

JAROSITE IN AN EAST AFRICAN SALINE-ALKALINE PALEOLAKE DEPOSIT: IMPLICATIONS FOR MARS. L. J. McHenry¹, V. F. Chevrier², and C. Schröder³, ¹Department of Geosciences, University of Wisconsin- Milwaukee, PO Box 413, Milwaukee, WI 53201, lmchenry@uwm.edu, ²W.M. Keck Laboratory for Space and Planetary Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, ³Institut für Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universität, Staudinger Weg 9, D-55099 Mainz, Germany, schroedc@uni-mainz.de.

Introduction: Jarosite was discovered in outcrop rocks at Meridiani Planum by Mars Exploration Rover (MER) Opportunity [1]. Jarosite typically indicates water limited rock alteration [2] and thus evaporation in acidic environments [3], or weathering of sulfide-rich deposits in oxidative environments [4]. Jarosite was taken as evidence for general acidic conditions with implications for the possibility of life during formation of the Meridiani Planum outcrop deposits [5].

Jarosite is also found in altered tephra in the saline-alkaline paleolake deposits of Olduvai Gorge, Tanzania. Zeolites (mainly phillipsite) and authigenic K-feldspar dominate the mineral assemblage, indicating saline-alkaline diagenetic conditions. As jarosite is ordinarily an indicator of acidic conditions on Earth and Mars, its association with such undisputed high-pH indicators is unexpected.

The Olduvai record includes a Plio-Pleistocene lacustrine deposit with abundant altered tephra layers. The saline-alkaline lake and groundwaters altered the tephra into zeolite-rich deposits near the center and clay dominated deposits at the margins of the lake, forming a classic “bulls-eye” alteration pattern.

Methods: 58 altered tephra samples were collected across the Olduvai basin to determine the authigenic assemblages and constrain the jarosite occurrence. Each sample was scanned quickly by XRD, followed by a 7-hour scan for samples with potential jarosite so that minor (<1%) jarosite could be measured with confidence. Rietveld refinement was used to quantify mineral abundances. Jarosite-bearing samples were analyzed by SEM to ascertain the textural relationship between jarosite and zeolites and to confirm jarosite using qualitative EDS. A subset of the samples was also analyzed by FTIR and Mössbauer to see if minor jarosite associated with zeolites is detectable using techniques more comparable to those used on Mars.

Fourier transform infrared (FTIR) reflectance spectra were taken using a Nicolet 6700 Smart Diffuse spectrometer with N₂ purge gas to remove atmospheric gases (H₂O and CO₂). Near-infrared (NIR) spectra were recorded in reflectance mode in the range of 200 – 12,500 cm⁻¹ (0.8 – 5.0 μm) with resolution of 4 cm⁻¹, although we subsampled the 1.0 – 2.6 μm range for easier comparison to data from OMEGA and CRISM available in the literature. The configuration used a quartz-halogen IR source, a CaF₂ beam splitter, and a

DTGS detector. Background spectra using a Spectralon white standard (NIR) were systematically taken before each sample's spectra to remove instrumental signal.

Mössbauer spectra were obtained at room temperature with a laboratory copy of the MER instruments [6]. These instruments are set up in backscattering geometry. The Mössbauer source was ⁵⁷Co in Rh matrix. Spectra were evaluated using Lorentzian lineshapes. Parameters are quoted relative to α-Fe⁰.

Results: Ten samples contained XRD-detectable jarosite. All jarosite-bearing samples came from near the lake center (where conditions would have been most alkaline), and also contained phillipsite (Fig 1), K-feldspar, and smectite ± analcime. Detected jarosite concentrations vary from 0.6% - 6%. SEM showed associated jarosite and phillipsite crystals ~1 μm across (Fig 2), and EDS peaks for S, K, and Fe confirm the identity of jarosite with some Al³⁺ substitution for Fe³⁺.

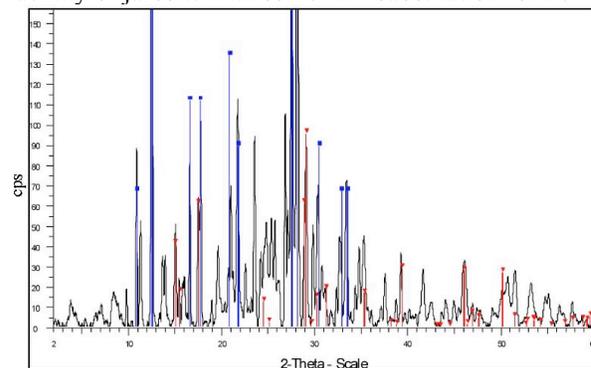


Figure 1: XRD for jarosite-rich (6%) sample. Blue = phillipsite, red = jarosite (other minerals not indicated).

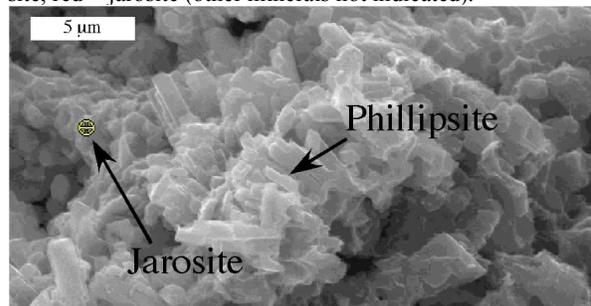


Figure 2: SEM BSE image of jarosite and phillipsite.

From the discussion below, the FTIR spectra of two samples show a clear smectite signal, with the two characteristic bands at 1.4 and 1.9 μm. There is also a

clear band at 2.3 mm due to the Fe-OH bond in the smectite. Last, there is a weaker band at 2.2 mm due to Al-OH in the structure. Thus the FTIR results confirm the presence of an Al,Fe³⁺-smectite, likely a nontronite.

Jarosite is identified by 4 major bands at 1.46, 1.85, 1.92 and 2.26 mm (there are several other minor bands). On the FTIR graph we observe a weak absorption band at 1.8 mm and several “humps” in other larger bands, at 1.46, 1.96 and 2.26 mm. These features are pretty close to jarosite, especially since jarosite is a minor phase which therefore has very small bands.

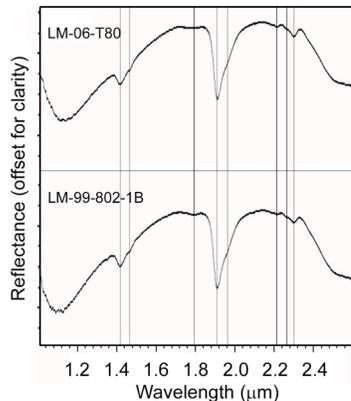


Figure 3: FTIR reflectance spectra of two jarosite-smectite bearing samples.

Five samples were investigated with Mössbauer spectroscopy. Four of these samples contained jarosite detected by XRD. The jarosite could be clearly identified in the Mössbauer spectra of these four samples (e.g., Fig 4). A second ferric phase, consistent with a smectite, was identified in all five samples. Jarosite at Meridiani Planum has average values for the isomer shift δ of 0.37 mm/s and the quadrupole splitting ΔE_Q of 1.20 mm/s. It has Na > K > H₃O as monovalent cation with possible Al³⁺ for Fe³⁺ substitution [7].

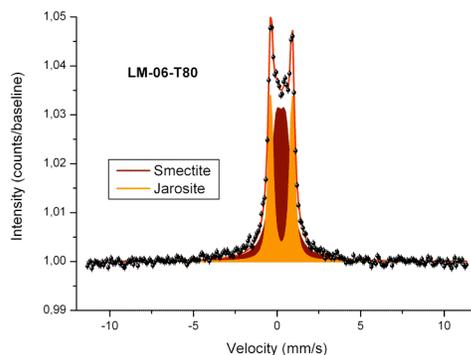


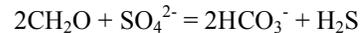
Figure 4: Mössbauer spectrum of a smectite and jarosite-bearing sample.

Olduvai jarosite has average values for δ of 0.37 mm/s and ΔE_Q of 1.30 mm/s. Jarosite ΔE_Q increases from H₃O to Na to K as dominant cation [8] and with

Al³⁺ for Fe³⁺ substitution [7]. The Olduvai data are therefore consistent with K as the dominant monovalent cation and possible Al³⁺ for Fe³⁺ substitution.

Discussion: The zeolite-rich assemblage excludes dominantly acidic conditions. Zeolites generally begin to crystallize in closed basin environment once the pH reaches 9-10 [9]. Associated moulds after trona suggest a pH between 9 and 10 [10]. Modern groundwater is highly alkaline, leading to salt efflorescences of sodium carbonate/bicarbonate consistent with a pH of 9.5-10 [10-11]. In contrast, jarosite forms at pH <4 [7].

A potential model for the formation of this deposit is as follows: Phillipsite and K-feldspar formed in tephra altered in the high-pH ground and lake water. Pyrite formed soon after deposition as water containing dissolved sulfate underwent sulfate reduction:



H₂S then reacted with Fe²⁺ in the muds (available after Fe³⁺ reduction of detrital material), forming pyrite (modified from [11]). More recently, perhaps in modern groundwater, pyrite was oxidized:



The sulfuric acid locally lowered the pH into the jarosite stability field. The acidic conditions caused by the oxidation of pyrite did not persist long enough to destroy the phillipsite. The formation of jarosite is most likely recent, as the pH 9.5-10 modern groundwater would likely destroy it over time. An alternative explanation for this assemblage is that jarosite may be a stable phase under the extreme saline-alkaline conditions present in Pleistocene or modern Olduvai.

Implications for Mars: Jarosite occurs ubiquitously in outcrops at Meridiani Planum and is not confined to a lake center as at Olduvai. However, these results suggest that jarosite can form as a late stage alteration product, superimposed upon a mineral assemblage indicative of much more alkaline conditions. Thus, the dominant conditions at Meridiani Planum could have been more alkaline than generally assumed.

References: [1] Klingelhöfer G. et al. (2004) *Science*, 306, 1740-1745. [2] Elwood Madden M.E. et al. (2004) *Nature*, 431, 821-823. [3] Tosca N.J. et al. (2005) *EPSL*, 240, 122-148. [4] Burns R.G., Fischer D.S. (1990) *JGR*, 95, 14415-14421. [5] Knoll A.H. et al. (2005) *EPSL*, 240, 179-189. [6] Klingelhöfer G. et al. (2003) *JGR*, 108(E12), 8067. [7] Morris R.V. et al. (2006) *JGR*, 111, E12S15. [8] Leclerc A. (1980) *Phys. Chem. Miner.*, 6, 327-334. [9] Langella et al. (2001) in Bish D.L., Ming D.W. (eds), *Natural Zeolites*, 235-360. [10] Hay R. L. (1964) *Am. Mineral.*, 49, 1366-1387. [11] Hay R.L., Kyser T.K. (2001) *GSA Bulletin*, 113, 1505-1521.

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