

THERMAL INFRARED AND VISIBLE TO NEAR-INFRARED SPECTRAL ANALYSIS OF CHERT AND AMORPHOUS SILICA. M. L. McDowell¹, V. E. Hamilton², S. L. Cady³, and P. Knauth⁴. ¹Hawai'i Institute of Geophysics and Planetology, University of Hawai'i, 1680 East-West Rd, Honolulu, HI 96822 (mcdowell@hawaii.edu), ²Southwest Research Institute, Boulder, CO, ³Portland State University, Portland, OR, ⁴Arizona State University, Tempe, AZ.

Introduction: Recent spectral observations of the Martian surface have discovered materials more rich in crystalline and amorphous silica (SiO₂) than previously known to be present [e.g., 1-6]. In the past, limited effort has been made to study and document the characteristics and variability of these phases in the thermal infrared (TIR) and visible to near-infrared (VNIR) wavelength ranges. This information is necessary to accurately identify silica phases in our data sets from Mars and to subsequently draw inferences about the geologic conditions or environments they represent.

In our study we consider these silica phases, focusing primarily on the spectral characteristics of various forms of chert and amorphous silica. Chert and opaline silica are targets of astrobiological interest because of their exceptional potential for microfossil preservation. They signify past activity of water and could represent deposits from surficial, diagenetic, or hydrothermal fluids.

Previous spectral studies of chert and amorphous silica include analysis of TIR emission spectra of four cherts by Michalski [7], TIR transmission spectra by Long et al. [8], and VNIR reflectance of lithic artifacts by Hubbard et al. [9].

Because the structures of chert and amorphous silica are different from that of plutonic quartz, their TIR spectra differ in shape and contrast, as described in Michalski [7, 10]. Figure 1 shows examples of the spectra of the samples analyzed. Plutonic quartz and chert exhibit a double emissivity minimum at ~1000-1300 cm⁻¹ (region in grey) due to Si-O stretching vibrations. However, the shape of these two minima are round or angle inward toward each other for plutonic quartz, while the two minima become more pointed and angle outward away from each other in chert. Other Si-O features at ~800 cm⁻¹ and ~500 cm⁻¹ are similar with the exception of the emissivity minimum at ~550 cm⁻¹, which may not be present in chert.

The more disordered structure of amorphous silica leads to a broader emissivity minimum in the ~1000-1300 cm⁻¹ region and a lack of the minima at ~550 and 400 cm⁻¹. The feature at ~800 cm⁻¹ may be absent.

Though the Si-O bond has no features in the VNIR region, it is likely that features attributable to hydration and other minerals in chert may be observable.

Approach: We improve upon the previous studies by including a more extensive sampling of geologic chert in hand sample representing various sources,

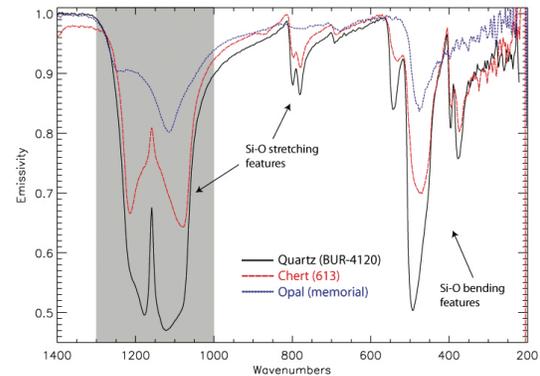


Figure 1: A comparison of quartz, chert, and opal spectra.

methods of formation, surface textures, and crystallinities. We analyzed the samples using TIR emission spectroscopy and VNIR reflectance spectroscopy. TIR emission spectra were collected over the range of 2000 - 200 cm⁻¹ with a ThermoElectron Nexus 470 FTIR spectrometer [11]. VNIR reflectance spectra were measured over the range of 350 - 2500 nm using an ASD field spectrometer. The following sections show results from our spectral studies. Further characterization (e.g. XRD, SEM) of these samples is currently underway.

TIR Spectra:

Spectral Variation in Chert and Amorphous Silica.

Variation in spectral character between different cherts also exists, as shown by the samples in our study. Features that may vary include the following: 1) relative depth of the two minima in the ~1000-1300 cm⁻¹ region, 2) angle of slope of the two minima in the ~1000-1300 cm⁻¹ region, 3) addition of local maxima/minima superposed on the larger emissivity minima in the ~1000-1300 cm⁻¹ region, 4) presence and depth of the feature at ~550 cm⁻¹, 5) depth and shape of the feature at ~350 cm⁻¹, 6) inclusion of a minimum at ~900 cm⁻¹ due to carbonate minerals within the sample.

Orientation Effects. The spectra of minerals may differ depending on the orientation of crystal axes relative to the viewing angle (e.g. [12,13]). In rocks where the crystals have a preferred orientation, spectral features vary when measured in differing orientations.

For the samples in our study the spectral features from different orientations are generally similar, but with slight differences in the depth and/or shape of the

$\sim 450\text{ cm}^{-1}$ band or the $\sim 1000\text{-}1300\text{ cm}^{-1}$ bands. The overall similarity of the spectra suggest that the grains in these samples have little preferred orientation, or alternatively, any crystal orientation present produces only slight differences in spectral shape for chert.

Effect of Viewing Angle. TIR spectra of the same surface may vary when measured at different angles, as illustrated in Figure 2. The same features are present in the spectra from all angles, but the overall and relative depth of the minima at $\sim 1000\text{-}1300\text{ cm}^{-1}$ change, as does the shape of these minima. A systematic change based on the degree of slope is not apparent, however. A similar characteristic has been observed previously in the spectra of amorphous silica [14]. Ruff et al. [3] attribute the spectral shape of the high silica material in Gusev Crater to a variation of an amorphous silica spectrum caused by differences in emission angle and sample porosity.

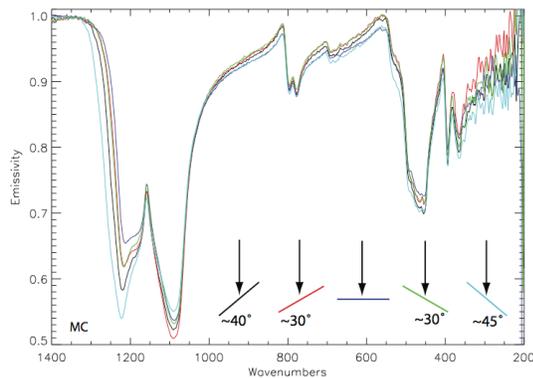


Figure 2: Spectra from the same surface of sample MC, each measured with the surface at different angles.

Surface Roughness Effects. Differences in surface roughness cause differences in spectral features for the same material, as discussed by Michalski [7]. Contamination of rough or natural surfaces with weathering products is likely, but not significant enough to be apparent in these spectra. We observe: 1) shallowing of features with increased surface roughness (or deepening of features in one case, sample 613), 2) change in relative depth of the minima in the $\sim 1000\text{-}1300\text{ cm}^{-1}$ region, 3) absence of the ~ 550 and $\sim 350\text{ cm}^{-1}$ feature in surfaces of rougher texture.

VNIR Spectra: VNIR spectra of our chert and amorphous silica samples show that the material is not featureless in this wavelength range (e.g., Fig 3). The number and position of observed features varies between samples. Although their strengths vary considerably, almost all spectra appear to have features at ~ 1410 and $\sim 1910\text{ nm}$, which are attributable to H-O-H and O-H bonds in the samples. The additional fea-

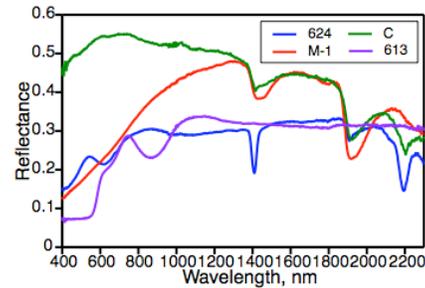


Figure 3: Examples of chert and amorphous silica VNIR spectra from our study.

ture(s) at $\sim 2200\text{-}2300\text{ nm}$ may be a result of M-OH bonds. Though a few samples have obvious narrow absorptions in this area indicative of clay minerals, most samples have a shallow, broad convex shape. Some samples also have features at shorter wavelengths ($<1000\text{ nm}$) that may be due to ferric oxides such as hematite.

These features suggest that hydration in chert and amorphous silica can be observed in VNIR data, along with other phases which may potentially be included in the material (e.g., clay minerals and ferric oxides), even though features from the Si-O bonds of the chert cannot be seen.

Summary & Ongoing Work: The TIR spectra of chert samples from a variety of geologic settings show that they have a range in spectral characteristics indicating differences in structure, physical character, and/or mineral inclusions. VNIR spectra show that most chert and amorphous silica samples exhibit hydration features. The spectra also indicate that some samples contain clay minerals in addition to silica.

Future work will focus on attributing spectral variation observed in chert to specific physical (e.g. surface roughness, grain size) or chemical characteristics (e.g. silica phase, mineral inclusions).

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