Supplementary Materials for

Alteration history of Séítah formation rocks inferred by PIXL x-ray fluorescence, x-ray diffraction, and multispectral imaging on Mars

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*Sci. Adv.* 8, eabp9084 (2022)
DOI: 10.1126/sciadv.abp9084

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**Supplementary Text**

**PIXL Diffraction Detection: Grain Size Dependence in the Flight Instrument**

To compare theoretical and ground-based experimental predictions of diffraction detection based on crystal grain size with performance on Mars by the flight instrument, we made use of a natural experiment offered by Dourbes olivine and pyroxene grain boundaries. In particular, a large region of Dourbes pyroxene produces diffraction peaks at 7.5 and 11.6 keV (25). These regions were large enough (many PIXL spot sizes in diameter) that many measurement spots were located along effectively straight boundaries between pyroxene and other grains, predominantly olivine. The spots were placed randomly with respect to these boundaries and thus contained varying amounts of pyroxene in the measurement volume. We find that, when the PIXL spot overlaps pyroxene by at least 20-30 µm, diffraction was observed at 7.5 and 11.6 keV (Fig. S1). These results are consistent with experimental observation of diffraction from halite crystals down to at least 40 µm in size.

**PIXL Diffraction Detection: Relative Grain Orientation**

The polychromatic micro-focused x-ray beam on the PIXL instrument has a convergence angle of approximately 8°. Therefore, if PIXL is aligned so that the center of the beam satisfies the Bragg condition for a given crystallographic plane and crystal orientation, the edges of the beam will be incident on the same crystallographic plane at a relative crystal orientation angle of ±4° and the Bragg condition will be satisfied at a different energy according to Eq.1:

$$E = \frac{hc}{2d_{hkl} \sin \theta}$$ (1)

where $d_{hkl}$ is the d-spacing of the crystallographic plane (hkl), $h$ is Plank’s constant, and $c$ is the speed of light. The constants $hc$ reduce to approximately 12.398 keV Å. Applying this to PIXL’s geometry with a 2θ angle of approximately 158° gives a maximum energy range that satisfies Eq. 1 for a relative crystal tilt of ±4° of ±14 eV for diffraction at 1 keV up to ±204 eV for diffraction at 15 keV.

As discussed in the Materials and Methods, the FWHM, and therefore the convergence angle, of the beam is energy dependent. This will reduce the degree of relative crystal tilt, and therefore the acceptable energy range, at lower energies by up to a factor of two. We note that the acceptance angle of each detector (22°) is significantly larger than that of the beam, and therefore the degree of acceptable crystal tilt that can still satisfy the Bragg condition is limited by the convergence of the incident beam.
Fig. S1. PIXL detection of diffraction from pyroxene in spots containing both pyroxene and olivine.

A) Pyroxene-containing scan regions having diffraction peaks detectable at 7.5 and 11.6 keV. B) Integrated photon counts for both diffraction peaks normalized to counts from the detector oriented away from the diffracting photons. Points from highlighted pyroxene shown in red. Modified from (25). C) Compositional ternary diagram as in Fig. 1 with pyroxene producing diffraction highlighted in (B) shown in red and blue. Diffracting points lie on a mixing trend from those observed when the PIXL spot lay entirely within pyroxene (augite; northeast-most points) to where the center of the spot (120 μm diameter) lay ~30-40 μm on the olivine side of an olivine:pyroxene contact (southwest-most points in blue). Pyroxene diffraction therefore originated from material in 20-30 μm on the edge of the spot. D) Locations of diffracting points highlighted in blue in C) demonstrating PIXL spot placement along the boundaries of pyroxene and olivine.
**Fig. S2. Diffraction Spectra.**

Normalized diffraction spectra belonging to each cluster presented in Fig. 6, together with the cluster center (solid line in each panel). Vertical shaded red lines highlight similar grains that differ only in a small energy shift, corresponding to an inter-grain rotation of less than 8° (see Materials and Methods), while spectra with a shaded gray overlay represent poorly defined clusters. These clusters are interpreted as regions without a clear grain orientation due to either multiple overlapping smaller grains, or multiple inter-grain rotations in excess of 8°. Asterisks in spectra D1 P1, D1 P4, D1 O1, and D1 O2 correspond to asterisk in Fig. 6.
Fig. S3. Mineral stripping assignment of oxides to mineral endmembers.

In each panel, spots in grey indicate no significant subtraction of oxide by assignment to merrillite, CaSO₄, MgSO₄, NaClO₄, or Fe,Cr,Ti-spinel. Spots in shades of yellow indicate partial or complete assignment of oxide to one of these minerals. A) CaO subtraction. Yellow spots are predominantly merrillite and CaSO₄. B) Na₂O subtraction. Yellow spots are almost entirely paired with Cl, are modeled as NaClO₄ for mineral stripping, and referred to generically as “perchlorate.” C) MgO subtraction. Yellow spots are almost entirely MgSO₄. D) FeO subtraction. Yellow spots are Fe,Cr,Ti-spinel. E) SO₃ subtraction. Yellow spots are CaSO₄ and MgSO₄. Almost complete lack of grey spots indicates that nearly all SO₃ was assigned to these minerals. F) Cl subtraction. Yellow spots are perchlorate. Light grey areas, particularly in areas with abundant alteration minerals, may indicate a small amount of excess Cl relative to NaClO₄.
Fig. S4. Mineral mixing model for effective spot size estimation.

Fitted mixing relationships (blue lines) from olivine (red star) to feldspar (blue star, A) and pyroxene (green star, B). All points selected from contacts between large endmember mineral grains. Green crosses are from the same regions but also have modeled NaClO₄ > 0.11 mmol/g. High inferred perchlorate abundances are associated with higher FeO/(SiO₂ + MgO), consistent with inferred partial oxidation of Fe and dissolution of olivine during perchlorate infiltration and precipitation. Best-fit mixing curves were therefore selected to closely match the left-most boundary of observed mixing arrays. Mixing relationships are non-linear because effective measurement spot sizes for these elements are MgO > SiO₂ > FeO, causing observed MgO and SiO₂ abundances to change before FeO as the PIXL measurement spot moves toward mineral contacts.
Fig. S5. Diffraction detection dependence on crystal grain size.

Halite (NaCl) with different grain sizes ranging from 45 µm to 500 µm all display significant diffraction. Panel (A) shows a complete spectrum, with Na and Cl fluorescence lines indicated with vertical red dashed lines. The region between 3.5 keV and 15 keV (shaded) has no fluorescence lines, yet several peaks are present resulting from crystalline diffraction (red arrows). Panels (B-E) show five independent measurements from different locations of samples comprised of the grain size fraction indicated in each panel. As the grain size decreases below the beam size (B), increased number of diffraction lines are present with decreased intensity, indicating that multiple randomly orientated grains are within the x-ray beam. Grains with sizes...
above 45 µm produce clear diffraction peaks (B). Results for grain sizes above 500 µm (not shown) show similar diffraction peaks to 300 µm to 500 µm grain sizes (E).
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