

## O, Si, Fe isotopes and Ge/Si constraints on the preservation of signatures inherited from the formation of Isua BIFs

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A 5.7 cm long sample, made of 9 alternating magnetite-rich and quartz-rich layers, of the oldest known example of archaean BIF (3.7-3.8 old Isua sample IF-G) was studied by ion microprobe for its O, Si and Fe isotopic compositions, and by laser ICP-MS for its trace element concentrations (Ge/Si ratios). Isotopic profiles across the layers were obtained with a resolution of 50-100 $\mu$ m (spot size 25 $\mu$ m) to look for systematic isotopic variations (total of 580  $\delta^{18}\text{O}$  data in quartz and magnetite, 441  $\delta^{30}\text{Si}$  in quartz and 641  $\delta^{56}\text{Fe}$  in magnetite). Ge contents in quartz were measured in parallel with a spot size of  $\sim$ 120 $\mu$ m.

$\delta^{56}\text{Fe}$  values range from -0.1 to +2.4‰ and are quite homogeneous ( $\pm$ 0.8‰,  $2\sigma$ ) within a given magnetite layer, with no significant differences between two successive layers, in agreement with previously published values [1, 2, 3]. Up to 3‰ variations in  $\delta^{18}\text{O}$  values are present in the magnetite and quartz layers (except one showing larger variations) with an average  $\sim$ 8‰ difference in  $\delta^{18}\text{O}$  between quartz (either in the quartz layers or in the magnetite layers) and magnetite, in agreement with isotopic equilibration under amphibolite facies metamorphism. In contrast to  $\delta^{18}\text{O}$  and  $\delta^{56}\text{Fe}$  values,  $\delta^{30}\text{Si}$  values show systematic "stratigraphic" isotopic variations (from -3.5 to 0‰) with significant differences between quartz in the quartz-rich and the magnetite-rich layers. Ge/Si ratios vary from 0.6 to  $1.2 \times 10^{-5}$  mole/mole (i.e., 7-14 ppm Ge). There are significantly lower than published data on bulk quartz layers from a Isua sample (Ge/Si  $> 2 \times 10^{-5}$  mole/mole [4]) due to the occurrence of Ge-rich amphiboles. Ge/Si variations seem to follow those of  $\delta^{30}\text{Si}$ . Because quartz is resistant to Si isotopic exchanges,  $\delta^{30}\text{Si}$  are likely to reflect variations in the conditions of formation and diagenesis of the Isua BIFs. Ge/Si ratios could trace temperature fluctuations and parent fluids of different origin.

[1] Dauphas, N. et al. (2007) *Geochim. et Cosmochim. Acta* **71**, 4745-4770. [2] Whitehouse M.J. and Fedo C.M. (2007) *Geology* **35**, 719-722. [3] Czaja, A.D. et al. (2013) *Earth Planet. Sci. Lett.* **363**, 192-203. [4] Frei R. & Polat A. (2007) *Earth Planet. Sci. Lett.* **253**, 266-281.

## How kimberlites form: Clues from olivine geochemistry

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The formation of olivine in kimberlites is not well understood. In most kimberlites, olivine occurs as large rounded single or polycrystalline nodules (1-10mm) and as small single crystals in the matrix. It is widely accepted that majority of them are xenocrysts produced by reaction and elimination of minerals from mantle peridotite either within kimberlite melts in transit toward the surface or within the mantle before. The compositions of the cores of olivines in polycrystalline nodules range widely, from about Fo92 to Fo83, whereas the rims have more restricted compositions, usually about Fo88.

In this study, we focus on very well preserved kimberlites from Kangamiut in Greenland. We conducted petrological studies and microprobe analyses along several profiles in one unusual polycrystalline nodule. This nodule is an assemblage of small closely packed fragments, most with the uniform composition Fo92, but some fragments have rims with lower Fo contents. Our results show that the fragment rims are complex and comprise an internal zone with variable forsterite contents (Fo88 to Fo92) but roughly constant minor element contents (e.g. 0.07 wt.% CaO and 0.35 wt.% NiO), and an external zone with near-constant Fo (Fo88) but variable minor element concentrations (0.09-0.41 wt.% CaO and 0.19-0.29% wt. NiO). This external zone is similar to the thin rim surrounding all the polycrystalline nodule. We attribute these compositions to two major processes. The first, which is responsible for the internal zone, occurred before the incorporation of the nodule in the kimberlitic magma and is related to "defertilisation" of peridotite in the lithosphere; i.e. reaction with CO<sub>2</sub>-rich fluids that removed pyroxene and garnet to produce a dunitic lithology. The second, which is responsible for the external zone, resulted from crystallization of olivine from the kimberlitic magma.