

**IMPLICATIONS OF MARTIAN AND TERRESTRIAL JAROSITE. A CRYSTAL CHEMICAL PERSPECTIVE.** J.J. Papike ([jpapike@unm.edu](mailto:jpapike@unm.edu)), J.M. Karner, and C.K. Shearer, Institute of Meteoritics, University of New Mexico, Albuquerque, New Mexico 87131-1126.

**INTRODUCTION.** The importance of the discovery of jarosite at the Meridiani Planum region of Mars [1] is discussed. Terrestrial studies demonstrate that jarosite requires a unique environment for its formation. Jarosite crystallizes from highly acidic ( $\text{pH} < 4$ ) aqueous solutions under highly oxidizing conditions from S-rich brines. A likely scenario for jarosite formation on Mars is that degassing of shallow magmas likely released  $\text{SO}_2$  that reacted with aqueous solutions in shallow aquifers or on the martian surface. This interaction forms both  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{S}$ . A martian oxidant must be identified to both oxidize  $\text{H}_2\text{S}$  to produce the required acidity of the fluid and  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ . We suggest that reactions involving both sulfur and  $\text{CO}_2$  reduction to CO may provide part of the answer. The jarosite crystal structure is truly remarkable in terms of its tolerance for the substitution of a large number of different cations with different ionic radii and charges. The structure accommodates hydrogen, oxygen, and sulfur whose stable isotope systematics are strong recorders of low-temperature fluid-rock-atmosphere interactions. Jarosite has been proven to be a robust chronometer for Ar-Ar and K-Ar dating techniques. There is every reason to believe that for older jarosite from Mars the U-Pb, Rb-Sr, and Nd-Sm techniques will also be robust. Although the discovery of jarosite on Mars alone, with no other analytical measurements on the phase, have given us insights to martian surficial processes, the true power of jarosite can not be exploited until jarosite is sampled and returned from Mars. Mars sample return is a long way off but, until then, we should be vigilant about examining martian meteorites for martian alteration assemblages that contain jarosite. A suite of jarosite samples representing a significant time span on Mars may hold the key to reading the record of atmospheric evolution.

**CRYSTAL CHEMISTRY.** Although there are more than 40 mineral species with basically the alunite crystal structure [2], we emphasize alunite,  $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ , natroalunite,  $\text{NaAl}_3(\text{SO}_4)_2(\text{OH})_6$ , jarosite,  $\text{KFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$ , and natrojarosite,  $\text{NaFe}_3^{3+}(\text{SO}_4)_2(\text{OH})_6$ . We use the general formula  $\text{AB}_3(\text{XO}_4)_2(\text{OH})_6$  [3] where A is a 12-fold coordinated site that can contain

monovalent cations K, Na, Rb etc., divalent cations Ca, Pb, Ba, Sr, etc., and trivalent cations, REE, etc. The B position represents an octahedral site that usually contains trivalent Fe and Al but can include  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$  etc.

Our discussion of the crystal structure is derived from the discussions of Menchetti and Sabelli (1976) [4]. The structure drawings (Figure 1 projected down c, and 2 projected down a) were kindly provided by Dr. Eric Dowty. The alunite-jarosite crystal structure is represented by space group  $\text{R}\bar{3}\text{m}$  and there are 3 formula units per unit cell. Therefore for alunite there are 3 K, 9 Al, 18 (OH) groups, 24 oxygens, and 6 sulfur atoms per unit cell.

The unit cell parameters (Menchetti and Sabelli) are alunite,  $a = 7.020 \text{ \AA}$ ,  $c = 17.223 \text{ \AA}$ ; Na-alunite,  $a = 7.010 \text{ \AA}$ ,  $c = 16.748 \text{ \AA}$ ; jarosite,  $a = 7.315 \text{ \AA}$ ,  $c = 17.224 \text{ \AA}$ ; Na-jarosite,  $a = 7.327 \text{ \AA}$ ,  $c = 16.634 \text{ \AA}$ . Therefore the a-axis increases with the substitution of  $\text{Fe}^{3+}$  for Al in the octahedral site. Also, the c-axis decreases with the substitution of Na for K in the 12-coordinated site. Thus these unit cell variations can be used for estimating the Na/K and Al/ $\text{Fe}^{3+}$  ratio in solid solution among the end-members alunite-natroalunite-jarosite-natrojarosite.

The jarosite-alunite crystal structure is truly remarkable (Figure 1) in that it can accommodate many elements in the period table. It is also beautiful by its simplicity. Figure 1 shows the jarosite structure projected down the c-axis. The K atom sits in a 12-coordinated site and is coordinated by 6 oxygen ligands and 6 OH ligands. All 6 oxygen ligands and all 6 OH groups are symmetrically identical. Thus this site has a highly symmetrical coordination with 6 identical K-OH bonds and 6 identical K-O bonds.

The bond energies for each cation in each site determines the partitioning behavior of the cations between the jarosite structure and the aqueous fluid from which it precipitated. Thus if we know the partition coefficient (Ds) for each cation (mineral/ fluid) we can calculate the concentration of the cation in the coexisting fluid if we know the concentration in the jarosite crystal. Likewise the systematics of the stable

isotope partitioning of sulfur, oxygen, and hydrogen between jarosite and fluid depends on how many distinct sites (and distinct bonds within a site) these atoms occupy and the associated bond strengths. Also, we should note that the jarosite-alunite structure enables several types of radiogenic geochronometers, U-Pb, Rb-Sr, K-Ar, and Sm-Nd. This is partly because all parent and daughter isotopes are nicely accommodated in the 12-coordinated A-site. Of course the viability of each of these chronometers

depends on how old the jarosite is (different half lives for different systems) and whether the isotopes have been reset by any process since crystallization.

**REFERENCES.** [1] Klingelhöfer et al. (2004) *Science*, 306, 1740-1745. [2] Alpers et al (2000) *Reviews in Mineral. and Geochem.* 40, 1-608. [3] Scott (1987) *American Min.*, 72, 178-187. [4] Menchetti S. and Sabelli C. (1976) *N. Jahrb. Mineral. Monatsh. H.* 9, 406-417.

Figure 1.

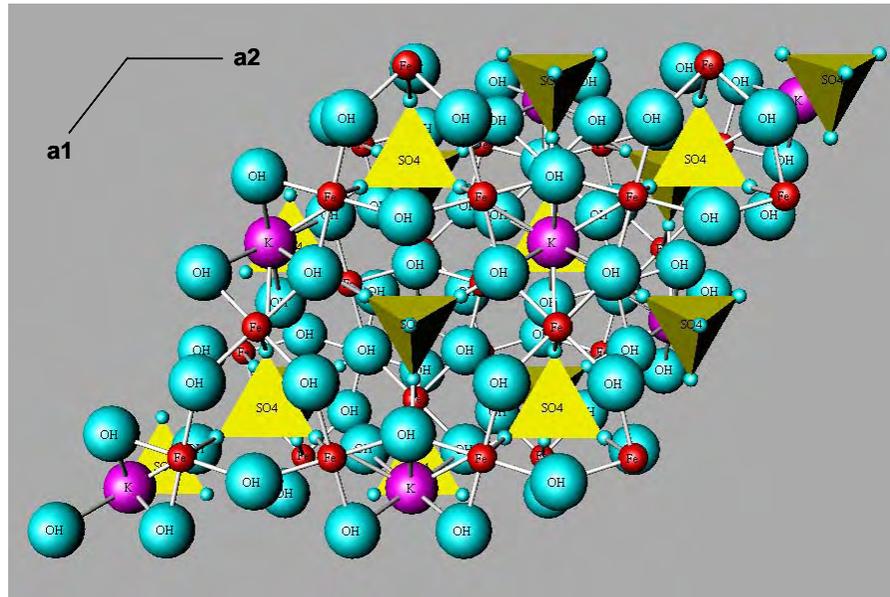


Figure 2.

