## Accessory Ba minerals as indicators of crystallization conditions in alkaline igneous rocks

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A number or rare Ba silicate and phosphate minerals occur as accessory minerals in peralkaline nephelinite at Nyiragongo, Democratic Republic of Congo, and in agpaitic nepheline syenite in the Pilanesberg Complex, South Africa. In both examples, the Baminerals formed as part of late magmatic to early post-magmatic / deuteric mineral assemblages. Although no thermodynamic data are available for these minerals, it is still possible to extract some indications about their relative stability in chemical potential space from chemographic analysis.

In the Nyiragongo nephelinite, andremeyerite (BaFe2<sup>2+</sup>Si<sub>2</sub>O<sub>7</sub>), fresnoite (Ba<sub>2</sub>TiOSi<sub>2</sub>O<sub>7</sub>) and "unknown" Na-Ba phosphate (Na<sub>0.7</sub>K<sub>0.3</sub>Ba<sub>0.7</sub>Sr<sub>0.2</sub>Ca<sub>0.1</sub>PO<sub>4</sub>), Na-Ti-Fe-Ba silicate [Na<sub>1.0</sub>K<sub>0.1</sub>Ca<sub>0.4</sub>Ba<sub>1.8</sub>Sr<sub>0.2</sub>(Fe,Mg,Mn)<sub>3.3</sub>(Ti,Nb)<sub>1.4</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>2</sub>(F<sub>1.6</sub>(O,OH)<sub>2.4</sub>] and Ba-Fe silicate (Ba<sub>2</sub>FeSi<sub>2</sub>O<sub>7</sub>) minerals occur in different late magmatic to postmagmatic / deuteric mineral assemblages together with combeite, kirschteinite, götzenite, cuspidine, delhayelite and umbrianite (Andersen et al. 2012; 2014). Andremeyerite is associated with extremely peralkaline silicate glass, and is undoubtedly of magmatic origin (Fig. 1). Some of the other minerals (in particular the phosphate and Na-Ba-Ti silicate mineral) may be late magmatic, or have formed by autometasomatic processes induced by degassing magma. Andremeyerite, Na-Ba-Ti silicate and Na-Ba phosphate minerals reflect increasing levels of peralkalinity, and a transition from andremeyerite through the Ba<sub>2</sub>FeSi<sub>2</sub>O<sub>7</sub> mineral and fresnoite to baryte a trend of increasing oxygen fugacity (Fig. 2a).



*Fig. 1.* Andremeyerite (bright green) with acicuar crystals of götzenite and silicate glass in nephelinite from Nyiragongo, DRC (Andersen et al. 2014). Width of frame: ca. 1mm

In the Pilanesberg complex, bafertisite  $[Ba_2Fe_4^{2+}Ti_2(Si_2O_7)_2O_2(OH)_2F_2]$  and jinshajiangite  $[BaNaFe_4^{2+}Ti_2(Si_2O_7)_2O_2(OH)_2F]$ , the latter forming epitaxial overgrowths on the former, occur as part of highly agpaitic interstitial mineral assemblages in white foyaite, together with astrophyllite, aenigmatite, lorenzenite and hilairite(Andersen et al. 2016).



**Fig. 2.** Stability relationships in log  $a_{Nds}$  – log  $a_{H20}$  –log  $f_{02}$  space (Nds: N $a_2Si_2O_5$  component) for accessory Ba minerals in a: Peralkaline nephelinite at Nyiragongo (Andersen et al. 2014) and b: Agpaitic nepheline syenite (white foyaite) in Pilanesberg (Andersen et al. 2016). Abbreviations: Ne: Nepheline, Ksl: Kalsilite, Leu: Leucite, Ap: Apatite, Gtz: Götzenite, Mag-Usp<sub>SS</sub>. Magnetite-ulvöspinel solid solution, Aen: Aenigmatite, Ast: Astrophyllite, Lor: Lorenzenite, Amph: Amphibole (arfvedsonite-magnesium arfvedsonite), Aeg: Aegirine, Bio: Biotite, Hil: Hilairite, Bft: Bafertisite, Jin: Jinshajiangite

Surkhobite [KBa<sub>3</sub>Ca<sub>2</sub>Na<sub>2</sub>Mn<sub>16</sub>Ti<sub>8</sub>(Si<sub>2</sub>O<sub>7</sub>)<sub>8</sub>O<sub>8</sub>(OH)<sub>4</sub>(F,O,OH)<sub>8</sub>] has formed as a late member of eudialyte-bearing magmatic mineral assemblages in green foyaite. These minerals reflect highly alkaline conditions during latest magmatic to early deuteric stages of the crystallization history, and in the case of the bafertisite-jinshajiangite transition, possibly a trend approaching a hyperagpaitic fluid regime in the intrusion (Fig. 2b).

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