

MECHANISMS FOR JAROSITE FORMATION AT CRYOGENIC TEMPERATURES ON MARS. P. B. Niles¹, Barbara Delmonte², Giovanni Baccolo², Christopher Snead³, Lindsay Keller¹, Joseph Michalski⁴ ¹NASA Johnson Space Center, Houston, TX 77058 (paul.b.niles@nasa.gov), ²Department of Environmental Sciences, University of Milano-Bicocca, Piazza della Scienza 1, 20126, Milano, Italy ³Jacobs, NASA Johnson Space Center, Houston, TX 77058; ⁴Department of Earth Sciences, University of Hong Kong, Hong Kong.

Introduction: Jarosite was one of the first minerals identified by the Opportunity rover at Meridiani Planum[1] and was ubiquitous within the outcrops investigated across most of the rover's 45 km traverse. Since the discovery by Opportunity, substantial new discoveries of jarosite on Mars have been made across the surface from orbital remote sensing as well as the Curiosity Rover in Gale crater[2]–[5]. Jarosite typically occurs within layered deposits and is frequently associated with the presence of other sulfate phases. Burns [6] proposed jarosite as a likely mineral to be present on Mars based on its extremely low solubility and the possibility that Fe(3+) hydrolysis on Mars was likely to occur in sulfate-rich solutions. In particular jarosite formation typically signals the presence of a low pH aqueous environment and the abundance of basaltic minerals, especially olivine, on Mars. Such conditions create an apparent paradox because basalt and olivine will act to neutralize acidic solutions and prevent jarosite formation[7]. This paradox is easily resolved if the jarosite deposits are either localized or derived from very short lived aqueous activity. Therefore, the challenge for Mars is to understand a global-scale process that deposits widespread layered, altered materials containing jarosite, while maintaining low activity of water.

The accumulation of sublimation residue from ice deposits is a well-recognized physical sedimentary process for creating widespread deposits on the martian surface, and ice/dust deposits have been proposed to provide an environment that could facilitate acidic weathering through cryoconcentration of sulfur-rich volcanic aerosols [8]. Experimental evidence shows that weathering rates of olivine are actually elevated at temperatures as low as -60° C [9]. However, because the experimental approach is challenging, jarosite formation has not yet been shown to be favored or even possible in this environment, even on Earth. Here we present definitive identification of abundant jarosite from mineral grains collected from an Antarctic ice core at depths of >1500 m. The ice core has been obtained at Talos Dome, an ice dome located in Northern Victoria Land (East Antarctica).

Methods: Mineral dust particles were extracted from sections of the TALDICE ice core. At Talos Dome, dust deposition is influenced by proximate active volcanic centers and doleritic-basaltic rock outcrops[10], [11]. SEM analysis of mineral dust through-

out the core was conducted at the EUROCOLD laboratory of the University Milano-Bicocca. Additional analyses were carried out on a selected dust sample from ice core sections at 1559 m depth. Ice at this depth was decontaminated, melted, and filtered through an Isopore 0.4 µm PC membrane under very clean conditions (ISO5) at the University of Milano-Bicocca. Two grains with reddish surface deposits were then picked from the filter and mounted embedded in low-viscosity epoxy for ultramicrotomy at NASA Johnson Space Center. Ultramicrotomed sections ~50 nm thick were analyzed on a JEOL 2500SE scanning and transmission electron microscope (STEM) equipped with a JEOL silicon drift detector for quantitative energy-dispersive X-ray (EDX) analyses.

Results: SEM analyses of mineral particles in the deeper sections of the core showed evidence for alteration including apparent precipitates forming on grain surfaces (Fig 1). These precipitates were not present on grains from shallower sections and showed enrichments in Fe, K, and S while the grain cores were commonly Si and Al rich (Fig 2). TEM analyses on two grains confirmed the presence of jarosite as sprays/rosettes of bladed crystals with diffraction spacings and chemical compositions consistent with jarosite (Fig 3). The jarosite crystals contain minor Al and P.

Discussion: The evidence from these preliminary analyses of the Talos Dome ice core shows definitive evidence for the presence of jarosite, and SEM analyses indicate that the jarosite is likely to be a common weathering product in deeper portions of the core. Fe-K-edge absorption shows steady increase with depth in the core indicating a progressive Fe-oxidation. The trend does not correlate with climate signals or dust content, suggesting a role played by post-depositional processes occurring *in situ* within the ice core itself[12]. The location of the Talos Dome ice core near volcanic centers and doleritic-basaltic outcrops provides a suitable comparison to Mars – in particular at 1500 m depth it is likely that the environment would be similar on Earth and Mars.

Thin film fluids at depth inside of Antarctic ice cores have been shown to be dominated by H₂SO₄ created by cryo-concentration of acidic aerosols[13]. At increasing depth, spatial chemical sorting of the impurities within the ice matrix occurs in tandem with progressive migration of dust grains and build-up of aggregates[14]. This environment, where volcanic dust

and sulphate-rich compounds meet, is clearly suitable for acid weathering and jarosite precipitation as the low temperatures preserve acidic environments and isolate them from the surrounding ice matrix. Similar conditions are found on Mars today and in fact its polar regions show enrichments in sulfate-rich material[15].

On Mars, volcanic and impact-generated dust would have been common, and ice deposition was also common throughout the planet's history. In the absence of a vigorous global hydrosphere, it is inescapable that ice/dust deposition would have been a driving sedimentary process, likely resulting in thick deposits of acidic, "dirty" ice. This could be a significant environment for jarosite formation on Mars throughout its history.

Conclusions: The existence of widespread jarosite on Mars almost certainly requires that aqueous activity remained short-lived and that the acidic solutions were prevented from long duration exposure to basaltic crustal materials. This can be accomplished through closed system weathering of dust grains by small amounts of immobile fluids inside of ice deposits as supported by our investigation of mineral dust from deep Antarctic ice.

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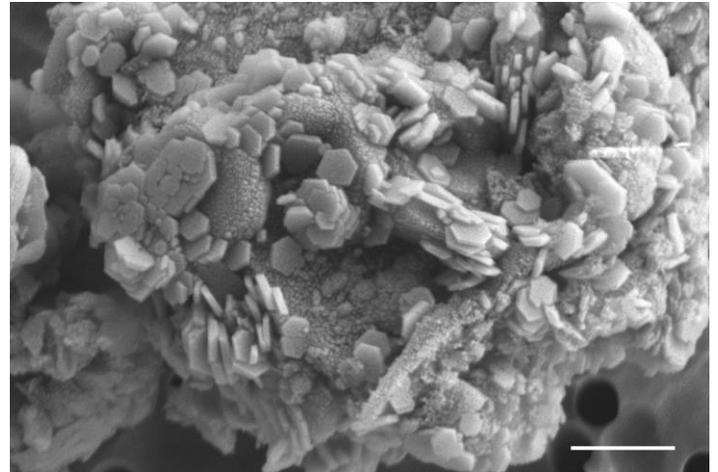


Figure 1. Secondary electron image of typical mineral grain from the deeper sections of Talos Dome ice core. Scale bar is 1 μm . Based on TEM results, hexagonal crystals are likely to be jarosite.

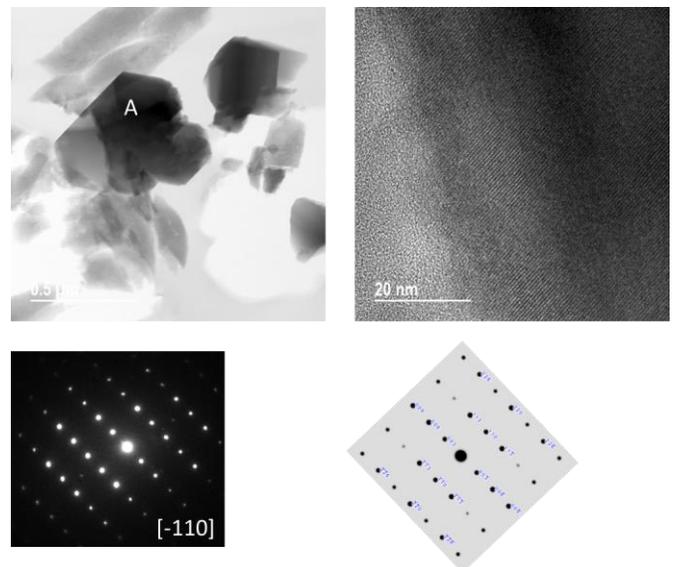


Figure 2. Brightfield STEM image and a selected area electron diffraction pattern from the crystal labeled A. The SAED pattern is from the $[-110]$ zone axis of jarosite.