

THERMAL INFRARED SPECTRA OF MICROCRYSTALLINE SEDIMENTARY PHASES: EFFECTS OF NATURAL SURFACE ROUGHNESS ON SPECTRAL FEATURE SHAPE. C. Hardgrove¹ and A. D. Rogers¹, ¹Stony Brook University, Department of Geosciences (255 Earth and Space Sciences Building (ESS) Stony Brook University, Stony Brook, NY 11794, craig.hardgrove@stonybrook.edu).

Introduction: Recent spectral observations from orbit and detailed studies of Gusev crater and Meridiani Planum by the Mars Exploration Rovers, have revealed that sedimentary rocks are common on the Martian surface [1-6]. On Earth, sedimentary rocks commonly include microcrystalline (<20 μm crystals) chemically precipitated minerals. Examples include the microcrystalline varieties of quartz (chert/chalcedony), gypsum (alabaster) and calcite (micrite). We note that silica, sulfate and carbonate mineralogies have all been identified on the Martian surface [6-8]. While infrared spectra of the macrocrystalline varieties of these minerals are available in existing spectral libraries, examples of microcrystalline spectra are absent or underrepresented. There is evidence to suggest that microcrystalline phases differ from their macrocrystalline counterparts in thermal infrared (TIR) spectra. For example, TIR spectra of chert show a significant change in the shape and relative band depths of the fundamental absorptions at $\sim 1200\text{ cm}^{-1}$ [9-10]. We have shown that these differences are due to, in part, the presence of the silica polymorph “moganite” which is commonly found within many terrestrial chert samples [10], as well as the roughness of the surface [9-10].

With this in mind, we conduct a thorough study of the TIR spectral features associated with common microcrystalline phases (chert, alabaster and micrite). As we will show, TIR spectra of natural microcrystalline materials are sensitive to both the mineralogy and micron-scale (e.g., $\sim 1\text{-}25\ \mu\text{m}$) roughness of the surface. Furthermore, due to their small crystal size, microcrystalline materials are likely to naturally form and weather to surfaces that are rough on the scale of TIR wavelengths.

Methods: To isolate the constituent microcrystalline phases within our samples, we use a Thermo Scientific Nicolet iN10 MX Imaging system equipped with a translating stage to collect microscopic Fourier transform infrared (FTIR) reflectance spectra (micro-FTIR). The iN10 MX can acquire hyperspectral image cubes with a 4 cm^{-1} spectral resolution and a nominal spectral range of $650\text{-}4000\text{ cm}^{-1}$. For bulk sample (macroscopic) emissivity analyses we use a Thermo Fisher Nicolet 6700 FTIR Michelson interferometer with an attached purged sample chamber and heater. Emissivity spectral measurements are acquired according to the methods of [11]. A petrographic microscope

was used to approximate crystal grain sizes within prepared thin sections of each sample. All thin sections were polished to $1\ \mu\text{m}$ (hereafter referred to as “smooth”). Samples were procured from the National Museum of Natural History as well as the Stony Brook Department of Geosciences mineral collections.

Micro-FTIR spectra were acquired for smooth chert, alabaster and micrite as well as for their corresponding natural surfaces. Emissivity spectra were acquired only for natural chert surfaces, including Jaspilite, Jasper, Banded Iron Formation (BIF), Chalcedony, Rose Chalcedony, and Novaculite. Because bidirectional reflectance spectra are not necessarily equivalent to emissivity spectra, emissivity spectra were acquired to verify spectral changes observed in the micro-FTIR reflectance data.

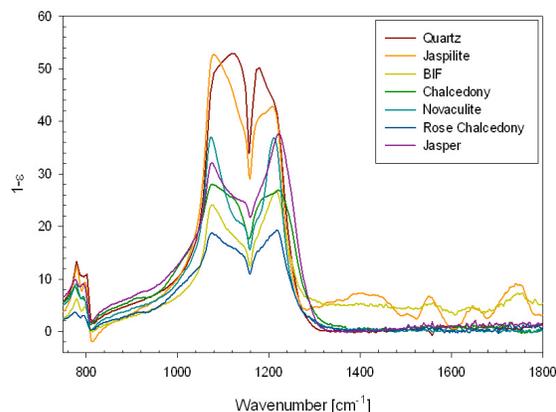


Figure 1: $1-\epsilon$ spectra for natural chert surfaces and macrocrystalline quartz. The Jaspilite has a markedly different spectral shape (inflection and restrahlen band ratio) than other natural chert surfaces and is more similar to macrocrystalline quartz. The larger crystal size of the Jaspilite relative to the other chert samples (Table 1) suggests that surface roughness (due to crystal size) affects TIR spectra when it approaches the scale of the wavelength.

Table 1: Approximate crystal size ranges for microcrystalline samples

Sample	Crystal Size Range [μm]
Alabaster	40 - 66
Jaspilite	25 - 33
BIF	14 - 25
Chalcedony	7 - 10
Chert	7 - 10
Rose Chalcedony	5 - 6
Jasper	3 - 5
Micrite	2 - 5

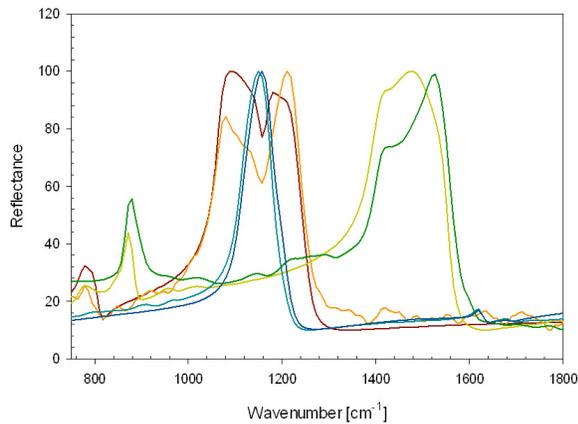


Figure 2: TIR reflectance spectra of natural microcrystalline surfaces and the same surfaces smoothed by polishing to a roughness of less than $1 \mu\text{m}$. Spectra shown are for smooth (red) and natural (orange) chert, smooth (olive) and natural (green) micrite, and smooth (blue) and natural (cyan) alabaster.

Results: Approximate crystal sizes for each sample are shown in Table 1. **Figure 1** shows TIR $1-\epsilon$ spectra for macrocrystalline quartz and natural chert (microcrystalline quartz) surfaces. This figure illustrates the typical spectral differences observed between microcrystalline and macrocrystalline quartz. Though many chert samples commonly contain other phases such as calcite or hematite, the spectral differences observed near $\sim 1000\text{-}1250 \text{ cm}^{-1}$ between macrocrystalline quartz and the chert samples cannot be explained by the presence of these additional phases. In addition, some of our samples are pure α -quartz (e.g., “Novaculite”). Rather, as has been shown [9-10, also, **Figure 2**], these spectral differences can be attributed to surface roughness. We note that the spectrum for “Jaspilite” looks more similar to the library spectrum of macro-quartz than any other in Fig. 1. Though the composition of the “Jaspilite” is most similar to that of the “BIF”, they do not have similar spectral shapes. The crystal grain size for “Jaspilite”, however, is between $25\text{-}33 \mu\text{m}$ while that of the “BIF” is between $14\text{-}25 \mu\text{m}$. This suggests that surface roughness, which is related to sample crystal size, may become significant below $\sim 25 \mu\text{m}$.

Figure 2 shows the micro-FTIR spectra for smooth and natural surfaces of chert, alabaster and gypsum. Both chert and micrite show significant changes in spectral shape, position, and the magnitude of fundamental absorption bands whereas there are no significant changes in the fundamental absorptions for alabaster between smooth and natural surfaces. Table 1 shows the crystal size for alabaster ($40\text{-}66 \mu\text{m}$) is significantly larger than both the micrite ($2\text{-}5 \mu\text{m}$) and chert ($7\text{-}10 \mu\text{m}$). This suggests that the alabaster crys-

tal size, which is likely linked to scale of surface roughness, may be too large for spectral changes to occur. An alabaster sample with smaller crystals will be analyzed in the future to confirm this hypothesis.

Samples labeled “smooth” in Fig. 2 have been polished to a roughness of less than $1 \mu\text{m}$ and their spectral features look most similar to that of their macrocrystalline counterparts. This suggests that it is the surface roughness, and not the microcrystalline nature of the minerals, that causes the observed spectral changes. In nature, however, microcrystalline materials will rarely form surfaces smooth on scales of $<1 \mu\text{m}$ and it is likely that weathering and erosion will result in surface roughnesses on the scale of the crystal size [9]. Therefore, TIR spectra may be an indirect indicator of crystal size (on the order of the TIR wavelength of $\sim 1\text{-}25 \mu\text{m}$) via surface roughness.

Summary and Future Work: Our results indicate that surface roughness controls the spectral shapes measured from natural microcrystalline surfaces. For microcrystalline materials, the surface roughness will be controlled by the average size of the crystal grains as well as the degree or type of surface weathering to which it has been exposed. We have shown that surfaces which are rough on a scale of $<25 \mu\text{m}$ can strongly affect the spectral shapes, positions and magnitudes of fundamental absorptions in the TIR. This also suggests that TIR spectra can be used to identify microcrystalline phases within sedimentary rocks and to place constraints on the size of the crystals that make up those phases. The ability to distinguish microcrystalline materials from macrocrystalline counterparts remotely could be a powerful tool for inferring formation environment of measured phases.

To understand the causes of these spectral changes, we will be using the computational light scattering model, Multiple Sphere T Matrix (MSTM), to simulate reflectance of TIR light from surfaces of varying crystal size [12].

References: [1] Squyres et al., (2006) *JGR*, 90, E02S11. [2] Christensen et al., (2004) *Science*, 306, p.1733-1739. [3] Grotzinger et al., (2005) *EPSL*, 240, p.11-72. [4] Glotch et al., (2006) *JGR*, 111, E12S03. [5] Bibring et al., (2005) *Science*, 307, p.1576-1581. [6] Ruff et al., (2011) *JGR*, 116, E00F23. [7] Gendrin et al., (2005) *Science*, 307, p.1587-1591. [8] Ehlmann et al., (2008) *Science*, 332, p.1828-1832. [9] Michalski, J. (2005) *ASU*, PhD dissertation. [10] Hardgrove C. and Rogers A. D., AGU 2011. [11] Ruff S. W. and P. R. Christensen (1997) *JGR*, 102, 14899-14913. [12] Mackowski D. and Mishchenko M (2011) *J. of Quantitative Spectroscopy. & Radiative Transfer*, 112, p.2182-2192.