American Mineralogist, Volume 108, pages 584–594, 2023

The occurrence of monoclinic jarosite in natural environments

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Abstract

Jarosite and related subgroup minerals are of high importance in mineral processing, as sources and sinks for metals and acidity in the environment, and they have the potential to preserve elemental and isotopic biomarkers relevant to the search for life in the solar system. The crystal structures and chemistry of jarosite minerals affect their stability and reactivity and thus the roles they play in natural and engineered systems. Rhombohedral symmetry has been documented in natural and synthetic jarosites, whereas monoclinic symmetry has only been documented in synthetic jarosites. This research reports the occurrence of monoclinic symmetry in a natural natrojarosite sample investigated using synchrotron powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and electron backscatter diffraction (EBSD). Splitting of several rhombohedral PXRD peaks (e.g., 012, 027, and 033) into pairs of peaks was observed, with the magnitude of the splitting and the relative intensities of the pairs of peaks being almost identical to those reported for synthetic monoclinic jarosite. Rietveld refinement with room-temperature PXRD data shows an ordering of iron-site vacancies on the Fe1 site consistent with monoclinic symmetry, space group C2/*m*. Conversion of monoclinic unit-cell parameters into pseudo-hexagonal unit-cell parameters, specifically β′, also supports the use of a monoclinic model to describe the natrojarosite structure. Structural analysis with increasing temperature is supportive of the thermal evolution previously described for synthetic monoclinic jarosite samples, with some indications of subtle differences between synthetic and natural materials including slower rates of thermal expansion and absence of $FeOHSO_4$ peaks for natural monoclinic jarosite. EBSD provides insight into the spatial–structural variation within the hand specimen from which the natrojarosite was sampled, demonstrating that there are areas of unambiguous monoclinic symmetry, but others where both monoclinic and rhombohedral natrojarosite coexist. The results of this study suggest that monoclinic symmetry in natural jarosites may be more prevalent than previous studies suggest. Monoclinic symmetry in jarosites is identifiable by an ordering of iron-site vacancies on the Fe1 site, splitting of specific rhombohedral XRD peaks into pairs of peaks, and an increase in jarosite symmetry (i.e., from monoclinic to rhombohedral) during heating. The splitting of peaks in monoclinic jarosites can be subtle so it is recommended that high-resolution XRD data are collected when studying the crystal structure of jarosites.

Keywords: Jarosite, natrojarosite, monoclinic symmetry, synchrotron powder X-ray diffraction, Rietveld refinement, electron backscatter diffraction