

Thermal emission spectroscopy of the silica polymorphs and considerations for remote sensing of Mars

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[1] The possible existence of silica-rich rocks on Mars requires consideration of all of the candidate forms of silica that might exist there. We synthesized coesite and cristobalite, and obtained natural samples of tridymite, opal-A, and opal-CT. The thermal emission spectra of these silica phases were analyzed and related to their crystal structure and crystallinity. Structural differences between the polymorphs result in unique spectral character and the degree and type of crystal ordering in opal-CT results in cristobalite- or tridymite-like spectral features. These spectra will be useful for analysis of Thermal Emission Spectrometer (TES) data from Mars. While silica polymorphs are not modeled in deconvolution of the two main TES surface-type spectra, this does not preclude the possible detection of local abundances of these minerals on Mars. Spectral detection of silica phases on Mars would have implications for the volcanic and alteration history of the planet. **INDEX TERMS:** 3934 Mineral Physics: Optical, infrared, and Raman spectroscopy; 5464 Planetology: Solid Surface Planets: Remote sensing; 6225 Planetology: Solar System Objects: Mars; 8450 Volcanology: Planetary volcanism (5480). **Citation:** Michalski, J. R., M. D. Kraft, T. Diedrich, T. G. Sharp, and P. R. Christensen, Thermal emission spectroscopy of the silica polymorphs and considerations for remote sensing of Mars, *Geophys. Res. Lett.*, 30(19), 2008, doi:10.1029/2003GL018354, 2003.

1. Introduction

[2] Thermal Emission Spectrometer (TES) data suggest that the Martian surface is dominated by two major rock types: a basalt component [Bandfield *et al.*, 2000; Christensen *et al.*, 2000] and an andesite [Bandfield *et al.*, 2000; Hamilton *et al.*, 2001] or weathered basalt [Wyatt and McSween, 2002] component. If andesite is present, it would have major implications for the evolution of Martian magmatic processes through time [Rogers and Christensen, 2003]. The TES andesite signature is interpreted as a silica-enrichment in the form of volcanic glass, based on spectral deconvolution results [Bandfield *et al.*, 2000; Hamilton *et al.*, 2001].

[3] Silica-enriched rocks were also detected at the Mars Pathfinder landing site (MPF) [Economou *et al.*, 2003], possibly suggesting that magmatic evolution has occurred. Singletary and Grove [2002] performed petrologic experiments on Mars Pathfinder andesite primary melt compositions and modeled the possible mineralogy of those rocks. The results suggest that, if the magma was oxidized,

tridymite could occur in abundances of up to ~10%. The plausibility of primary silica minerals occurring in Martian volcanics is supported by the existence of silica phases in the most evolved basaltic Martian meteorite, Los Angeles [Rubin *et al.*, 2000]. The primary silica phases cristobalite and tridymite should be considered as plausible mineralogical components in surface spectra, but to date, only quartz has been used in deconvolution modeling.

[4] Secondary silica minerals formed by weathering and hydrothermal alteration should also be considered in interpretation of Mars remote sensing data. Silica-enrichment at MPF could also be interpreted as secondary enrichment due to the occurrence of significant bound water in rock surfaces [Economou *et al.*, 2003]. McLennan [2003] suggests that alteration of Martian rocks over a range of conditions should produce abundant free silica. Theoretical [Griffith and Shock, 1997] and experimental [Baker *et al.*, 2000] simulations of hydrothermal alteration on Mars produce silica phases. Purely amorphous opal-A and partially crystalline opal-CT are candidate forms of secondary silica in either scenario.

[5] Any primary or secondary silica minerals on Mars may have been shock-metamorphosed to high-pressure phases such as coesite during impacts. Though coesite typically does not occur in large abundances, high-pressure silica should still be considered as a possible constituent of the Martian surface. Even if coesite cannot be detected in large abundances over regional areas with TES, it might be detected in local environments with future instruments such as mini-TES.

[6] Of the silica polymorphs, quartz has been the most widely studied spectrally, and is therefore not directly considered in this study. Perhaps the earliest detailed analysis of the silica polymorphs was performed by Lippincott *et al.* [1958], who related the thermal infrared (TIR) absorptions to crystal structure and specific bonds. More recent studies have used transmission spectroscopy to understand the detailed crystal structure of the silica polymorphs [Etchepare *et al.*, 1978; Hofmeister *et al.*, 1992; Cellai *et al.*, 1995; Rokita *et al.*, 1998]. Rice *et al.* [1995] applied TIR transmission spectroscopy to determine the crystallinity of opal-CT samples from band ratios. In this study, we perform TIR emission spectroscopy on synthetic and natural samples of silica. TIR emission spectroscopy is analogous to spectral measurements observed with TIR remote sensing instruments, and the self-absorptions observed from emitted radiation produce different spectral features than are observed with transmission spectroscopy. Our goal is to characterize the thermal emission spectral features of the polymorphs cristobalite, tridymite, and coesite, as well as amorphous opal and partially crystalline opal-CT. These

data will aid in interpretation of TES and mini-TES data from Mars, as well as data from future planetary and terrestrial remote sensing missions.

2. Methods

2.1. Sample Acquisition

[7] Natural mineral specimens were acquired from vendor sources or teaching collections at Arizona State University (ASU). Natural coarse particulates of cristobalite and coesite were not available and were synthesized in the laboratory.

2.1.1. Natural Samples

[8] Tridymite was purchased from David Shannon Minerals in Mesa, AZ. The specimens occur on basaltic rock faces, where they probably formed from fumarolic vapor deposition. The 0.5–3 mm crystals and crystal aggregates were plucked from rock surfaces, and then washed over a 125 μm sieve to remove any fines that could have been produced in the extraction. Opal and opal-CT samples represent a small range of crystallinities. Samples 02-011, 02-020, and 02-015 were obtained from the teaching collection at ASU. Sample 02-031 was purchased from Ward's Natural Science. All opal samples were crushed and washed over a 125 μm sieve to remove fine particulates. The final particle size range for each sample was 125 μm to approximately 2 mm.

2.1.2. Synthesis of Coesite and Cristobalite

[9] Coesite was synthesized in a single experiment at 700°C and 3.2 GPa using an end-loaded piston-cylinder apparatus with a 19 mm piston (95 hour run duration). The furnace assembly consisted of a graphite furnace with NaCl, Pyrex, and MgO sleeves and plugs. The starting material, 0.13 g of powdered opal-A, was encapsulated in a 5 mm outer diameter sealed gold capsule that held H₂O from the dehydration of opal during the experiment. Cristobalite was synthesized by heating 50–70 μm quartz particulates at 1535°C for 163 hours in an iron-free platinum crucible. The products of both experiments were polycrystalline particulates approximately 50 μm to 1 mm in diameter.

2.2. Sample Characterization

[10] Powder X-ray diffraction (XRD) was performed to confirm the mineralogies of natural and synthetic silica polymorphs and to estimate the crystallinities of opal-CT samples. Opal-CT consists of amorphous silica with short range order in the form of tridymitic and cristobalitic stacking [Graetsch, 1994]. Overall crystallinity increases with duration and degree of diagenesis. Cristobalitic ordering begins to dominate over tridymitic ordering with increased diagenetic “ripening.” To estimate the crystallinity, full-width half-maximum (FWHM) measurements, similar to those of *Herdianita et al.* [2000], were made of the broad tridymite-cristobalite X-ray diffraction peak between 18–24° 2 θ . In addition, the relative degrees of cristobalitic versus tridymitic stacking were estimated qualitatively from the relative intensities of the tridymite peak at 4.12 Å and the cristobalite-tridymite peak at 4.04 Å.

2.3. Spectrometer Setup

[11] High resolution emission spectra of samples were recorded at the ASU Mars Spaceflight Facility. The spec-

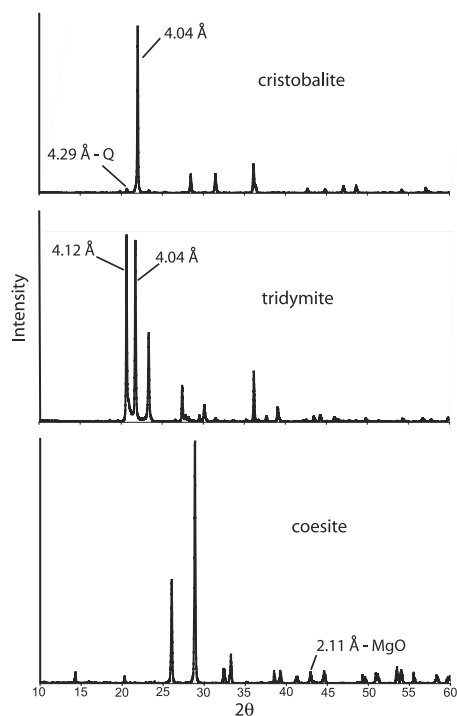


Figure 1. X-ray diffraction data for the silica polymorphs used in this study. Synthetic cristobalite displays a minor peak at 21° 2 θ , which is interpreted as residual quartz (Q) starting material. Coesite is mostly pure with a minor MgO peak at 43° 2 θ , which is due to contamination from our experimental apparatus.

trometer used is a Nicolet Nexus 670, which was adjusted to 4 cm^{-1} spectral resolution. This instrument has been modified to measure emitted energy, rather than reflected energy [Christensen and Harrison, 1993; Ruff et al. 1997]. The sample chamber of the instrument was purged with N₂ gas to minimize spectral contributions from CO₂ and water vapor during sample collection. The instrument field of view is an ellipse with a major axis that is adjustable from approximately 1 to 4 cm length.

[12] Emission spectra were recorded during several sessions over a 2-month period. Sample temperature was maintained at 80° C during spectral acquisition with a small heating element placed below the copper sample cup to increase the signal to noise ratio. Samples were placed in the instrument sample chamber and 270 scans were recorded over approximately 5 minutes. Midway through each session, spectra of two blackbody targets were recorded. Blackbody targets at temperatures of 70°C and 100°C were used to calibrate the raw data to radiance. Radiance data were processed to emissivity according to Ruff et al. [1997]. Samples of cristobalite, tridymite, and coesite were run on five separate occasions and the emissivity data were averaged to increase the signal to noise ratio.

3. Results

3.1. XRD and Petrographic Results

[13] XRD characterization indicates that our synthetic samples are nearly pure [Figure 1]. Cristobalite is low-cristobalite (tetragonal) and tridymite is low-tridymite (monoclinic). The cristobalite has a slight brown color

suggesting an impurity, but the only impurity evident in our X-ray data is indicated by an anomalous peak at 4.29 Å, corresponding to quartz. A minor peak is observed at 2.11 Å in the coesite X-ray pattern, which we attribute to MgO from the high-pressure experiment assembly. X-ray results for cristobalite, tridymite, and coesite and the observed crystal habit of tridymite indicate that all are well crystalline and contain no amorphous material.

[14] XRD patterns of opal samples are shown in Figure 2. FWHM measurements (in degrees 2θ) are: 5.6 for sample 02-011, 1.8 for samples 02-031 and 02-015, and 1.6 for sample 02-020, indicating that 02-011 is completely amorphous and 02-020 is the most crystalline. The relative intensities of the tridymite versus cristobalite-tridymite peaks indicate that 02-015 has the most cristobalitic stacking and borders between opal-CT and opal-C. Samples 02-020 and 02-031 are opal-CT. Sample 02-020 has minor quartz, indicated by the presence of a small peak at 3.34 Å.

3.2. Spectroscopy Results and Interpretation.

[15] Thermal infrared emissivity spectra for the silica polymorphs are shown in Figure 3. The spectral contrast was normalized to the shallowest spectrum. All of the polymorphs have broadly similar spectral features in the 1400–400 cm^{-1} region, but they are distinguishable with high spectral resolution. Band assignments are based in those of *Lippincott et al.* [1958].

[16] The spectrum of opal is the simplest, with a single broad Si-O stretching absorption between 1300 and 950 cm^{-1} and a Si-O bending absorption centered at 474 cm^{-1} . Tridymite is characterized by a broad absorption doublet between 1300 and 950 cm^{-1} . A poorly developed Si-O stretching absorption is observed at 785 cm^{-1} and well developed Si-O bending absorptions are observed at 540, 513, 482, and 413 cm^{-1} . Cristobalite has a more complex spectral structure with distinct asymmetric Si-O stretching absorptions at 1213 and 1103 cm^{-1} , separated by a local emissivity peak at 1192 cm^{-1} . A symmetric Si-O stretch is observed at 793 cm^{-1} and Si-O bending absorptions occur at 621, 527, 500, and 476 cm^{-1} . A broad, shallow trough is observed in the 600–800 cm^{-1} region that is likely the result of minor volume transmission. Coesite exhibits four

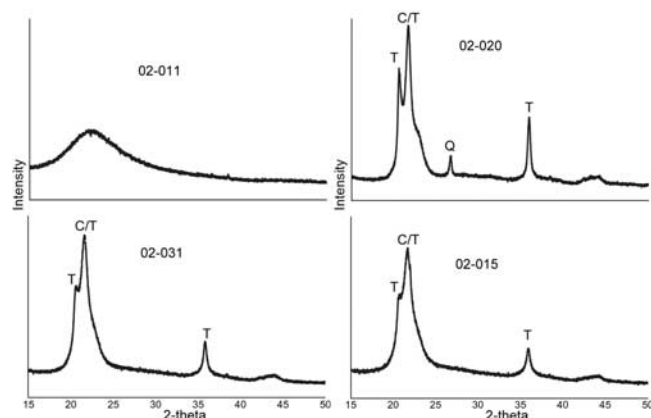


Figure 2. X-ray diffraction data for opal-A and opal-CT samples used in this study. Tridymite peaks are labeled “T,” cristobalite-tridymite peaks are labeled “C/T,” and the quartz peak is labeled “Q.”

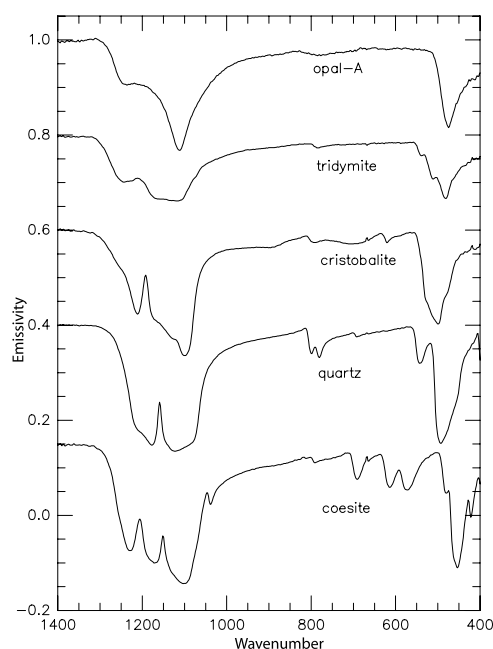


Figure 3. Thermal infrared emission spectra of the silica polymorphs tridymite, cristobalite, quartz, and coesite, compared to opal-A.¹

distinct asymmetric Si-O stretching absorption bands at 1227, 1169, 1103, and 1038 cm^{-1} , separated by three distinct local emissivity peaks at 1205, 1151, and 1047 cm^{-1} . Symmetric Si-O stretching absorptions occur at 813, 796, and 683 cm^{-1} . Si-O bending absorptions occur at 598, 557, 442, and 430 cm^{-1} .

[17] Spectra of opal-A and several samples of opal-CT are shown in Figure 4. All opal samples have a single broad absorption between 950 and 1300 cm^{-1} . Almost all of the variance in the opal-CT spectra occurs between 1300 and 1175 cm^{-1} . With increasing crystallinity, the absorptions become broader and develop cristobalite-tridymite-like spectral structure. The spectral shoulder near 1250 cm^{-1} is steeper for opal-A and becomes shallower with increasing tridymitic stacking. An absorption near 1175 cm^{-1} is observed primarily in 02-015 and is interpreted to result from dominance of cristobalite-like stacking. The 476 cm^{-1} band becomes deeper with increasing crystallinity and a slight inflection on the high-wavenumber side of the 476 cm^{-1} band is indicative of tridymite-like structure.

4. Discussion and Conclusions

[18] In all of the polymorphs studied, Si^{4+} is in 4-fold coordination and all display similar Si-O stretching absorptions between 1300–950 cm^{-1} and bending absorptions between 500–400 cm^{-1} . However, despite the identical chemistry of cristobalite, tridymite, and coesite, the structural differences result in slightly different vibrational absorptions that can be used to distinguish the minerals from each other. Coesite has the most spectral structure of

¹ Auxiliary material is available at <ftp://ftp.agu.org/apend/gl/2003GL018354>.

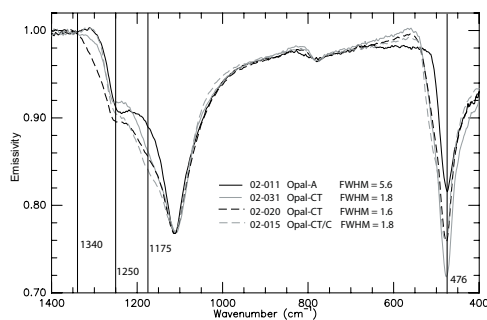


Figure 4. Thermal infrared emission spectra of opal-A and opal-CT samples. FWHM measurements indicate the relative degree of crystallinity¹.

the polymorphs, with four restrahlen bands separated by local emissivity peaks. Cristobalite has comparable spectral character to quartz, though it is obviously different from quartz. Tridymite has the least amount of spectral structure of the crystalline polymorphs, and is more similar to opal-A than it is to the other crystalline varieties.

[19] Opal-A and opal-CT spectra are slightly different from each other, though not significantly so. With increasing overall crystallinity and increasing cristobalite-tridymite stacking order, the spectra of opal become more tridymite- and cristobalite-like, suggesting that emission spectroscopy could be used to investigate the diagenetic history of opaline materials remotely. Amorphous and partially crystalline silica is expected to form on Mars if chemical alteration has occurred [McLennan, 2003]. Opaline silica should be considered as a potentially important component of Mars surface spectra (Kraft et al., Effects of pure silica coatings on thermal emission spectra of basaltic rocks: Considerations for Martian surface mineralogy, submitted for publication, 2003).

[20] We included the silica polymorphs along with a general mineral library (of Rogers and Christensen [2003]) in spectral deconvolution of basalt and andesite TES spectra (see Bandfield et al. [2000] for a description of deconvolution). The results are generally unchanged from previous interpretations, suggesting that the presence of pure silica polymorphs is not a likely alternative to silicate glass as a major component of the Martian andesite. However, if the silica enrichment is primary, it may be possible to detect local abundances of the polymorphs tridymite and cristobalite in Martian volcanic rocks. On the Moon, cristobalite and tridymite are common phases in basaltic rocks. They occur more frequently in areas of flows with coarser texture and more rapidly cooled flows of the same composition have a significant glass component [Mason, 1972]. A similar situation could occur at Mars, where more silicic volcanic rocks are dominantly glassy, but may contain crystalline silica phases locally. Identification of silica polymorphs in Martian rocks would have petrologic significance and provide important information about the magmatic evolution of the planet.

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