

CRYSTALLOGRAPHY ON MARS: IDENTIFICATION OF CRYSTALLINE ANHYDRITE AS A SECONDARY MINERAL FILLING CAVITIES AND VEINLETS IN THE WESTERN JEZERO DELTA FRONT. M. W. M. Jones¹, D. A. Flannery², B. J. Orenstein², J. A. Hurowitz³, D. C. Catling⁴, M. M. Tice⁵, A. C. Allwood⁶, C. Heirwegh⁶, B. C. Clark⁷, S. J. VanBommel⁸, and A. L. Knight⁸, ¹School of Chemistry & Physics and Central Analytical Research Facility, Queensland University of Technology, Brisbane, QLD 4000, Australia, ²School of Earth & Atmospheric Sciences, Queensland University of Technology, Brisbane, QLD 4000, Australia, ³Department of Geosciences, Stony Brook University, Stony Brook, NY 11794-2100, USA, ⁴Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195, USA, ⁵Dept. of Geology & Geophysics, Texas A&M University, College Station, TX 77843, USA, ⁶Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109, USA, ⁷Space Science Institute, Boulder, CO 80301, USA, ⁸McDonnell Center for the Space Sciences, Department of Earth and Planetary Sciences, Washington University of St. Louis, St. Louis, MO 63130, USA, ⁹Department of Earth and Planetary Sciences, Washington University of St. Louis, St. Louis, MO 63130, USA.

Introduction: We investigate sulphate veinlets and masses from two abraded patches in outcropping sedimentary rocks of the Jezero delta front (Berry Hollow and Uganik Island) using the PIXL instrument (Planetary Instrument for X-ray Lithochemistry) on the Perseverance rover [1]. Analysis of the diffraction data [2,3] collected in the two energy-dispersive X-ray detectors using a forward simulation look up table method [4] provides in-situ crystallographic orientation information for the first time on Mars. This analysis revealed crystalline anhydrite (CaSO₄) that, combined with a suite of additional analyses, we interpret as the result of secondary cavity-filling cements after removal of a more soluble precursor material that formed earlier in the authigenic/diagenetic history of these rocks. Precipitation of crystalline anhydrite implies a fluid that had low water activity, was warm, or both.

Diffraction Peak Identification and Crystal Orientation: Investigation of the raw spectra reveals diffraction in one detector (det A) at an energy of ~2.71 keV, which for the PIXL geometry corresponds to a d-spacing of ~2.33 Å in thin, hairline veinlets (0.1-0.2 mm wide by >15 mm long) in the Berry Hollow target. A similar peak is observed in thicker (up to 1 mm wide and 7 mm long) veins and equant masses at Uganik Island, and a second peak, at ~3.31 keV corresponding to a d-spacing of ~1.90 Å is also observed in some Uganik Island spectra. Further investigation of diffraction in PIXL can be done using a forward simulated look up table (LUT), which is used in determining crystallographic orientations from low quality Laue diffraction data [4]. Creating a forward simulation LUT for gypsum (CaSO₄·2H₂O), bassanite (CaSO₄·½H₂O), and anhydrite for PIXL reveals that the observed diffraction at around 2.7 keV is from the anhydrite (202) reflection, with the crystal orientation in one of two directions. No single orientation from gypsum, bassanite or anhydrite matches both peaks observed at Uganik Island, therefore the peaks must come from two populations of crystallites. Treating the two Uganik

Island peaks independently reveals two anhydrite populations aligned orthogonally to the vein wall. LUT simulations do not match any random orientations, suggesting the anhydrite crystallite vein is highly ordered/aligned on a common c-axis.

Anhydrite Textures and Petrogenesis: Crystal textures were examined by mapping roughness-corrected excess counts in the energy range between ~2.46-2.97 keV [5] (**Fig. 1**). A large veinlet and a cm-scale equant mass in Uganik Island contain thin (<120 µm) rims of anhydrite showing diffraction peaks at 2.7 keV detected in det A, det B, or both, with detection in the same detector persisting for up to ~800 µm along the rims. Contiguous regions become larger in the interior of the mass and are not concentrically organized with respect to the rim. This pattern is inconsistent with crystal growth from the center out to the rims, but most likely reflects growth of an initially isopachous and fibroradial cavity-lining rim followed by infilling with blocky crystallites. Observed diffraction patterns thus imply that anhydrite in this part of the delta front formed as a secondary cavity-filling precipitate after removal of an unknown early diagenetic material.

An estimate of the bulk chemical composition of the large mass in Uganik Island (**Table 1**) required consideration of the following factors: 1) To avoid mixing effects with the surrounding rock, XRF analysis points interior to the mass were selected; 2) Na has significant diffraction-related effects in this target that result in an overestimate of its abundance, and was set to 0; 3) high total element abundances (108 wt%) remaining after Na-subtraction, which likely result from diffraction-related effects on our model of the Rh-background, were dealt with by normalizing to 100%.

Subtraction of CaSO₄, SrSO₄, and MgSO₄ yields a residuum composition (**Table 1**). This residuum may reflect a small quantity (<10 wt%) of Mg-Al silicate derived from the host rock during fluid migration through fractures but does not constrain the composition of the anhydrite precursor.

TABLE 1. UGANIK ISLAND CAVITY FILL

	Bulk* (wt%)	Residuum (wt%)
N=226 spots		
MgO	3.21	1.37
Al ₂ O ₃	1.23	1.23
SiO ₂	4.19	4.19
SO ₃	54.6	0
Cl	0.61	0.61
K ₂ O	0.03	0.03
CaO	35.6	0
TiO ₂	0.01	0.01
MnO	0.01	0.01
FeO _T	0.28	0.28
SrO	0.11	0
TOTAL	99.9	7.73

*Na₂O removed from bulk composition and remaining abundances normalized to 100% to correct for diffraction.

Diagenetic Conditions During Anhydrite Precipitation: Calcium sulphate can exist in three different hydration states: gypsum, hemihydrate or bassanite, or anhydrite. In turn, anhydrite can exist in phases I-III [6]. However, cubic anhydrite I is unstable below 1180 °C and turns into stable, orthorhombic anhydrite II. Also, anhydrite III is metastable and converts into anhydrite II with heating or hydrates to bassanite. Consequently, anhydrite II is the expected stable phase on Mars, consistent with our findings.

Anhydrite II ('anhydrite') sets constraints on the paleoenvironment of its formation because it is thermodynamically favored by warmth and/or low water activity. The thermodynamic transition temperature producing anhydrite rather than gypsum (*via* $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(s) \rightleftharpoons \text{CaSO}_4(s) + 2\text{H}_2\text{O}(l)$) is ~40–60 °C in dilute solutions, or ~18 °C in saturated sodium chloride solution (11). In the subsurface, the geothermal gradient can reach the transition temperature, making anhydrite rather than gypsum common below ~400 m depth on Earth, especially in more ancient rocks [7]. On the other hand, because of heat and/or low water activity, anhydrite is found in Earth's near-surface in tropical sabkhas (coastal supratidal plains) [8, Chap. 3]. But even in today's surface conditions on Mars, gypsum should be stable against dehydration to anhydrite [9], suggesting a mechanism other than simple surface dehydration from gypsum exposure to form martian anhydrite veins. The slow crystallization kinetics of anhydrite relative to the other CaSO₄ salts complicates the simple picture deduced from thermodynamics; nonetheless, warmth and/or low water activity remain robust general conditions for anhydrite formation.

Two other factors relevant to anhydrite formation concern its solubility. First, anhydrite has retrograde solubility, i.e., less solubility at warmer temperatures.

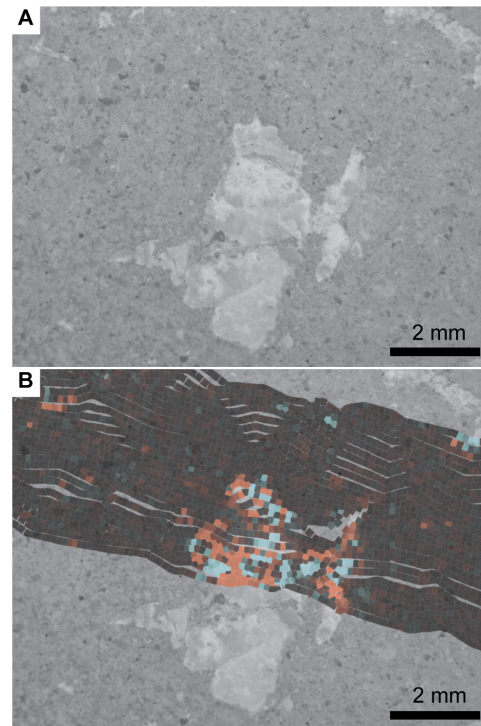


Figure 1. Diffraction peak detections in anhydrite masses. **A)** WATSON mosaic showing light-toned anhydrite mass and vein (upper right) in Uganik Island abrasion patch. **B)** Distribution of diffraction peak detections in detector A (red) and B (cyan). Note thin rim with alternating detections and blocky interior.

On Earth, such behavior causes anhydrite to precipitate in the seafloor when sulphate-rich seawater encounters hot, Ca²⁺-rich hydrothermal fluid. Also, anhydrite precipitates in the summertime capillary zone of sabkhas when a rising brine warms [10]. Second, the concentration of other dissolved salts affects the solubility of anhydrite non-linearly. For example, anhydrite is stable than gypsum in a CaSO₄ brine above ~4 molal dissolved NaCl at 25 °C [11]. So, concentration changes of other dissolved salts can cause anhydrite to precipitate.

Acknowledgments: Contributions by JPL co-authors were funded under contract with the National Aeronautics and Space Administration (80NM0018D0004).

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