



New insights into the structure and crystal-chemistry of arrojadite-group minerals

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The crystal-chemistry of arrojadite-group minerals had not been satisfactorily defined yet. The available works deal with the ideal compositions $\text{KNa}_4\text{Ca}(\text{Fe,Mn,Mg})_{14}\text{Al}(\text{PO}_4)_{12}(\text{OH,F})_2$ [1,2,3] and $\text{BaNa}_3[\text{Ca}(\text{Fe,Mn,Mg})_{14}\text{Al}(\text{PO}_4)_{12}(\text{OH,F})_2]$ [sigismundite, 4], which are related by a coupled heterovalent exchange at the large X sites hosting alkaline elements. Although all the cited works report detailed single-crystal refinements, there are some oddities in the structure and some inconsistencies in the chemical characterisation. In particular, refinements in the monoclinic $C2/c$ space group imply the presence of disordered PO_4 groups (with vertices alternately pointing to opposite directions when seen along b), and of partial occupancy at 10 out of the 49 sites in the asymmetric unit.

Arrojadites are the most chemically complex of primary pegmatite phosphates, and the coexistence of P, Fe and F strongly hinders accurate EMP analyses. In addition, some previous analyses suggest the presence of significant Li contents, which may also explain the reported cation vacancies.

Recent developments in microanalytical techniques and in the efficiency of the area detectors may allow clarification of all these issues. New EMP analyses were done based on a careful choice of the standards, and generally yielded a homogeneous stoichiometry of $\text{P} = 12$ apfu and $(\text{Mg,Mn,Fe}) = 13\text{-}14$ apfu. Accurate data collections on a number of arrojadite compositions ($R_{\text{sym}} = 2\text{-}3\%$) followed by full-matrix least squares structure refinements ($R_{\text{all}} = 2.8\text{-}3.8\%$) showed that the space-group symmetry should be lowered to Cc . In this model, all the P sites

are fully occupied and ordered, and all the X sites are fully occupied in arrojadite s.s. samples. A crystal of the newly found Sr-dominant variety shows a clear $X^5K_{-1} X^4Na_{-1} X^5Sr_1 X^4[]_1$ coupled heterovalent substitution. In addition, the coupled exchange $X^{2a}Na_{-1} X^6Na_{-1} X^{2a}[]_1 X^6Fe_1$ explains the presence of (Mg,Mn,Fe) in excess of the 13 M sites pfu. Moreover, there is a clear indication for the presence of 3 OH groups pfu, one of which is at the apex of the [P1bO₄] tetrahedron. The lowering in the space-group symmetry may be related to cation (Mg,Mn,Fe) and anion (F) ordering between formerly equivalent sites.

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