

## MÖSSBAUER AND REFLECTANCE SPECTROSCOPY OF SYNTHETIC JAROSITE WITH VARIABLE COMPOSITIONS AND TEMPERATURES.

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**Introduction:** The Mars Exploration Rover Mössbauer spectroscopy team identified jarosite, a sulfate which forms in the presence of water, in spectra of a layered outcrop in Meridiani Planum [1]. They made this assignment based on a doublet with quadrupole splitting of  $\sim 1.22$  mm/s at  $T=200-280$ K that was assigned to either K- or Na-jarosite with the possibility of some Al substituting for Fe in octahedral sites. In order to further characterize this jarosite at Meridiani and search for jarosite elsewhere, careful spectroscopic characterization of the Mössbauer parameters of jarosite over a range of compositions and temperatures is needed, which is the goal of this study.

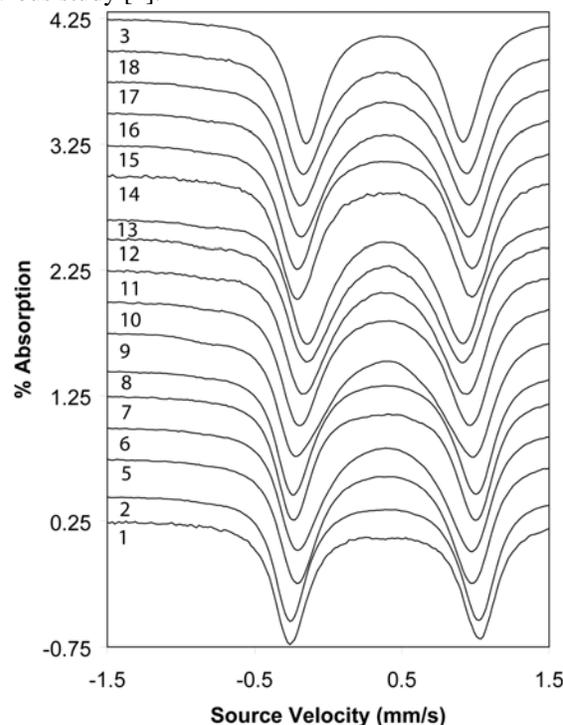
**Table 1. Compositions of Synthetic Jarosites**

Number, from [2]	Formula
1	$(K_{.86}Na_{.04}(H_3O)_{.10})_3Fe_9(SO_4)_6(OH)_{18}$
2	$(K_{.74}Na_{.02}(H_3O)_{.24})_3Fe_9(SO_4)_6(OH)_{18}$
3	$(K_{.74}Na_{.01}(H_3O)_{.25})_3Fe_9(SO_4)_6(OH)_{18}$
5	$(K_{.70}Na_{.01}(H_3O)_{.29})_3Fe_9(SO_4)_6(OH)_{18}$
6	$(K_{.67}Na_{.01}(H_3O)_{.32})_3Fe_9(SO_4)_6(OH)_{18}$
7	$(K_{.60}Na_{.07}(H_3O)_{.34})_3Fe_9(SO_4)_6(OH)_{18}$
8	$(K_{.57}Na_{.10}(H_3O)_{.33})_3Fe_9(SO_4)_6(OH)_{18}$
9	$(K_{.56}Na_{.02}(H_3O)_{.42})_3Fe_9(SO_4)_6(OH)_{18}$
10	$(K_{.55}Na_{.03}(H_3O)_{.42})_3Fe_9(SO_4)_6(OH)_{18}$
11	$(K_{.49}Na_{.16}(H_3O)_{.35})_3Fe_9(SO_4)_6(OH)_{18}$
12	$(K_{.47}Na_{.02}(H_3O)_{.51})_3Fe_9(SO_4)_6(OH)_{18}$
13	$(K_{.4}Na_{.68}(H_3O)_{.28})_3Fe_9(SO_4)_6(OH)_{18}$
14	$(K_{.3}Na_{.78}(H_3O)_{.19})_3Fe_9(SO_4)_6(OH)_{18}$
15	$(K_{.2}Na_{.72}(H_3O)_{.27})_3Fe_9(SO_4)_6(OH)_{18}$
16	$(K_{.1}Na_{.65}(H_3O)_{.34})_3Fe_9(SO_4)_6(OH)_{18}$
17	$(K_{.1}Na_{.83}(H_3O)_{.16})_3Fe_9(SO_4)_6(OH)_{18}$
18	$(Na_{.83}(H_3O)_{.17})_3Fe_9(SO_4)_6(OH)_{18}$

**Background:** The jarosite group has the formula  $AM_3(SO_4)_2(OH)_6$ , where A is usually a monovalent cation ( $K^+$  and  $Na^+$  are most common, although  $Pb^+$ ,  $Ag^+$ ,  $NH_4^+$  and  $H_3O^+$  are also observed). M is primarily  $Fe^{3+}$  for jarosite,  $Al^{3+}$  for alunite or another trivalent cation. The structure is composed of  $SO_4^{2-}$  tetrahedra and  $MO_2(OH)_4$  octahedra, both somewhat distorted and each forming a layer in the *a* direction. Each  $SO_4^{2-}$  tetrahedron has one O bound to Al or Fe, producing a symmetry of  $C3v$  instead of  $Td$ .

**Methods:** The jarosite samples used in this study were synthesized by Brophy [2] and were generously

provided to us by him. They represent a series of 17 compositions (Table 1) in which the values of potassium (K), sodium (Na), and hydronium ( $H_3O$ ) all vary. Mössbauer spectra of all samples were acquired at room temperature (Figure 1); sample #2 was also measured over a range of 16 temperatures from 12-295K at low He gas pressure. A source of 100-70 mCi  $^{57}Co$  in Rh was used on a WEB Research Co. model W100 spectrometer equipped with a Janus closed-cycle He refrigerator. Run times ranged from 1-12 hours; results were calibrated against  $\alpha$ -Fe foil. Spectra were fit with quadrupole splitting distributions (QSD) and hyperfine field distributions using the method of [3]; an average correlation between the isomer shift and quadrupole splitting of  $Fe^{2+}$  was assumed. Reflectance spectra were measured as in a previous study [4].



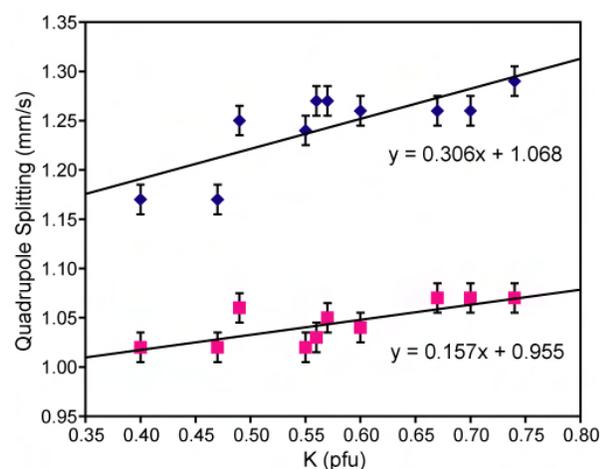
**Figure 1.** Mössbauer spectra of the 17 jarosites at room temperature.

**Mössbauer Results:** Using the QSD method, the 293K jarosite spectra were found to be composed of three sub-components with  $\delta = 0.37-0.39$  mm/s and  $\Delta$  (QS) values of 1.13-1.29, 1.02-1.09, and 0.64-0.94 mm/s, respectively. At compositions with  $>0.40$  pfu K, there is a systematic *positive* correlation between K and  $\Delta$  for the dominant doublets (sub-components #1

and 2) with areas >20%. Thus, our results suggest that the Mars MER jarosite would have <50 mol% K, consistent with APXS results of [11] and the suggestion of [12] of hydronium jarosite on Mars.

At low K contents, Na and  $\text{H}_3\text{O}^+$  were co-varied, so the trends are not clear. These data contrast with the much older work of [5] and [6], who suggested that the QS values of jarosite are *negatively* correlated with K contents. However, those earlier studies used Lorentzian doublets rather than QSD's, employed natural samples that were part of mixtures of minerals, and/or had far fewer compositions represented.

Our multi-temperature Mössbauer spectra show that magnetic ordering in jarosite with a composition of  $\text{K}_{0.74}\text{Na}_{0.02}(\text{H}_3\text{O})_{0.24}$  occurs at 90 K. Further measurements of ordering temperature in other compositional extremes are in progress, as are calculations of the recoil-free fraction,  $f$ .



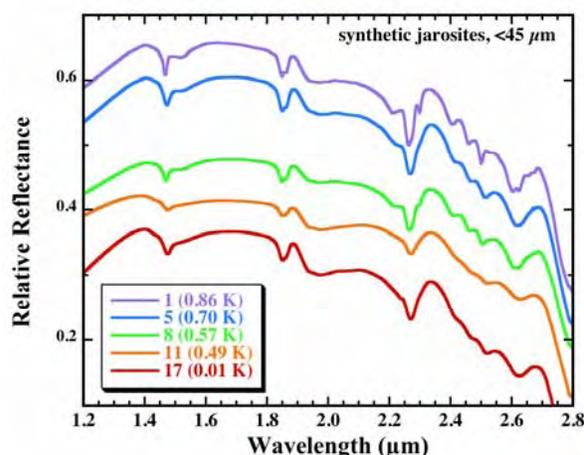
**Figure 2.** Change in quadrupole splitting as a function of K content (given in terms of formula units).

**Reflectance Results:** Jarosite exhibits several near-infrared (NIR) overtone and combination bands due to OH and  $\text{SO}_4$  groups [4]. These bands differ greatly if Al (alunite) is substituted for Fe. The new spectra of this jarosite suite with a range of K, Na and  $\text{H}_3\text{O}$  abundances also show variations in the NIR features (Figure 3). These data are somewhat complicated because of the three cations present, however, a clear trend is observed for K-rich jarosite and Na-rich jarosite.

The NIR spectrum of K-jarosite exhibits an OH stretching band at  $1.47 \mu\text{m}$ , an OH stretch + 2 bend combination doublet at  $1.849$  and  $1.864 \mu\text{m}$ , plus an OH stretch + bend combination triplet at  $2.215$ ,  $2.265$ , and  $2.300 \mu\text{m}$  and additional OH and  $\text{SO}_4$  combination features near  $2.40$ ,  $2.46$ ,  $2.50$ ,  $2.60$  and  $2.62 \mu\text{m}$ .  $\text{H}_3\text{O}$ - and Na-jarosite spectra exhibit broader features and the doublet is less resolvable. The spectrum of Na-

jarosite contains a band at  $1.48 \mu\text{m}$ , a broad asymmetric band near  $1.85 \mu\text{m}$  and a triplet near  $2.235$ ,  $2.275$ , and  $2.310 \mu\text{m}$ , plus additional features near  $2.42$ ,  $2.47$ ,  $2.52$ ,  $2.62$  and  $2.64 \mu\text{m}$ .

**Implication for Mars:** Diagnostic NIR absorptions of the sulfate minerals kieserite and gypsum have been identified in data from the OMEGA instrument in several locations on Mars [7-9]. The deposits range from small, light-toned outcrops in Valles Marineris to regional layers rich in sulfate in the Meridiani region. These recent discoveries highlight the importance of studying sulfate minerals in particular as direct tracers of the alteration history of the red planet. The CRISM spectrometer on the Mars Reconnaissance Orbiter will evaluate these sulfate-bearing sites at even smaller spots sizes on the surface [10]. Thus, it is necessary to characterize potential sulfate minerals such as jarosite in order to identify them on Mars.



**Figure 3.** Near-infrared spectra of synthetic jarosites with a range of  $\text{K}^+$  abundance in the monovalent sites.

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**References:** [1] Klingelhofer G. et al. (2004) *Science* 306, 1740-1745. [2] Brophy, G.P. & Sheridan, M.F. (1965) *Amer. Mineral.*, 50, 1595-1607. [3] Wivel C. & Mørup, S. (1981) *J. Phys.*, E14, 605-610. [4] Bishop, J. L. & E. Murad (2005) *Amer. Mineral.*, 90, 1100-1107. [5] Johnson J.H. (1977) *GCA*, 41, 539-544. [6] Hryniewicz A. Z. et al. (1965) *J. Inorg. Nucl. Chem.*, 27, 2513-2517. [7] Arvidson R. E. et al. (2005) *Science*, 307, 1591-1594. [8] Bibring J.-P. et al. (2005) *Science*, 307, 1576-1581. [9] Gendrin A. et al. (2005) *Science*, 307, 1587-1591. [10] Murchie S. et al. (2003) *Sixth Int'l Conf. on Mars*, CD-ROM #3062. [11] Clark B.C. *EPSL*, 240, 73-94. [12] Tosca N. J. et al. (2005) *EPSL*, 240, 122-148.