Data Repository Item
for
"Opaline Silica in Young Deposits on Mars"
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Methods for CRISM Data Reduction

We processed the CRISM data for this work using standard techniques employed by the CRISM team. To convert CRISM measurements to apparent I/F, the instrument background is subtracted from raw data using measurements in which an internal shutter is closed. The result is scaled to radiance by dividing by comparably processed measurements of an internal integrating sphere and multiplying by a radiometric model of the sphere constructed during ground calibration. Radiance is then divided by solar irradiance convolved through the bandpasses of each pixel, scaled for solar distance. We assume a Lambertian surface and divide I/F values by the cosine of the incidence angle to correct for photometric effects. To correct for atmospheric effects, data are divided by a scaled atmospheric transmission spectrum obtained during an observation crossing Olympus Mons. This procedure leaves broad residual trends if the aerosols' nature and abundance has shifted over time relative to the volcano scan, but these trends do not influence our results, which are based on narrow vibrational absorption features. This atmospheric correction technique is also used by the Mars Express OMEGA team. Map projection uses a camera model, gimbal attitude, and spacecraft and planetary ephemeris to calculate the planetocentric latitude and longitude for each pixel.

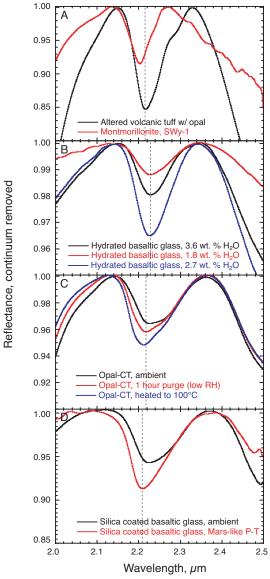**Spectral Characterisitics of Opaline Silica and Glass**

The Si-OH bands in reflectance spectra of opal and chalcedony are commonly wider than their counterparts in unaltered hydroxylated glasses and exhibit band minima centered at ~2.21 and ~2.26 µm, whereas metal-OH bands in spectra of unaltered glasses commonly exhibit a single band with a minimum near ~2.22 – 2.23 µm (DR Figure 1)." The Si-OH absorption band near ~2.21 µm in opal and chalcedony is often broader than its hydrated glass counterpart due to weak hydrogen bonding of relatively greater numbers of H_2O molecules to surface silanol groups. Dehydration of opal through heating or lowering the relative humidity (RH) weakens absorptions due to hydrogen-bonded silanol while strengthening those due to non-hydrogen bonded silanol, thus reducing the overlap responsible for the original broad absorption envelope (DR Figure 1).

The presence of a longer wavelength band in opal, near ~2.25-2.26 µm, accounts for the broader and slightly asymmetric appearance of the ~2.21 µm band in opals and chalcedony with higher H_2O contents. Removing H_2O from opal changes the center of the OH-stretch overtone from ~1.41 µm to ~1.38 µm, an additional indication that H_2O is hydrogen bonded to some of the surface silanol groups. Similar spectral characteristics have not yet been observed in the laboratory for unaltered hydroxylated glasses. Therefore, spectral indicators of H_2O hydrogen bonded to silanol groups, such as the width and number of Si-OH bands near ~2.21-2.26 µm and the center of the OH^- overtone near ~1.38-1.41 µm, can aid in distinguishing between opaline silica and hydroxylated glass.
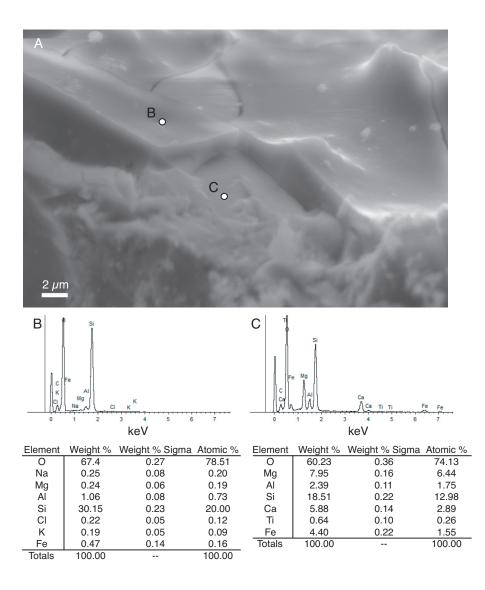
Dehydration of Fe-Sulfates

As discussed in text, the only materials in our current spectral libraries that exhibit a narrow absorption near 2.23 μm, coupled with features at 0.8 μm and an inflection at ~2.4 μm, are Fe-sulfates that have been partially dehydrated. Several hundred milligrams of ferricopiapite (verified by XRD) were heated in air to 250°C to examine spectral changes caused by dehydration. This partially dehydrated ferricopiapite exhibits all of the major spectral features we observe in the CRISM data for the hydrated phases near Juventae Chasma (see Figure 2 in main text). Similary, it has been noted that H_3O-bearing jarosite produces a similar absorption feature at 2.23 μm when heated in air. The phases produced by the dehydration of these materials is currently unknown, but XRD patterns show that they are not XRD amorphous. The pattern for the heated jarosite resembles an $Fe-SO_4$-OH bearing material. Therefore, the material associated with these spectral features in the CRISM data is likely an Fe-sulfate that has experienced partial dehydration.
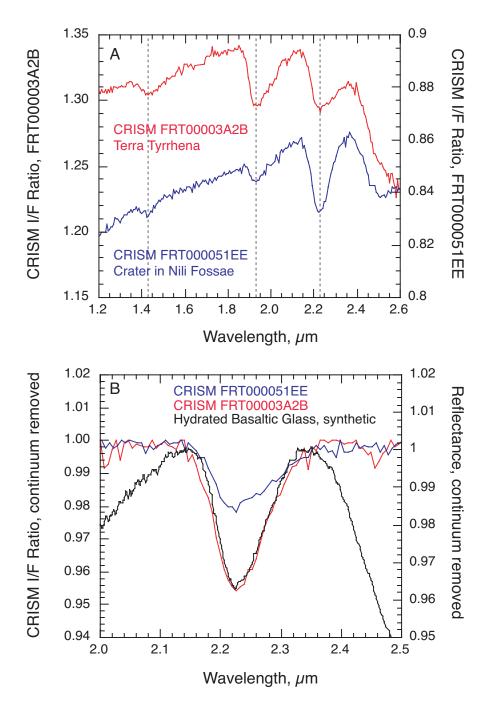
In the case of phases such as ferricopiapite, this can occur as a result of changing relative humidity and is apparently reversible (the partially dehydrated ferricopiapite rehydrated in the lab back to ferricopiapite after several weeks). Conversion of jarosite to this unknown $FeSO_4$ phase may require heating (e.g. by impact) on Mars. Because we have not yet examined the dehydration effects for all Fe sulfates, we use the general term 'partially dehydrated Fe sulfate" to refer to the material on Mars. Finally, we note that spectral signatures of other Fe-sulfates (most similar to copiapite, ferricopiapite, and ferrihydrite) have been observed in association with opaline silica in CRISM data for Noctis Labyrinthus, and these spectra also exhibit weak features centered at 2.23 μm, strengthening the argument that this material is likely related to Fe-sulfates.

Data Repository Figure 1.   Comparison of laboratory reflectance spectra for various H_2O and SiOH-bearing phases. Original spectra were divided by a straight-line continuum fit over the 2.2 μm band to produce continuum-removed spectra. Hydrated silica-bearing materials are easily distinguished from phyllosilicates such as montmorillonite (A) by the width of the metal-OH absorption centered near ~2.2 μm. Unaltered hydrated glass, such as the unaltered synthetic hydrated basaltic glasses in (B), exhibit a single band centered at 2.22-2.23 μm, whereas opaline silica phases exhibit a slightly wider band centered at 2.21 μm (C, D). Opaline phases also exhibit an absorption centered near ~2.26 μm, indicative of SiOH hydrogen bonded to relatively greater quantities of H_2O. The great number of these hydrogen-bonded silanol groups causes this absorption to weaken and the 2.21 μm absorption to increase in strength as H_2O is removed from opal by lowering the relative humidity (C, D) or through heating (C). This is in contrast to removing H_2O from hydrated glasses, which only affects the strength and not the position or width of the SiOH absorption at ~2.22-2.23 μm. Therefore, the position, width, and number of absorptions in the ~2.2 μm region can be used to distinguish between unaltered hydrated glass and opaline phases.

Element	Weight %	Weight % Sigma	Atomic %
O	67.4	0.27	78.51
Na	0.25	0.08	0.20
Mg	0.24	0.06	0.19
Al	1.06	0.08	0.73
Si	30.15	0.23	20.00
Cl	0.22	0.05	0.12
K	0.19	0.05	0.09
Fe	0.47	0.14	0.16
Totals	100.00	--	100.00

Element	Weight %	Weight % Sigma	Atomic %
O	60.23	0.36	74.13
Mg	7.95	0.16	6.44
Al	2.39	0.11	1.75
Si	18.51	0.22	12.98
Ca	5.88	0.14	2.89
Ti	0.64	0.10	0.26
Fe	4.40	0.22	1.55
Totals	100.00	--	100.00

Data Repository Figure 2.   Secondary electron microscope (SEM) (A) and energy dispersive spectrometer (EDS) data analysis points for the silica-coated basalt whose spectra are presented in Figures 2-4 and Supplementary Figure 1. The entire sample is altered to some extent, but the outer surface is covered by a several micrometers-thick coating of silica-rich material that is several-micrometers thick (A). B) EDS results for the spot marked B show the coating is dominated by Si and O. C) EDS results for the underlying material (spot C) suggest this region contains more glass and less silica. EDS results are forced to sum to 100%. Unlike the underlying less altered glass-rich material, the coating is fractured, possibly as a result of dehydration. The reflectance spectrum of the coating is most consistent with opaline silica. The sample is from a 3-5 kyr old lava flow on Mauna Loa, HI.

Data Repository Figure 3.   Example of CRISM spectra for hydrated silica deposits in southern highland craters. A) CRISM ratio spectra for deposits in Terra Tyrrhena and Nili Fossae. B) Spectra from (A) continuum-removed and compared to synthetic hydrated basaltic glass. The Si-OH absorptions are centered at slightly longer wavelengths (2.22 – 2.23 µm) than comparable Si-OH absorptions in opal (2.21 and 2.26 µm), and they are also slightly narrower. These CRISM ratio spectra are most consistent with unaltered or weakly altered glass of either volcanic (B) or impact origin.