

## SPATIAL VS. TEMPORAL DISTRIBUTION OF K-JAROSITE IN A SALINE-ALKALINE PALEOLAKE DEPOSIT: IMPLICATIONS FOR THE DISTRIBUTION AND LONGEVITY OF JAROSITE ON MARS.

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**Introduction:** The presence of jarosite at the MER Opportunity landing site at Meridiani Planum [1] and elsewhere on Mars [2,3,4] has emerged as an important indicator of early saline-acidic aqueous conditions followed by a long history of aridity [5,6]. To understand the implications of this discovery, researchers have sought natural jarosite occurrences on Earth to provide constraints about the environmental conditions on early Mars. Our analog, a Pleistocene aged volcanic ash layer (Fig. 1) altered under saline-alkaline conditions, is unusual because it places a jarosite occurrence in an otherwise saline-alkaline context far from the accepted stability field for this mineral [7]. Whether jarosite is an ephemeral phase in this environment, changing in abundance seasonally, or can be stable over longer periods of time in contact with groundwater of pH ~9.5, has implications for the range of environments in which Martian jarosite could have formed and how long it could have lasted.



Figure 1: outcrop photo of Tuff IF, with sampling spots for the 2011 samples indicated.

**Background:** Olduvai Gorge in Tanzania, East Africa exposes a Pleistocene saline-alkaline lacustrine deposit, which preserve layers of altered volcanic ash including Tuff IF (Fig. 1). While zeolites dominate these tuffs, abundant jarosite has also been observed. In samples collected from the same layer in the same outcrop from 2006 to 2010, the abundance of jarosite appeared to decrease from year to year [7].

**Methods:** To test whether these changes were temporal (an actual change in the abundance of jarosite from year to year) or spatial (a spatially limited occurrence of jarosite that was not re-sampled exactly each

year), we collected additional samples in 2011. Eight adjacent samples were collected from the soft layer within Tuff IF (Fig. 1) that had yielded jarosite in previous years. These samples were analyzed by XRD for mineral assemblage (non-clay constituents quantified using the Rietveld method) and by XRF for bulk chemical composition (methods of [7]).

**Results:** The overall mineral assemblage matched that observed in previous years [7], with phillipsite and K-feldspar dominating the authigenic minerals, anorthoclase representing the original volcanic composition, and K-jarosite varying between 0.4 (barely detectable) and 7.9% (Fig. 2 and 3, Table 1). Besides the variable abundance of jarosite, the rest of the assemblage is more consistent. The Fe<sub>2</sub>O<sub>3</sub> concentration is highest in the jarosite-rich samples (Table 2), which makes sense since jarosite contains Fe and none of the other non-clay minerals in the assemblage do.

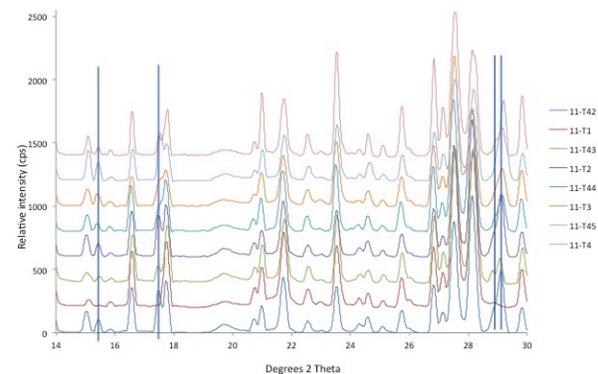


Figure 2: Diffraction patterns (14-30° 2 Theta) for all eight 2011 samples. Blue lines indicate jarosite peaks. Note the similarity between the patterns for the other peaks- the main difference between the samples is jarosite abundance.

**Table 1: Rietveld % of non-clay minerals**

Sample	Orthoclase	Anorthoclase	Phillipsite	Analcime	Jarosite
11-T42	20.2	26.3	43.8	2.9	5.8
11-T1	21.1	30.1	45.0	3.3	0.6
11-T43	24.5	27.1	44.1	2.7	1.6
11-T2	27.4	27.8	41.1	3.2	0.4
11-T44	22.5	29.4	42.7	2.7	2.7
11-T3	25.1	34.3	34.1	2.9	3.7
11-T45	25.3	28.7	34.8	3.2	7.9
11-T4	33.1	29.5	32.0	3.3	2.1

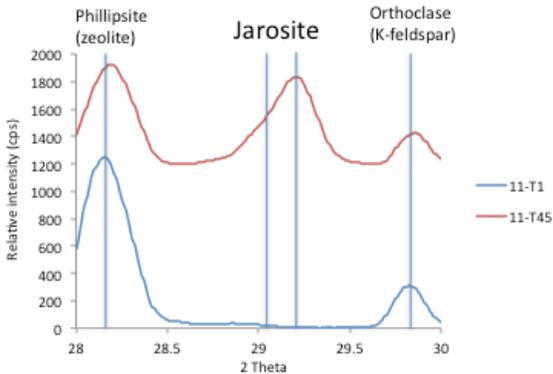


Figure 3: Zoom on the diffraction pattern (28-30° 2 Theta) for a jarosite-free (11-T1) and a jarosite-rich (11-T45) sample from 2011.

**Table 2: XRF results and jarosite abundances**

	11-T1	11-T2	11-T3	11-T4	11-T42	11-T43	11-T44	11-T45
SiO <sub>2</sub>	60.17	61.95	57.58	59.97	53.92	59.70	58.08	50.32
TiO <sub>2</sub>	0.29	0.29	0.32	0.30	0.22	0.29	0.31	0.28
Al <sub>2</sub> O <sub>3</sub>	16.42	16.74	15.75	16.30	14.76	15.75	16.13	14.30
Fe <sub>2</sub> O <sub>3</sub>	4.19	2.51	6.32	4.44	8.34	5.04	5.20	9.90
Mn	0.03	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	0.52	0.58	0.76	0.60	0.72	0.69	0.58	0.69
CaO	0.12	0.12	0.25	0.13	0.08	0.10	0.11	0.11
Na <sub>2</sub> O	4.40	4.46	3.92	3.56	4.01	3.91	4.18	3.17
K <sub>2</sub> O	8.44	9.05	8.87	9.82	8.38	8.87	8.81	8.95
P <sub>2</sub> O <sub>5</sub>	0.05	0.05	0.06	0.06	0.07	0.06	0.06	0.07
LOI	5.26	4.73	5.27	5.58	8.55	5.49	6.27	10.11
Total	100.01	100.63	99.28	100.93	99.22	100.08	99.89	98.07
Jar %	0.63	0.42	3.70	2.10	5.81	1.56	2.74	7.93

**Discussion:** The presence of saline-alkaline minerals (phillipsite, analcime, authigenic K-feldspar) points towards long-term saline-alkaline conditions, and modern groundwater analyzed from nearby springs yields a pH of ~9.5 [7]. Since jarosite typically forms at much lower pH [e.g. 8], its presence in this type of deposit is unexpected. Our favored mechanism for its formation is the oxidation of lacustrine pyrite from the surrounding paleolake deposit. While we have yet to observe actual pyrite in the paleolake beds, we do occasionally find cube-shaped, rust-colored voids that were likely once pyrite in the surrounding claystones. Pyrite oxidation would supply sulfur, iron, and the locally low pH conditions needed for jarosite formation in pore spaces, even under larger scale saline-alkaline conditions [7].

The dramatic variation in jarosite abundance observed in the 2011 samples points to spatial heterogeneity. Within a single layer over two meters we see a randomly distributed range from barely detectable to abundant jarosite, which would make sense if the jarosite results from very localized condition changes. While it is possible that the jarosite abundance does

change seasonally or year-to-year, with the currently available samples this cannot be separated from a purely spatially-controlled, long-lasting occurrence of jarosite. No obvious association between jarosite occurrences and cracks or other distinctive features was observed.

**Future research** will involve re-sampling all eight sampled spots in August 2012 to see if any annual changes are discernable, plus the analysis of the 2011 sample series by FTIR and Mössbauer for comparison to the 2006-2010 samples [7] and MER Opportunity results. We will also determine the sulfur concentrations of the 2011 samples and observe the textural associations between the jarosite and zeolite minerals using SEM. Further sampling, XRD analysis, and SEM imaging will also address the potential presence of pyrite or pseudomorphs after pyrite in the surrounding claystones.

**In conclusion,** the more detailed sampling in 2011 lends support to the hypothesis that the inter-sample variability in jarosite abundance is due to spatial variability rather than temporal variability. The age and longevity of the jarosite is unconstrained, and its distribution is likely attributable to the availability of the appropriate ingredients along cracks or in association with unevenly distributed sources of iron (lacustrine pyrite?).

The Olduvai jarosite occurrence differs substantially from that observed at Meridiani Planum, in the overall chemical composition, the rest of the authigenic mineral assemblage, and other indicators of low vs. high pH. However, it does illustrate that jarosite can form under diverse conditions on Earth and that its presence alone cannot show for certain that overall regional-scale conditions were acidic. Localized, small-scale occurrences of jarosite can occur and persist under quite varied more global conditions.

**References:** [1] Klingelhöfer G. et al. (2004) *Science* 306, 1740-1745. [2] Milliken, R.E. et al. (2008) *Geology* 36, 847-850. [3] Wray J.J. et al. (2009) *Geology* 37, 1043-1046. [4] Farrand, W.H. et al. (2009) *Icarus* 204, 478-488. [5] Knoll A.H. et al. (2005) *EPSL* 240, 179-189. [6] Elwood Madden et al. (2009) *Geology* 37, 635-638. [7] McHenry, L.J., Chevrier, V., Schröder, C. (2011) *JGR* 116, E04002. [8] Morris R.V. et al. (2006) *JGR* 111, E12S15.