

ENCODING OF WATER-ROCK-ATMOSPHERE INTERACTIONS IN JAROSITE: IMPLICATIONS FOR MARS. V. W. Lueth, New Mexico Bureau of Geology & Mineral Resources, New Mexico Tech, 801 Leroy Place, Socorro, NM 87801, vwlueth@nmt.edu

Introduction: The reported existence of jarosite, $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$, on Mars provides an exciting opportunity to study water-rock-interactions on the planet's surface. Low pH and a highly oxidizing environment are required for the formation of the mineral. Jarosite can form in a variety of environments ranging from hydrothermal (hypogene) to surface weathering (supergene). Each environment of formation appears to encode a unique stable isotope [1], textural [2], and microchemical signature [3]. In addition, the ability to date the mineral by K/Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ methods [4] allows the opportunity to study the timing of processes responsible for the formation of the mineral.

Stable Isotope Characteristics: The stable isotope values for sulfur, hydrogen and oxygen in both the SO_4 and OH sites can be measured with precision. Individual preparation techniques are required for the determination of $\delta^{34}\text{S}$, $\delta^{18}\text{O}_{\text{SO}_4}$, $\delta^{18}\text{O}_{\text{OH}}$, and δD values.

Sulfur: Sulfur isotope analyses can be used to ascertain origin of the sulfur in jarosite (Fig. 1).

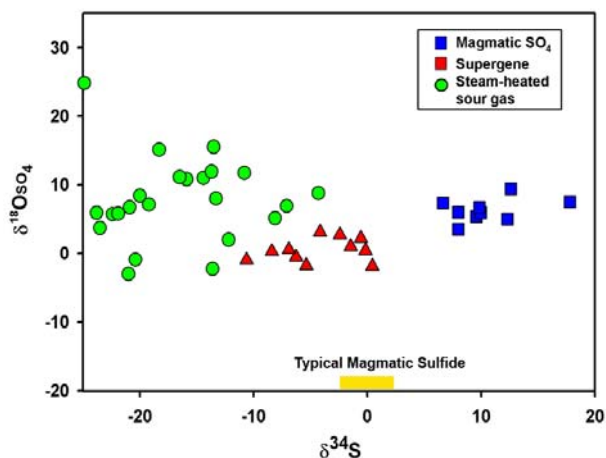


Figure 1 - $\delta^{34}\text{S}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ plot for sulfate minerals from various geological environments. Blue squares represent magmatic gypsum, anhydrite, and alunite. Red triangles are supergene jarosites. Green dots represent jarosites from steam-heated sour gas deposits. All values as ‰ relative to their appropriate standard.

Weathering or supergene types reflect the $\delta^{34}\text{S}$ value of the preexisting sulfide [5,6]. In magmatic systems the value for the precursor sulfide is around 0 ‰ (CDT). If the sulfur in jarosite is derived from H_2S in the hydrothermal environment (steam-heated [1]), it

should reflect the same value as the precursor H_2S unless exchange occurs with aqueous sulfate prior to formation of the jarosite.

Oxygen: Oxygen in the SO_4 site reflects the source of oxygen during oxidation of the sulfide. This value will depend on whether water or air provides the oxygen and if any biogeochemical (microbial) processes are involved. Earlier workers defined an important reference field, the supergene jarosite field (SJSF) [1], for almost all weathering derived jarosites. Jarosites from Lake Tyrell, Australia, are an exception. These samples show significant shifts in both oxygen and hydrogen as a result of equilibration of aqueous sulfate with low pH, highly evaporated water [7]. Hydrothermal jarosites have $\delta^{18}\text{O}_{\text{SO}_4}$ values that typically plot outside the SJSF. Comparison of supergene and hypogene jarosite of similar ages illustrates how oxygen and hydrogen isotopes discriminate between supergene and hypogene jarosite (Fig. 2).

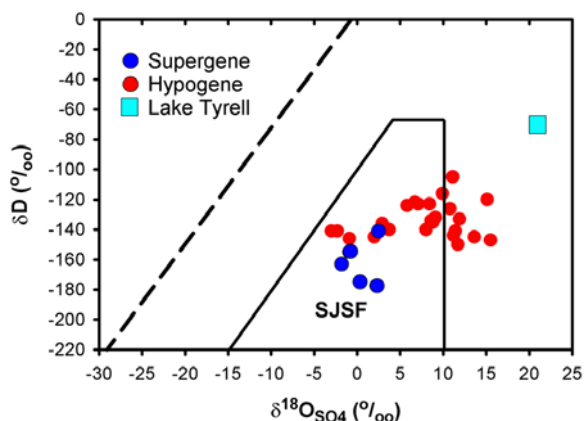


Figure 2 - δD and $\delta^{18}\text{O}_{\text{SO}_4}$ plot for jarosites from various geological environments. Data for Lake Tyrell from [7]. Supergene data from [6] and hypogene data from [4]. See [1] for definition of the SJSF and for additional data for hypogene (steam-heated) and supergene jarosites. Dashed line represent meteoric water line.

Oxygen in the OH site is more complex and reflects the character of the parent fluid, equilibrium exchange processes, and temperature. Most $\delta^{18}\text{O}_{\text{OH}}$ values should plot in a band parallel to the meteoric water line for supergene types. In conjunction with $\delta^{18}\text{O}_{\text{SO}_4}$ it can be used as a single mineral geothermometer [8, 4].

Hydrogen: δD values are controlled by similar processes as those for $\delta^{18}O_{OH}$. Importantly, if equilibrium exchange can be established, both δD and $\delta^{18}O_{OH}$ can be used to infer palaeoclimatic conditions. If temperatures can be constrained by other methods, or assumed, the isotopic composition of the water in equilibrium with the jarosite can also be calculated in conjunction with $\delta^{18}O_{SO_4}$.

Texture and Paragenesis: Specific mineral textures, associations, and paragenetic sequences are characteristic of different environments of jarosite formation. Typically jarosite appears within a specific paragenetic sequence that also includes goethite/hematite and gypsum.

Supergene. Jarosite is finely crystalline with the largest crystallites up to approximately 1mm often intermixed with hypogene phases, especially quartz and clays. Jarosite is early in the supergene paragenesis then alters to goethite and gypsum with subsequent weathering. Supergene jarosites are often destroyed at the surface unless fortuitously preserved.

Hypogene. Large crystals (up to 3 cm) or crystalline masses characterize hypogene jarosite occurrences. Common mineral impurities encountered in these samples are other ore/gangue minerals like barite, fluorite, and quartz. The mineral paragenesis is opposite that of supergene environments where hematite (rather than goethite) and gypsum are typically replaced by jarosite sometimes with apatite.

Chemistry: Most jarosites are typically pure end-members, even when both jarosite and natrojarosite occur together. In supergene types, oscillatory banding of jarosite and natrojarosite is common [9]. In hydrothermal types greater solid solution is apparent, consistent with thermodynamic predictions.

Studies correlating trace element compositions to specific geologic/geochemical environments have recently been initiated and may provide a fruitful avenue for characterizing jarosite. A wide variety of trace elements have been shown to be accommodated into the jarosite structure [9]. For example, arsenic is fairly abundant (up to 12,000 ppm) in hypogene steam-heated sour gas type jarosites [4]. Phosphorous, vanadium, and molybdenum have also been documented in jarosite and may be specific to particular types of mineralization.

$^{40}Ar/^{39}Ar$ Geochronology: The chemistry and structure of jarosite allows for reliable age dating [11, 4]. The grain size, contaminants, and composition have significant affect on the analytical spectra (Figure 3). Small crystallite sizes and incorporation of other minerals results in less than optimal age spectra. Poor crystallinity, recoil, Ar loss, and contamination are

endemic to supergene samples. Difficult and sophisticated separation techniques and chemical treatments are required to obtain reliable results. Samples from the surface of Mars will probably require similar types of separation techniques to produce reliable age dates.

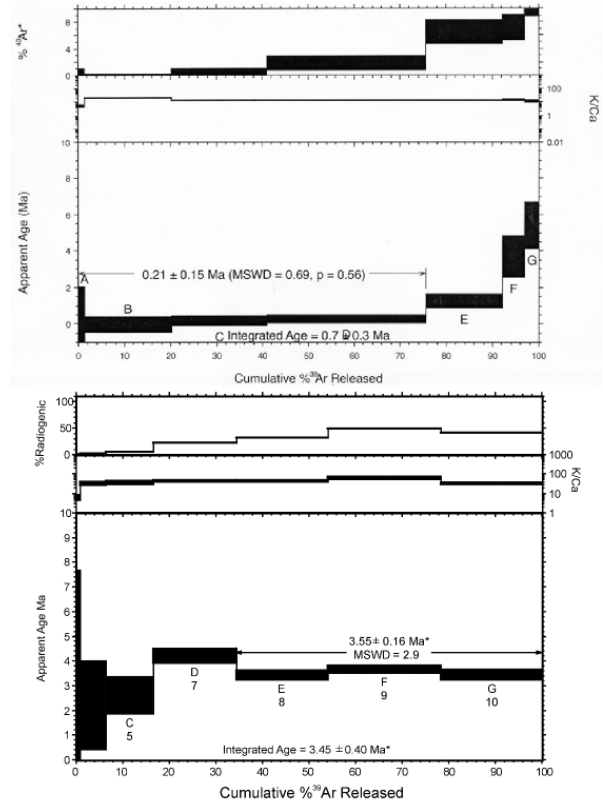


Figure 3 - Comparison of Ar spectra for supergene (top) and hypogene (bottom) jarosites [2]. Note the lower radiogenic yields for supergene types (top most plot) and greater analytical error. The “stepping up” of the apparent age for the supergene jarosite also suggests contamination of the sample by older clays.

Geochemical, geochronological, and stable isotope studies on jarosite from returned samples is a potentially powerful tool for characterizing past water-rock-interactions on the Martian surface.

References: [1] Rye and Alpers, 1997, *USGS OFR* 97-88. [2] Lueth (2006) *LPIC* #1331, p.51. [3] Papike et al. (2007) *Am. Mineral.* 92, 444-447. [4] Lueth, et al. (2005) *Chem. Geol.*, 215, 339-360. [5] Field (1966) *Econ. Geol.* 61, p. 1428-1435. [6] Campbell and Lueth (2008) *Appl. Geochem.* 23, p. 308-319. [7] Alpers et al. (1992) *Chem. Geol.* 96, p. 203-226. [8] Rye and Stoffregen (1995) *Econ. Geol.* 90, p. 2336-2342. [9] Papike et al. (2007) *Am. Min.* 92, p. 444-447. [10] Vasconcelos et al. (1994) *Geochim. Cosmochim Acta* 85, p. 401-420.