

## Garnet pyroxenite melting at the break-up of Gondwana (Karoo LIP) to present day (Bouvet TJ)

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Compositions of olivine phenocrysts in primitive magmas were inferred to support substantial contributions from a pyroxenitic mantle to oceanic and intracontinental basalts and picrites, the critical feature being a high-Ni/low-Mn signature [1]. Here we examine a picrite sample [2] from the Nuanetsi province (Karoo, S. Africa), for evidence of pyroxenite-sourced components. This large igneous province is related to the opening of the southern Atlantic Ocean. Primitive olivine phenocrysts (F<sub>0.84-9.1</sub>) have significantly higher NiO/MgO (0.008-0.012) and FeO/MnO (74-84) than in other continental flood basalts, suggesting up to 80% of the “pyroxenite” in the mantle source. Olivine-hosted melt inclusions confirm this signature for the primary (15 wt% MgO) melts: high-SiO<sub>2</sub> (52-54 wt%), high-Ni (~660 ppm), low-CaO (5-6 wt%), enrichment in K<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub> and incompatible trace elements (La/Sm ~5), and strong depletion in HREE (“garnet” signature; Gd/Yb ~ 6). Unusual source compositions are also reflected in initial Pb-Sr-Nd isotope ratios (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.262, <sup>87</sup>Sr/<sup>86</sup>Sr = 0.70588, εNd = -9, εHf = -10.0, at 190 Ma).

Very similar geochemical signature is found in a zero-age primitive (8.5 wt% MgO) SiO<sub>2</sub>- and Ni-rich glass [3] recovered from the MAR near the Bouvet Triple Junction. This glass (<sup>206</sup>Pb/<sup>204</sup>Pb = 17.188, <sup>87</sup>Sr/<sup>86</sup>Sr = 0.71209, εNd = -18) records melting of a pure garnet pyroxenite source [1] with an ancient lithospheric (lower crustal ?) LOMU isotopic flavor [3]. Based on tectonic reconstructions, the Karoo LIP and Bouvet TJ were closely spaced at the time of opening of the South Atlantic. We argue that pyroxenite-derived primitive melts were not only an important component during the initiation and development of LIP activity in the region, but continue to supply melts to the modern ridge system.

[1] Sobolev *et al.* (2007) *Science* **316**, 412-417. [2] Cox & Jamieson (1974) *J Petrology* **15**, 269-301. [3] Kamenetsky *et al.* (2001) *Geology* **29**, 243-246.

## Nano-scale phenomena in the interaction between apatite and aqueous Pb

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Apatite is an useful mineral for sequestering Pb in environments, and hydroxyapatite (Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH, HAP) is an important component of bone and teeth. In general, Pb immobilization by apatite is considered to take place by either cation exchange between Ca<sup>2+</sup> and aqueous Pb<sup>2+</sup> or precipitation of low solubility Pb phase following phosphate released due to apatite dissolution. In order to understand the nano-scale phenomena in the Pb immobilization process taking place at the interface, powder HAP (Synthetic, Wako Pure Chemical) and bulk single crystal of natural fluorapatite ((Ca<sub>4.915</sub>Na<sub>0.014</sub>)(P<sub>3.029</sub>Si<sub>0.010</sub>)O<sub>12</sub>(F<sub>0.930</sub>Cl<sub>0.098</sub>); FAP), which was mechanically polished normal to *c* axis, were reacted with Pb nitrate solution (2 mM) at pH of 5.0 at room temperature.

For the bulk FAP, cross sectional TEM reveals preferential leaching of Ca from the surface, while the secondary Pb-phosphate, chlorpyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>Cl; CPY), precipitates on the surface without epitaxial growth. Cation exchange mechanism does not operate in the present experimental condition.

In the experiment using powder HAP, the secondary Pb-phosphate, hydroxypyromorphite (Pb<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>OH; HPY), precipitates epitaxially parallel to *b* axis of HAP. Two types of mechanism are observed in the HPY formation; (i.) epitaxial growth of HPY needle on HAP only parallel to *b* direction from the solution supersaturated with respect to HPY; (ii.) direct replacement of HAP by HPY synchronizing the HAP dissolution.

The epitaxial growth was not observed in bulk FAP in contrast to the case in powder HAP, possibly because of the mechanically polished surface of bulk FAP, while the powder HAP has euhedral crystalline face. The results of the present study suggest that nano-scale process in Pb immobilization by apatite strongly depends on its crystallographic characteristics.