The arrojadite enigma: I. A new formula and a new model for the arrojadite structure

FERNANDO CÁMARA,1 ROBERTA OBERTI,1,8 CHRISTIAN CHOPIN,2 AND OLAF MEDENBACH3

1CNR Istituto di Geoscienze e Georisorse (IGG), unità di Pavia, via Ferrata 1, I-27100 Pavia, Italy
2Laboratoire de Géologie, UMR 8538 du CNRS, Ecole normale supérieure, 24 rue Lhomond, F-75005 Paris, France
3Institut für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, 44780 Bochum, Germany

ABSTRACT

A re-examination of the chemistry and structure of nearly all the known occurrences of arrojadite and related minerals ( dickinsonite and sigismundite) allowed understanding of the main substitution vectors and cation ordering schemes ruling the crystal-chemistry of these very complex phosphates. Electron microprobe analyses were done with a careful choice of the standards and of experimental conditions, and were coupled with LA-ICP-MS in situ analysis for Li, Be, and B. Structure refinement was done in a space group (Cc) with a lower symmetry than those used in previous studies (C2/c and its equivalents), which allowed a better understanding of the structure details and of cation ordering. The combined approach yielded a new formula for the arrojadite group, namely A2B2Ca1Na2+xM4(PO4)11(PO3OH) W(OH,F)2, where A are either large divalent cations (Ba, Sr, Pb) plus vacancy, or monovalent (K, Na) cations; and B are either small divalent cations (Fe, Mn, Mg) plus vacancy, or monovalent (Na) cations. The number of hydroxyl groups in the arrojadite formula is generally 3 apfu, and can be lowered to 2 apfu in particular when the sum of non-(P,Al) cations is higher than 20 apfu.

We present in this paper the complete characterization of three samples (two of which are new members) that are crucial to fix the cornerstones of arrojadite crystal-chemistry. The sample from Rapid Creek (Yukon Territory) is the holotype for arrojadite-(KNa), and has unit formula K0.83Na5.01(Ca0.91Sr0.01)Mn4(PO4)8[PO3(O,F,H)]4(OH)2 (Z = 4). The sample from Horrsjöberg (Värmland, Sweden) is the holotype material for arrojadite-(SrFe), and has unit formula K0.50Na5.78(Ca0.51Sr0.05Ba0.01Pb0.01)Mn4(PO4)11P1x(PO3OH) W(OH,F)2 (Z = 4). The sample from Branchville (Connecticut) is the holotype material for arrojadite-(SrFe), and has unit formula Sr1.03Na2.24Ca0.03Ba0.01K0.03Fe2+xMg5.16Mn2xZn0.55Li0.33(Al0.03Fe0.03)2.51(Fe1.03SO3)1.51F0.02O32.05P1x(PO3OH) W(OH,F)2 (Z = 4). 

Keywords: Crystal structure, arrojadite, analysis (chemical), new minerals, arrojadite-(KNa), arrojadite-(SrFe), dickinsonite-(K MnNa), optical properties, Raman spectroscopy, XRD data

INTRODUCTION

“Arrojadites are infernally complex structures, with several partly occupied cations sites, and the complete details of their structures exceed our spatial parameters.” This quotation is taken from Huminicki and Hawthorne (2002), page 186, in their review of known phosphate structures. In this pair of papers, we present the results of a general reconsideration of the known occurrences of arrojadite-group minerals (namely arrojadite, dickinsonite, and sigismundite), which is based on complete chemical analyses done with electron microprobe (EMP) and laser ablation-ICP-mass spectrometry (LA-ICP-MS), on single-crystal X-ray structure refinement (SREF), and on Raman spectroscopy.

This first paper focuses on a new model for the crystal structure of arrojadite, and on the crystallographic details that allowed us to fix the cornerstones of arrojadite crystal chemistry and thus, the basis for a new nomenclature scheme to be dealt with in Part II (Chopin et al. 2006, this volume).

The crystal structure of arrojadite was first determined in the B2/b space group on a sample from the Nickel Plate mine (Keystone, South Dakota) by Krutik et al. (1979), who did an isotropic refinement to R = 14% and proposed the formula Na3(Na, K, Ba, Sr)(Na, Ca)(Fe, Mn)4Al[Li, Mg, Ca, Al, Fe, Mn]4[PO4]6[PO4](O, F, OH)6(OH), Z = 4. The refined model has three independent sevenfold- to eightfold-coordinated sites occupied by large alkaline cations, one smaller octahedral site occupied by Al, seven independent fourfold- to sixfold-coordinated sites mainly occupied by Fe and Mn, six fourfold-coordinated sites occupied by P, and six OH groups per formula unit.

Merlino et al. (1981) did the anisotropic refinement (R = 8%)