

## Reversal of Sillimanite-Corundum-Quartz: Competition Between Stable and Metastable Reactions

<sup>1</sup>DANIEL HARLOV AND <sup>2</sup>RALF MILKE

<sup>1</sup>GeoForschungsZentrum Potsdam, Telegrafenberg, D-14473 Potsdam, F.R. Germany dharlov@gfz-potsdam.de

<sup>2</sup>Mineralogisch-Petrographisches Institut Universität Basel, Bernoullistr. 30 CH-4056 Basel, Schweiz

The equilibrium  $\text{Sil} \leftrightarrow \text{Crn} + \text{Qtz}$  (1) has been metastably reversed, approximately 700 - 800 MPa inside the Ky stability field, at 600 °C-1575 MPa; 700 °C-1725 MPa; 800 °C-1825 MPa; and 900 °C-1925 MPa using NaCl furnace assemblies in the non-endload piston cylinder press. Charges consisted of gem quality, inclusion-free Sil, synthetic  $\alpha$ -Crn, and synthetic dry Qtz ground together in molar amounts. The well mixed charge (10 - 15 mg) + H<sub>2</sub>O (2 - 3 mg) was placed in a 3 mm/1.3 cm Pt capsule which was welded shut, folded and placed such that the Ni-Cr thermocouple tip touched the capsule thereby minimizing thermal gradients [1]. The slope of the Sil-Crn-Qtz equilibrium is found to approximately parallel both that of Ky-Crn-Qtz and Ky-Sil [1].

The metastability of the assemblage  $\text{Sil} + \text{Crn} + \text{Qtz}$  implies that Reaction (1) is always in competition with  $\text{Crn} + \text{Qtz} \rightarrow \text{Ky}$  (2) and  $\text{Sil} \rightarrow \text{Ky}$  (3). Early on it may be assumed that a steady state between dissolution and growth rates is established. However, due to sluggish nucleation of Ky there is an induction period which is P-T dependent. Once Ky does appear, the reaction proceeds very fast to Ky via reactions (2) and (3). This supports the conclusions of [2] that reactions (2) and (3) are controlled by Ky surface reactions and thus dependent on the Ky surface area. However the overall reaction rate is also influenced by the dissolution rate of Crn and the transport of Al-species in the fluid. If Sil is metastable with respect to Crn + Qtz, Reaction (1) is faster than both (2) and (3) as long as the Ky surface area is small. When the Ky surface area increases beyond a certain critical point, reactions (2) and (3) outrun (1). Under constant P and T, the system evolves from metastable Sil formation to Sil consumption, only dependent on the Ky surface area. Similar competition between stable and metastable reactions could occur during contact metamorphism where metastable mineral growth is observed. It could also help explain metastable Crn+Qtz +/- Al<sub>2</sub>SiO<sub>5</sub> assemblages or 2-3 co-existing Al<sub>2</sub>SiO<sub>5</sub> phases in high-grade aluminous metamorphic rocks.

[1] D. Harlov, R. Milke, *Am Mineral*, 2002, 87, 424.

[2] G. Ostapenko et al., *Geochim Int*, 1991, 7, 936.

## Crystal Chemistry of the Na<sub>2</sub>(Mn<sub>1-x</sub>Fe<sup>2+</sup><sub>x</sub>)<sub>2</sub>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub> alluaudite-type solid solution

F. HATERT AND A.-M. FRANSOLET

University of Liège, Laboratory of Mineralogy B.18, B.4000 Liège, Belgium. fhatert@ulg.ac.be

Alluaudite, a Na-Mn-Fe-bearing phosphate mineral, is known to occur in Li-rich granitic pegmatites. Moore [1] determined the crystal structure of alluaudite in the C2/c space group and derived the general structural formula, recently modified by Hatert *et al.* [2]:  $[\text{A}(2)\text{A}(2)'][\text{A}(1)\text{A}(1)'\text{A}(1)'']_2[\text{M}(1)\text{M}(2)]_2(\text{PO}_4)_3$ .

During the past decade, several alluaudite-type compounds containing In, Cr, Ga or Cd were synthesized, in order to better understand the crystal chemistry of these phosphates [3]. However, the crystal chemistry of alluaudites with natural compositions was never investigated to date.

Compounds of the Na<sub>2</sub>(Mn<sub>1-x</sub>Fe<sup>2+</sup><sub>x</sub>)<sub>2</sub>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub> series (x = 0.00 to 1.00) were synthesized between 400 and 800°C at 1 kbar, using horizontally arranged Tuttle-type cold-seal bombs. Pure alluaudite-type compounds are obtained at 400°C.

The X-ray Rietveld refinements indicate

the presence of Na on the A(1) and A(2)' sites, Mn and Fe<sup>2+</sup> on the M(1) site, and Mn, Fe<sup>2+</sup> and Fe<sup>3+</sup> on the M(2) site. The presence of small amounts of Na on the M(1) site, and of Mn on the A(1) site, indicates a partially disordered distribution of these cations. An excellent linear correlation has been established between the M(1)-M(2) distance and the energy of the infrared band attributed to M<sup>2+</sup>-O vibrations.

Mössbauer spectra, measured between 85 and 295 K, were analyzed in terms of a model which includes the next-nearest neighbor interactions at the M(1) and M(2) crystallographic sites. The isomer shifts and quadrupole splittings of Fe<sup>2+</sup> on the M(1) site are larger than those of Fe<sup>2+</sup> on M(2), indicating that the M(1) site is both larger and more distorted than the M(2) site.

[1] P.B. Moore, *Am. Min.*, 1971, 56, 1955-1975.

[2] F. Hatert, P. Keller, F. Lisner, D. Antenucci, A.-M. Fransolet, *Eur. J. Mineral.*, 2000, 12, 847-857.

[3] D. Antenucci, 1992. Ph. D. Thesis, University of Liège.