A Revision of the Structure and Crystal-Chemistry of the Arrojadite-Group

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Arrojadite, dickinsonite and sigismundite define a group of phosphates with a very complex structure and crystal-chemistry, which has not been satisfactorily characterized so far. Previous works described the structure in the $C2/c$ space group which implies the presence of half-occupied P1 phosphate groups sharing basal faces and with the apical oxygen atoms pointing in opposite directions, and of partial occupancy at 10 out of the 49 sites in the asymmetric unit. Electron microprobe analyses suffer from severe interference problems due to the coexistence of P, Fe and F.

Single-crystal refinement, Raman spectroscopy and well-controlled *in situ* microchemical analysis of selected samples allowed a better interpretation of the structure and crystal-chemistry of the arrojadite group. The correct space group is Cc, and the lowering in symmetry implies recognition of strong cation ordering among the 21 cationic sites besides the 12 PO_4 groups. The correct number of OH groups *pfu* is 3 and not 2 (2 OH are bonded to octahedral sites and 1 to a PO_4 group), and a selectivity is shown for F incorporation at one of these sites. The active exchange vectors were identified, and a new nomenclature has been proposed on crystal-chemical basis.

The $C2/c$ derives from the presence in some samples of Cc domains related by a diad along *b* plus a ½ shift along *c*. This feature cannot be treated by X-ray structure refinement, and may be related to growth defects occurring during high-*T* crystallisation (in pegmatites).

Keywords: phosphate crystal-chemistry, mineralogy, crystal-structure