

THE FORMATION AND DESTRUCTION OF JAROSITE IN A 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, ³Center for Applied Geoscience, Eberhard Karls Universität, Sigwartstr. 10, D-72076 Tübingen, Germany, christian.schroeder@ifg.uni-tuebingen.de.

Introduction and Background: Jarosite was discovered in outcrop rocks at Meridiani Planum by 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, 5]. Jarosite was taken as evidence for general acidic conditions with implications for the possibility of life during formation of the Meridiani Planum outcrop deposits [6].

However, jarosite has recently been observed in other environments, not all acidic. These include the local oxidation of pyrite in generally neutral freshwater spring environments [7,8], and in microenvironments in carbonate-buffered systems in cold, arid contexts [9,10]. The current study strives to explain the unexpected occurrence of jarosite in the altered tephra of a Pleistocene saline-alkaline paleolake deposit at Olduvai Gorge, Tanzania [11] that is dominated by zeolites phillipsite and chabazite further out, and clays at the lake margin. Mg- and Fe- rich smectite clays are present throughout.

The Olduvai Paleolake: This paleolake deposit follows a typical “bull’s-eye” pattern of saline-alkaline authigenic mineralization (Fig 1), with K-feldspar and the zeolite mineral phillipsite dominating the altered tephra of the central basin, zeolites phillipsite and chabazite further out, and clays at the lake margin. Mg- and Fe- rich smectite clays are present throughout.

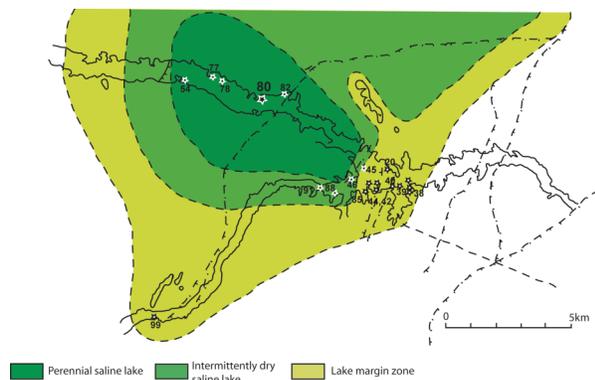


Figure 1: Map of Olduvai Gorge with superimposed Plio-Pleistocene lacustrine environments. Jarosite was only found in the lake center (dark green) sites. Map after [13]

Methods: 65 samples of altered tephra and four of lacustrine claystone from above and below jarosite-bearing altered tephra were collected over five field seasons at Olduvai. Sampling covered a transect from the central lake to the margin. The pH and conductivity

of two modern springs at Localities (Locs) 78 and 82 were also measured. One jarosite-bearing site (Loc 80) was sampled during three visits. Each sample was powdered and analyzed by X-ray Diffraction (XRD). Samples from each environment were also analyzed by Mössbauer, and jarosite-bearing samples by Scanning Electron Microscopy (SEM) and Fourier transform infrared (FTIR) reflectance spectroscopy (methods of [11]). Jarosite composition for one Loc 80 sample was measured directly by electron microprobe (EPMA). Mössbauer spectra were obtained at room temperature with a laboratory copy of the MER instruments [14].

Results: Jarosite occurred, in concentrations ranging from 0.3 to 6%, in samples of altered tephra from all of the central lake basin localities. These samples were dominated by phillipsite and authigenic K-feldspar (with minor clays). Jarosite was not observed in all lake-altered tephra samples, and was not recognized in the lacustrine clays, intermittent, or lake margin environments. SEM images indicate that the jarosite is in textural association with smectite and phillipsite (Fig 2). The EPMA analyses reveal a K-rich jarosite with minor substitution of Al for Fe (Table 1). FTIR and Mössbauer results are presented and discussed in Figures 3 and 4.

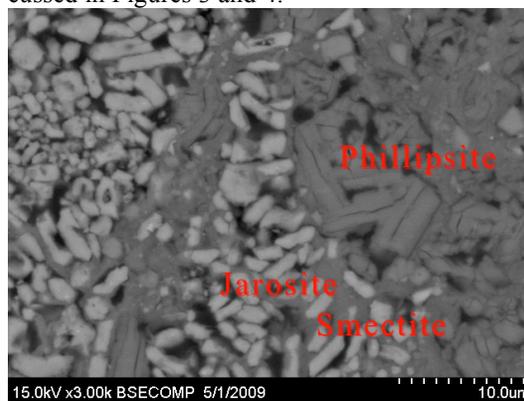


Figure 2: SEM backscatter image of a jarosite and phillipsite-bearing sample from Loc 80. Jarosite is brightest, phillipsite forms laths, and smectite occurs in the matrix.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	SO ₃	SUM
1.00	3.33	39.07	0.33	8.12	29.84	81.85
0.50	0.53	1.51	0.23	0.62	0.96	1.53

Table 1: EPMA compositions for Loc 80 jarosite (average of 8 analyses and standard deviation). Low totals attributed to small grain size (<1 μm) and hydration.

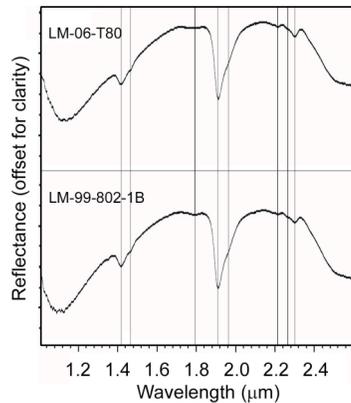


Figure 3: The FTIR spectra show two characteristic smectite hydration bands at 1.4 and 1.9 μm , a clear band at 2.3 μm due to the Fe-OH bond, and a weaker band at 2.2 μm due to Al-OH in the structure, indicating a Al,Fe³⁺-smectite, likely nontronite. Jarosite is identified by 4 major bands at 1.46, 1.85, 1.92 and 2.26 μm . A weak absorption band at 1.8 μm and several “humps” in other larger bands at 1.46, 1.96 and 2.26 μm are consistent with jarosite as a minor phase.

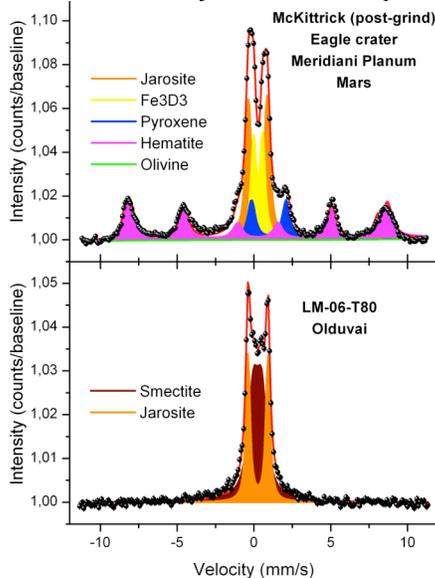


Figure 4: Comparison of a typical Meridiani Planum, Mars, sulfate-rich evaporitic outcrop spectrum (top) with a jarosite-rich sample from Olduvai Gorge, Tanzania (bottom). Both spectra show two central ferric doublets, jarosite, and an unidentified phase designated as Fe3D3 in the Meridiani spectrum [1, 15] and jarosite in combination with an Fe-bearing smectite in the Olduvai spectrum.

Modern Springs: The modern springs are saline-alkaline, with pH ranging from 9.29 to 9.54 with conductivities of 14.6 and 25.6 mS at 17.5°C. Trona actively precipitates at the margins of spring-fed pools.

Year-to-year variability: The three samples collected from the same spot in three different years showed declining jarosite concentrations over time:

6% in 2006, 2% in 2008, and 0.3% in 2009. This suggests that the jarosite occurrence is ephemeral and related to the modern weathering environment rather than the ancient depositional environment.

Model: Potential explanations for this unusual jarosite occurrence include a potential new high-pH stability field for jarosite, formation from modern groundwater, or formation in acidic microenvironments caused by modern weathering. The alkalinity of the modern groundwater makes it an unlikely source for the jarosite. Our favored hypothesis is that the jarosite formed from local oxidation of ancient lacustrine pyrite, formed initially in a saline-alkaline reducing environment and now exposed to oxidizing fluids. This oxidation reaction produces sulfuric acid in local pore spaces (producing an acidic microenvironment), and provides Fe³⁺ and sulfate for the formation of jarosite. As jarosite is not stable in the large-scale saline-alkaline groundwater environment, it is gradually destroyed upon exposure. Only the continued oxidation of pyrite allows jarosite to persist in this environment.

Implications for Mars: The Olduvai paleolake is not the best analog for Mars, except for the jarosite occurrence. The tephra is phonolitic rather than basaltic, and the rest of the assemblage of zeolites and other saline-alkaline minerals is at odds with the saline-acidic assemblage observed at Meridiani. However, the presence of jarosite in a deposit dominated by saline-alkaline minerals shows that jarosite can occur in a variety of environments, not all dominated by acidic conditions. The presence of jarosite alone should not be used as an indicator of predominantly acidic conditions or to rule out the possibility of zeolites or other phases in co-existing mineral assemblages.

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] Chevrier V.F. et al. (2004) *Geology* 119, 1477. [6] Knoll A.H. et al. (2005) *EPSL*, 240, 179-189. [7] Ashley G.M. et al. (2004) *Sedimentology* 51, 1301-1321. [8] Adelsberger K.A., Smith J.R. (2009) *GSA Abst. w. Prog.* 41, 436. [9] Darmody R.G. et al. (2007) *GSA Bull.* 119, 1477-1485. [10] Leveille R.J. (2007) *GSA Abstracts w. Programs* 39, 284. [11] McHenry L.J. et al. (2009) *LPS XL*, Abstract #1635. [12] Langella et al. (2001) in Bish D.L., Ming D.W. (eds), *Natural Zeolites*, 235-360. [13] Hay R.L. (1976) *Geology of the Olduvai Gorge*. U. California Press, Berkeley. [14] Klingelhöfer G. et al. (2003) *JGR*, 108(E12), 8067. [15] Morris R.V. et al. (2006) *JGR*, 111, E12S15.

Acknowledgements: We thank G. Klingelhöfer for access to the MER-like Mössbauer spectrometers.