where amphibole fractionation is most pronounced, high Sr/Y signatures develop [2]. Elevated Sr/Y magmas have an association with porphyry mineralisation (e.g. [3]) – most likely an indicator that water-rich, amphibole stable melts are fertile for porphyry formation [4].

Clinopyroxene is an early and abundant fractionating phase in most arc magmas, and unlike amphibole is common in the erupted rocks. New data from the Solomon Islands suggest that the early-formed clinopyroxene cumulates can react with evolving magmas, forming amphibole as a secondary metasomatic phase. The “cryptic” fractionation of amphibole may in fact be clinopyroxene cumulate–melt reactions, generating REE profiles characteristic of amphibole removal without it being a major modal phase in the crystallising magma.

Furthermore, the Solomon Islands data show that these metasomatic amphibole cumulates can be contrasted with true amphibole cumulates (i.e. directly crystallised and fractionated amphibole), with only the true amphiboles generating strong Y depletion (and by extension, high Sr/Y) in the daughter magmas.

The clinopyroxene cumulates are potentially acting as a sponge, modifying the daughter magma’s REE signature, and locking up water as they react to form amphibole. More hydrous magmas, able to directly crystallise amphibole and generate high Sr/Y, may only form where the sponge has been entirely metasomatised, and is no longer capable of locking up water. The clinopyroxene sponge possibly limits water content and magma fertility under normal arc-fractionation conditions. Fertile magmas are either more hydrous at source (able to directly crystallise amphibole), or only develop after repeated cycles of intrusion and cumulate–melt reaction.

### References

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