

Refinement of the Jarosite-Alunite Cell Parameters as a Function of Compositional Variance

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Introduction: The jarosite-alunite mineral group consists of (among others) four common rock-forming minerals:

alunite	$\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$
natroalunite	$\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$
jarosite	$\text{KFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$
natrojarosite	$\text{NaFe}^{3+}_3(\text{SO}_4)_2(\text{OH})_6$

These sulfate minerals are commonly found on Earth and jarosite has been identified on Mars using the Mössbauer spectrometer aboard the Opportunity rover. On Earth, jarosite has specific conditions of formation, and is only found in certain environments, specifically those which contain low pH waters. The chemical formula for jarosite is commonly written as $\text{AB}_3(\text{SO}_4)_2(\text{OH})_6$ because of the high amount of isomorphic substitution that occurs in the A and B sites. Site A can be occupied by either Na or K, and site B can be occupied by either Fe or Al.

The main goal of this project is to determine whether the cell parameters in the alunite mineral group vary systematically as a function of composition. We will attempt to determine whether that variation is conclusive enough to use as a method for precise mineral identification, so that compositions might be deduced on the basis of remote measurements such as those from ChemMin on Mars Science Laboratory.

Samples: The samples were prepared at SUNY Stony Brook by Podratz, et al. [1]. They were synthesized by heating a supersaturated solution rich in sulfate and the desired cations in Teflon jars at 90°C with constant stirring for 5-48 hrs. The samples were allowed to rest for one hour to cool and precipitate. The remaining solution was decanted using a centrifuge. All samples were filtered/washed with deionized water and dried overnight at 110°C.

The mineral precipitates were analyzed with x-ray diffraction and scanning electron microscopy to ensure that only the single, desired phase was present. The synthetic set of minerals varies both parameters of the solid solution systematically. Solid solutions among these four minerals represent possible combinations of the cations Al and Fe^{3+} in the 6-coordinated site of the structure, and K and Na in the 12-coordinated site

Scanning electron microscopy showed that there was a visible variation in crystal habit as the composition of the mineral changed. Figure 1 shows photomicrographs of two samples.

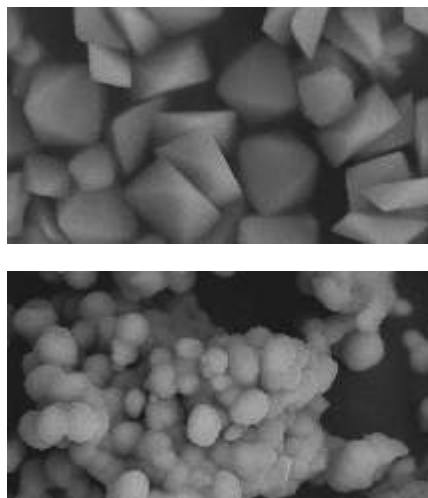


Figure 1: SEM photomicrograph of synthetic jarosite (top) and alunite (bottom) crystals, showing their variable morphology.

Results: Detailed XRD patterns are being collected using the Siemens D5000 X-Ray Diffractometer at the University of Idaho. Cell parameters and d -spacings are being calculated using Siroquant Version 3, a Rietveld Refinement program. The c and a axes in the jarosite structure vary as the average radius of the included cation changes.

So far, we have analyzed the four end members, and the results show a systematic trend:

Mineral Name	c axis (Å)	a axis (Å)
Jarosite	17.045	7.305
Natrojarosite	16.496	7.321
Alunite	17.032	6.999
Narroalunite	16.592	6.980

The above data show that the substitution of K for Na in site A (12-fold coordination), increases the c axis by about 0.495 Å. The substitutions of Fe for Al in site B (octahedral site) causes the a axis to increase by approximately 0.324 Å. These data are consistent with the model presented by Papike, et al. [2]. We will

continue to analyze the remaining samples, and see if the model holds for the intermediate compositions of the solid solutions.

Figure 2 shows why the c and a axes are affected by this substitution. Increasing the size of the cation represented by the purple sphere (site A) will increase the c axis, and increasing the size of the brown octahedron (site B) will increase the a axis.

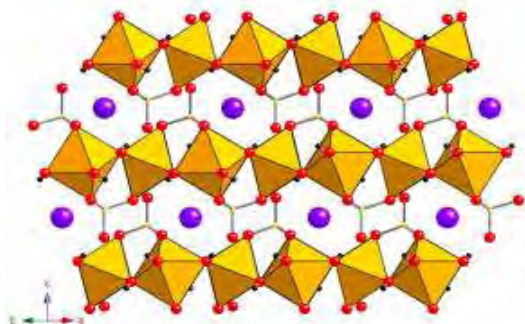


Figure 2: Schematic diagram showing the relative placement of the atoms and tetrahedra that comprise the alunite crystal structure. Na or K shown as purple sphere, Fe or Al shown as brown octahedron, O shown as red sphere, S shown as yellow sphere, H shown as black sphere.

Implications for Mars: NASA is planning the Mars Science Laboratory for 2009, which is expected to include an X-Ray Diffractometer among its analytical instruments. Knowing the precise placement of the minerals in this solid solution set on a ternary diagram should prove valuable in understanding how jarosite precipitates and/or crystallizes on the Martian surface, leading to a better understanding of the surface processes on Mars.

References:

- [1] L. A. Podratz, et al. "Synthesis and Stability of the Alunite-Jarosite Series" *NASA Idaho Space Grant Consortium Research Symposium*. 2006.
- [2] J. J. Papike, et al. "Jarosite-Alunite Crystal Chemistry". *Martian Sulfates as Recorders of Atmospheric-Fluid-Rock Interactions*. 2006. Abstract # 7003

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