

**EPHEMERAL K-JAROSITE IN A SALINE-ALKALINE PALEOLAKE DEPOSIT: IMPLICATIONS FOR THE LONG-TERM SURVIVAL OF JAROSITE ON EARTH AND MARS.** L. J. McHenry<sup>1</sup>, V. F. Chevrier<sup>2</sup>, and C. Schröder<sup>3</sup>, <sup>1</sup>Department of Geosciences, U. Wisconsin- Milwaukee, PO Box 413, Milwaukee, WI 53201, lmchenry@uwm.edu, <sup>2</sup>W.M. Keck Laboratory for Space and Planetary Simulation, Arkansas Center for Space and Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, <sup>3</sup>Center for Applied Geoscience, Eberhard Karls Universität, Sigwartstr. 10, D-72076 Tübingen, Germany, christian.schroeder@ifg.uni-tuebingen.de.

**Introduction:** Jarosite, a hydrous Fe-sulfate mineral generally indicative of water-limited [1] acidic [2] conditions on Earth, has been detected on Mars by the MER Opportunity at Meridiani Planum [3] and from orbit elsewhere [4,5,6]. Its occurrence is used as a line of evidence in support of widespread acidic conditions early in Mars' history [7]. The presence of jarosite also limits water abundance, since long-term exposure to water would destroy the jarosite [8]. The ease with which jarosite breaks down in terrestrial environments suggests that conditions on Mars must have been very dry since its formation, or that the jarosite formed much more recently than the outcrops in which it is found [9]. However, jarosite in certain non-acidic environments on Earth [e.g. 10] shows that jarosite alone does not always indicate large-scale acidic conditions.

**Background:** Olduvai Gorge, Tanzania, exposes a transect of a Pliocene-Pleistocene saline-alkaline paleolake deposit containing altered phonolitic and trachytic tephra dominated by zeolites and Fe- and Mg-rich clay minerals [11], with occasional jarosite. This jarosite is unexpected, since it occurs within a mineral assemblage dominated by phases favored by high-pH conditions [10].

**Methods:** 52 samples of altered tephra from the Olduvai paleolake were analyzed by XRD as part of the study, 11 of which contained measurable jarosite. Select samples were also analyzed by XRF, VNIR, Mössbauer, EPMA, and SEM, results reported in [10] and [12]. This study focuses on four samples, collected from the same spot in four different years (Figure 1).

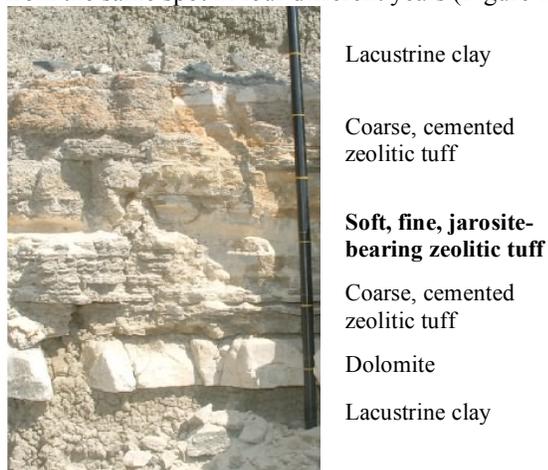


Figure 1: outcrop photo of jarosite-bearing tephra

One specific part of a single layer of Tuff IF at Locality 80 was initially sampled in 2006 and then re-sampled in 2008, 2009, and 2010 to determine whether the jarosite is long-lasting or ephemeral. Figure 1 is a photograph of the main Locality 80 exposure, including sample positions. The exact sample spot was identified and re-sampled each year, at approximately the same time (July-August, during Tanzania's dry season). The hole left from sampling the previous year was located, and the new sample was collected directly adjacent, no more than centimeters (laterally) from the previous sample and within the same thin, soft layer. About 200 g per sample were collected.

**Results:** In the 2006 sample (06-T80) jarosite was a prominent phase in the XRD pattern (Figure 2), accounting for 4.5% of the sample (based on Rietveld refinement, excluding the clay component). In the 2008 sample (08-T4) the jarosite XRD peaks are still obvious, accounting for over 0.7% of the sample, but by 2009 (sample 09-T23) jarosite was less observable, with about 0.3%. No jarosite was detected in the 2010 sample (10-T43). Mössbauer results of the 2006 and 2008 samples show both jarosite and an Fe-smectite [10]. EPMA, XRD, and Mössbauer results agree that this jarosite is K-rich. SEM imaging shows that the jarosite is fine-grained ( $\sim 1\mu\text{m}$ ) and in close association with the zeolite mineral phillipsite (Figure 3). XRF results (Table 1) reveal a decrease in the bulk concentration of  $\text{SO}_3$  and  $\text{Fe}_2\text{O}_3$  (and relative increase in  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ ) between 2006 and 2010.

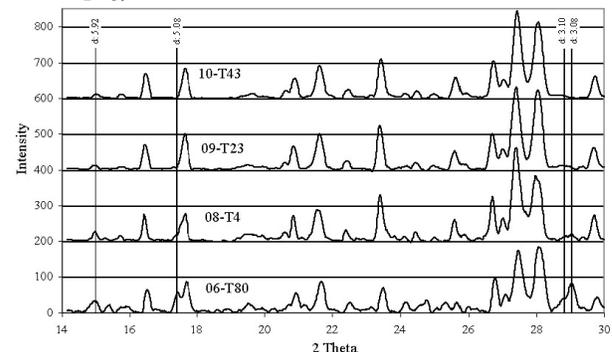


Figure 2: XRD plot (intensity vs. 2 theta) for the 2006 (06-T80), 2008 (08-T4), 2009 (09-T23), and 2010 (10-T43) samples for Olduvai Locality 80, with four jarosite peaks indicated. The main difference between the three samples is the jarosite abundance.

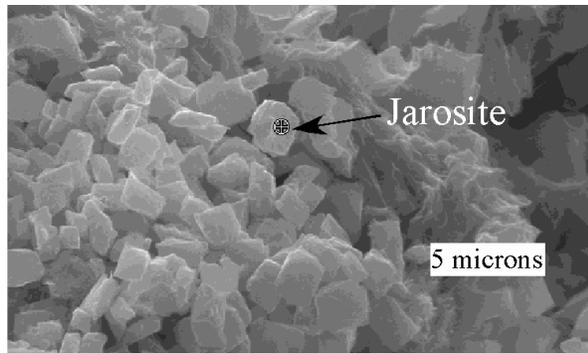


Figure 3: SEM SE image of jarosite crystals in sample 06-T80. The substrate is Fe-rich clay and the zeolite phillipsite.

Table 1: Bulk composition (XRF)

Sample	06-T80	08-T4	09-T23	10-T43
SiO <sub>2</sub>	54.70	55.81	61.03	60.76
TiO <sub>2</sub>	0.27	0.31	0.33	0.35
Al <sub>2</sub> O <sub>3</sub>	14.60	15.43	15.89	16.32
Fe <sub>2</sub> O <sub>3</sub>	7.32	6.29	4.32	2.87
MnO	0.01	0.02	0.01	0.03
MgO	0.68	0.85	0.95	0.78
CaO	0.16	0.37	0.21	0.55
Na <sub>2</sub> O	4.12	3.80	4.13	4.47
K <sub>2</sub> O	8.05	8.59	8.79	8.57
P <sub>2</sub> O <sub>5</sub>	0.05	0.06	0.05	0.05
SO <sub>3</sub>	1.72	1.02	0.15	0.09
LOI	9.54	5.87	6.09	4.28
SUM	101.23	98.42	101.95	99.21

**Discussion:** The jarosite in this saline-alkaline lacustrine deposit likely formed recently, as Pleistocene lacustrine pyrite oxidized, providing sulfur and locally acidic conditions that could allow jarosite to form within pores [10]. However, the overall mineral assemblage and the composition of modern groundwater (pH ~9.5) are far from jarosite's stability field, and after formation the jarosite could be degraded rapidly.

The trend we see in the jarosite content of the four samples could be spatial rather than temporal. It is impossible to collect the exact same sample four years in a row, since the original sample was removed. However, we contend that the close spacing of our sampling (see methods above) provides samples more affected by temporal than spatial differences. While we see mineralogical differences between different layers of the tephra, the only major difference between samples from the fine, soft layer is the jarosite abundance.

One observation that could support the spatial (rather than temporal) hypothesis is the difference in Fe and S content between jarosite-rich and jarosite-poor samples. This could indicate a heterogeneous

distribution of pyrite in the original alteration assemblage. The lack of jarosite breakdown products (goethite, etc.) in the jarosite-poor samples suggests either that Fe was somehow lost to solution as jarosite altered or that jarosite was not originally present.

We favor a model in which jarosite formed recently, and was not part of the original saline-alkaline mineral assemblage. It is unlikely that jarosite has existed in these rocks for the last 1.79 Ma (age of Tuff IF, [13]), only to vanish in the four years under investigation. This points to a short-term, local process. This potentially ephemeral occurrence of jarosite is similar to seasonal jarosite efflorescence observed at Rio Tinto in Spain, where hydronium jarosite precipitates from evaporating acidic river water under dry conditions and is seasonally destroyed by exposure to wet conditions [14]. K-rich jarosite is, however, typically more resistant to weathering; on Mauna Kea, K-jarosite has persisted for over 4000 years under non-equilibrium conditions at near neutral pH [15]. The apparent rate of dissolution for the Olduvai jarosite is at the extreme short end of the range determined experimentally by [8] (1.5 years to 1 Ma). The smaller grain size (~1 μm vs. 10 μm) of the Olduvai jarosite and higher pH (>9 vs. neutral) could account for this difference.

**Conclusions:** These observations are relevant to the interpretation of the role and history of jarosite on Mars. First, jarosite can occur in deposits that are far from its normal stability field; thus jarosite cannot be used in isolation as an indicator of dominantly acidic conditions. Second, even K-rich jarosite can degrade rapidly in contact with alkaline fluids. The presence of jarosite on Mars suggests either a recent origin [9] or an exceptionally dry history since formation [8]. While it strongly suggests acidic conditions for both its formation and preservation, it can be formed and found in other settings.

**References:** [1] Elwood Madden M.E. et al. (2004) *Nature* 431, 821-823. [2] Tosca N.J. et al. (2005) *EPSL* 240, 122-148. [3] Klingelhöfer G. et al. (2004) *Science* 306, 1740-1745. [4] Milliken, R.E. et al. (2008) *Geology* 36, 847-850. [5] Wray J.J. et al. (2009) *Geology* 37, 1043-1046. [6] Farrand, W.H. et al. (2009) *Icarus* 204, 478-488. [7] Knoll A.H. et al. (2005) *EPSL* 240, 179-189. [8] Elwood Madden et al. (2009) *Geology* 37, 635-638. [9] Fairén, A.G. et al. (2009) *Planet. Space Sci.* 57, 276-287. [10] McHenry, L.J. et al. (in press) *JGR*. [11] McHenry, L.J. (2010) *Clays Clay Miner.* 58, 627-643. [12] McHenry et al. (2010) *LPS XLI Abstract #1476*. [13] Hay R.L. and Kyser T.K. (2001) *Geol. Soc. Am. Bull.* 113, 1505-1521. [14] Fernández-Remolar et al. (2005) *EPSL* 240, 149-167. [15] Morris R.V. et al. (1996) In Dyar, M.D. et al. (eds), *Spec. Publ. Geochem Soc.* 5, 327-336.