

Fe³⁺. Rietveld refinements of selected samples, Na₂Mn₂Fe³⁺(PO₄)₃, Na_{1.5}Mn_{1.5}Fe³⁺_{1.5}(PO₄)₃, and Mn_{2.25}Fe³⁺_{1.5}(PO₄)₃, have been performed in order to tackle the cation distribution between the A(2)', A(1), M(1) and M(2) crystallographic sites. The ⁵⁷Fe-Mössbauer spectra indicate the presence of small amounts of Fe²⁺ in the Fe-rich alluaudites-like compounds, confirming the wet chemical analyses realised by Hatert *et al.* (in press). This method also sheds some light on the distribution of Fe atoms between the M(1) and M(2) sites.

Fransolet AM, Antenucci D, Fontan F & Keller P, *I.M.A. 16th General Meeting, Abstract volume*, 125-126, (1994).

Hatert F, Keller P, Lissner F, Antenucci D & Fransolet AM, *Eur. J. Mineral., in press*

CRYSTAL CHEMISTRY OF THE TRIVALENT CATION IN THE ALLUAUDITE STRUCTURE: THE NaMnM³⁺(PO₄)₃ (M³⁺ = Al, Cr, Ga, Fe³⁺, Sc, In, La) SOLID SOLUTIONS

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Alluaudite, a phosphate mineral occurring in granitic pegmatites, has been subject to numerous experimental studies during the past decade. In order to tackle the behaviour of the trivalent cation in this structure, we investigate the NaMnM³⁺(PO₄)₃ solid solutions, starting from the synthetic compound NaMnFe³⁺(PO₄)₃ which has a chemical composition close to that of the alluaudite from Buranga, Rwanda. The phosphates have been synthesized by solid state reaction in air, between 900 and 950°C. The powder diffraction patterns show the presence of M³⁺PO₄, as impurity with a berlinite structure, when Fe³⁺ is progressively replaced by Al, Cr, Ga and La. Whereas NaMnSc₂(PO₄)₃ exhibits the fillowite structure, the NaMn(Fe³⁺_{1-x}In_x)₂(PO₄)₃ solid solution terms are pure and crystallize with the alluaudite structure. The unit-cell parameters of the NaMn(Fe³⁺_{1-x}In_x)₂(PO₄)₃ alluaudite-like compounds regularly increase with x. The Rietveld refinement of the NaMnIn₂(PO₄)₃ endmember confirms the following cationic distribution: A(2)' is empty, A(1) is occupied by Na, M(1) by Mn, and M(2) by In. This ordered distribution, with Na confined on A(1), is similar to the distribution observed by Antenucci *et al.* (1993) for the alluaudite-like compound NaCdIn₂(PO₄)₃. However, this situation is very different for the compound NaMnFe³⁺(PO₄)₃, with Na localized on both the A(2)' and A(1) crystallographic sites (Hatert *et al.*, in press). The infrared spectra of the NaMn(Fe³⁺_{1-x}In_x)₂(PO₄)₃ solid solution terms show very sharp bands for the In-rich samples, which confirm the ordered distribution of Na on the A-sites. The ⁵⁷Fe-Mössbauer spectra elucidate the replacement mechanisms of Fe³⁺ by In on the M(2) site.

Antenucci D, Mieke G, Tarte P, Schmahl W & Fransolet AM, *Eur. J. Mineral.*, **5**, 207-213, (1993).

Hatert F, Keller P, Lissner F, Antenucci D & Fransolet AM, *Eur. J. Mineral., in press*

AN *IN SITU*, SYNCHROTRON RADIATION STUDY OF THE HYDROTHERMAL CRYSTALLIZATION OF GYROLITE

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Disordered calcium silicate hydrate (C-S-H) gel phases of similar compositions to gyrolite (Ca₁₆Si₂₄O₆₀(OH)₈·(14+xH₂O)) are primary constituents of hydrated Portland cement and play an import role in the cement setting process. Environmental scientists have recently been researching the formation of C-S-H phases as they are thought to form around cementitious nuclear waste sites. This study reports *in situ* studies of the hydrothermal formation and dehydration of gyrolite using energy dispersive powder diffraction (EDPD) methods at the Daresbury Synchrotron Radiation Source, UK. Starting materials for hydrothermal synthesis reactions consisted of alk-oxide gels with the stoichiometric composition of gyrolite (Ca/Si=0.66). Concentrated calcium hydroxide solution (pH=13) is added to this gel to give a solution to solid ratio of 5. Experiments were performed from 190°C to 250°C, with a diffraction pattern taken every 1-2 minutes. All the reactions were completed within 2 hours and all produced gyrolite as their final reaction product. The first diffraction peaks to form are a broad peak at approximately 3.1 Å and a sharper peak at 1.8Å; these peaks are associated with the presence of poorly ordered C-S-H gel. The second stage in the crystallization process involves the formation of a broad Bragg peak at 15Å and a sharp peak at 4.2 Å indicating the presence of the synthetic Z-phase (Ca₉Si₁₆O₄₀(OH)₂·(14+xH₂O)). After about 10 minutes, the intensity of the 15 Å peak begins to decrease with the formation of peaks at 22 and 11Å. This stage of the reaction involves breakdown of Z-phase and crystallization of gyrolite. Kinetic and reaction mechanism data were obtained by fitting the time-resolved data with an Avrami type kinetic model, and Arrhenius plots were used to calculate activation energies. The gyrolite formation mechanism is believed to be a 2-dimensional, diffusion-controlled growth mechanism with an activation energy of between 76 and 91 kJ/mol.