

## TRACE ELEMENT CRYSTAL CHEMISTRY OF JAROSITE: AN ION MICROPROBE PILOT STUDY

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### Introduction

Jarosite on the martian surface was first identified in a jarosite/hematite rich outcrop at Meridiani Planum by the Opportunity Rover [1]. Papike et al. [2,3,4] reviewed the potential of martian jarosite as a recorder of rock-fluid interactions by using terrestrial examples. Understanding the trace element crystal chemistry of terrestrial jarosite will further our understanding of martian near-surface processes and our ability to better interpret current martian surface data sets. Here, we discuss the approach behind the microbeam trace element analysis of jarosite from two terrestrial hydrothermal environments on Earth, the trace element crystal chemistry of jarosite, and relevance to Mars.

### Major Element Crystal Chemistry of Jarosite

The general formula for jarosite is  $AB_3(XO_4)_2(OH)_6$  [2] where A is a 12-fold coordinated site that can contain monovalent cations such as K, Na, and Rb, divalent cations such as Ca, Pb, Ba, and Sr, and trivalent cations such as the REE. The B position represents an octahedrally coordinated site that usually contains trivalent Fe and Al, but can include Zn and Mg. The X position represents the tetrahedrally coordinated site and contains S, P, As, Sb, V and Mo. The major element compositions of the terrestrial jarosites analyzed in this study can be predominantly represented within the compositional space defined by alunite ( $KAl_3(SO_4)_2(OH)_6$ ), natroalunite ( $NaAl_3(SO_4)_2(OH)_6$ ), jarosite ( $KFe^{3+}_3(SO_4)_2(OH)_6$ ) and natrojarosite ( $NaFe^{3+}_3(SO_4)_2(OH)_6$ ).

### Analytical Parameters

**Electron Microprobe** – Samples were initially documented using backscattered electron imaging (BSE) at an accelerating voltage of 15 kV and a beam current of 10 nA, using UNM's JEOL 8200 electron microprobe. Once suitable regions were identified, wavelength dispersive (WDS) scans were conducted to determine the major and minor element composition of the jarosite crystals. Spectrometer configurations were optimized for the chosen elements, and standardized using Taylor mineral standards. Spot analyses were gathered using a 10  $\mu$ m beam.

**SIMS** – Iron, trace elements (Sr, Ba, Th) and REE (La, Ce, Nd, Sm, Eu, Dy, Er and Yb) were analyzed on the Cameca 4f secondary ion mass spectrometer at the Institute of Meteoritics at the University of New Mexico. Intensities were normalized to  $^{54}Fe$  intensities and total Fe; total Fe was independently determined by electron microprobe. Analytical spots were chosen to coincide with electron microprobe points, and a primary accelerating voltage of 10 kV, a beam current of 20 nA, and a voltage offset of -75 V were used during analyses. Several standards were used to obtain a calibration curve including the NIST-610 glass standard, WU A and B, and basaltic glass standards KL2 and ML3B. Sr, Ba and Th were each individually calibrated, while one curve, defined by the basaltic glass standards, was used for all of the REE. A homogenous Peña Blanca jarosite was used as a secondary standard to evaluate the relevance of the glass calibration. Due to a high Ba concentration in the unknowns, there was a substantial BaO interference on Eu. By

comparing each of the Eu isotopes intensities with Ba intensity, we determined that the Eu concentration is 0.45 ppm at a minimum (or 4.63 times greater than CI) in the case of the Apex Mine sample, but cannot place more precise constraints at this time. Future analyses will incorporate a more robust Ba correction. Ba in the Peña Blanca sample is low, therefore, the Eu concentration measured for this sample is likely more robust. Additionally, Gd for each of the samples was inferred using the slope of line defined by La and Dy.

### Results

**Major Elements in Jarosite** – Both Peña Blanca and Apex Mine have similar major element compositions; Peña Blanca and Apex Mine have an average  $Fe_2O_3$  concentration of 45.2 wt.% and 48.2 wt.% with very little (<1.3 wt.%) standard deviation in both cases (Table 1). Both jarosite samples show minimal deviation from the jarosite endmember composition. Apex Mine analyses indicate an elevated amount of  $Na_2O$ ; average concentration is ~1.15 wt.%, and values as high as 1.5 wt.% occur at the periphery of the vein, with lower concentrations (~0.6 wt.%) occurring in the interior (Fig. 1). Peña Blanca has a slightly higher concentration of  $Al_2O_3$ , where average values are ~1.48 wt.%, in comparison to ~0.03 wt.% in Apex Mine.

**Trace Elements in Jarosite** – In both Peña Blanca and Apex Mine, V concentration was below the detection limit. As was similar in both samples, approximately 1042 ppm and 1313 ppm in Peña Blanca and Apex Mine, respectively. Other minor and trace elements show more variability. Peña Blanca has ~1461 ppm Mo, while it was below the detection limit in Apex Mine. Sr was lower in Peña Blanca, with an average concentration of 9 ppm, and ranged from 17 ppm in the interior of the jarosite vein in Apex Mine, to ~33 ppm at the periphery of the vein. Ba was also low in Peña Blanca, with an average of 4 ppm, whereas Apex Mine had an average of 706 ppm in the center of the vein, down to 201 ppm

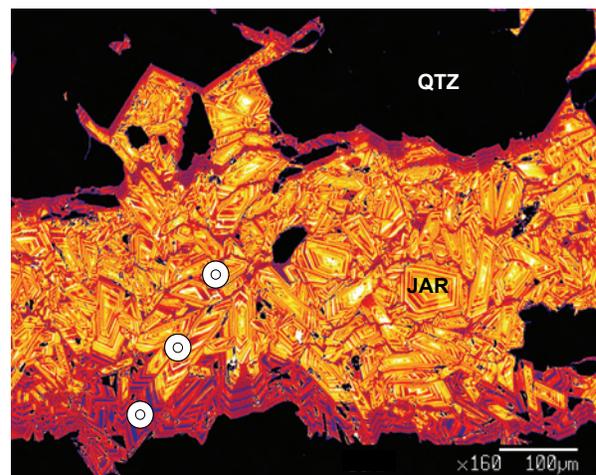


Figure 1. False-color BSE image of jarosite vein in Apex Mine. SIMS analyses are indicated by white circles. Increased Na concentration is apparent at the periphery of the grain, where colors are darker than at the center.

<b>Major Elements by EMP, measured in Wt.%</b>			
	Peña Blanca		Apex Mine
Al <sub>2</sub> O <sub>3</sub>		1.48	0.03
SO <sub>3</sub>		31.58	31.08
Na <sub>2</sub> O		0.02	1.15
Fe <sub>2</sub> O <sub>3</sub>		45.24	48.20
K <sub>2</sub> O		9.31	7.03
CaO		0.00	0.00
F		0.00	N/A
Cl		0.01	0.01
H <sub>2</sub> O		11.97	9.17
<b>Total</b>		<b>100.00</b>	<b>100.00</b>

<b>Minor Elements by EMP, measured in PPM</b>			
	Peña Blanca		Apex Mine
P		27.88	246.45
V		b.d.	b.d.
As		1042.39	1313.09
Mo		1460.82	b.d.

<b>Trace Elements and REE by SIMS, measured in PPM</b>				
	Peña Blanca	Apex Mine		
	Average	Inner	Middle	Outer
Sr	8.96	16.94	24.50	33.25
Ba	3.80	706.49	311.25	200.78
La	0.35	0.98	0.63	0.31
Ce	0.08	0.07	0.07	0.03
Nd	0.09	0.28	0.25	0.14
Sm	0.07	0.19	0.18	0.08
Eu	0.08	0.45	0.45	0.45
Dy	0.07	0.08	0.11	0.06
Er	0.04	0.07	0.06	0.04
Yb	0.06	0.06	0.09	0.06
Th	0.13	0.10	0.07	0.06

Table 1. Major, minor, trace and REE compositions of Peña Blanca and Apex Mine. Eu concentration for Apex Mine represents a minimum value, b.d. = below detection.

(cont.) at the periphery. Th was similar in both samples, Peña Blanca had an average of 0.13 ppm, whereas Apex Mine ranged from 0.1 to 0.06 ppm from center to periphery. REE (Fig. 2) also showed systematic variation in Apex Mine, from most enriched at the center of the vein, to lower concentrations toward the periphery (Fig. 3). Jarosites from both locations have a flat REE pattern with the exception of a negative Ce anomaly and a positive Eu anomaly. Results are in general agreement with bulk INAA analyses conducted on our jarosite sample, with the exception of Sm which seems to be higher in our observations in comparison to INAA (Fig. 3).

### Discussion

**Trace Element Crystal Chemistry of Jarosite** – It is apparent from the observations that fluid chemistry plays an important role in determining the trace element compositions of jarosite. Mo shows the greatest variability between the two jarosite samples and appears to reflect the provenance of the samples. Sr and Ba appear to be more closely linked to fluid chemistry; both of these elements show a correlation and vary systematically from the center of the vein in Apex Mine, toward the periphery of the vein. This may reflect a

change in fluid chemistry with increased jarosite precipitation, and is complemented by the increase in Na concentration at the boundary of the vein, observed by the electron microprobe analyses (Fig. 1). The Ce and Eu anomalies in the REE patterns of the jarosites reflect the conditions under which jarosite crystallized and the fluid composition. Under the oxidizing conditions of jarosite precipitation, significant Ce will exist as Ce<sup>4+</sup> (~0.97 Å) rather than Ce<sup>3+</sup> (1.29 Å). The Ce anomaly could potentially represent contrasting behavior of Ce<sup>4+</sup> vs. REE<sup>3+</sup>. Alternatively, and perhaps more likely, Ce<sup>4+</sup> may have been depleted in the solution due to the precipitation of another phase (e.g. Mn oxides) [5] prior to jarosite precipitation. Eu likely exists as Eu<sup>3+</sup> in these oxidizing environments, therefore, the Eu anomaly does not reflect preferential partitioning of different Eu valences. It is more likely that the Eu anomaly is a fingerprint of the fluid and reflects an earlier stage in fluid evolution.

**Relevance to Mars Surface Processes** – This study illustrates the potential of trace elements in jarosite for fingerprinting the evolution of martian fluids. Additionally, Th analyses suggest that the Th concentration in jarosite is relatively low and therefore does not make a substantial contribution to the Th abundance observed by Mars Odyssey in the martian regolith [6,7,8,9].

### References

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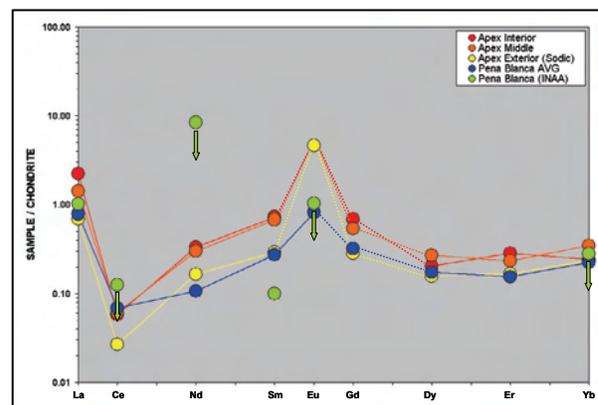


Figure 2. REE concentration of Apex Mine and Peña Blanca. Dashed lines connect inferred concentrations, arrows suggest possible concentration range as measured by INAA.