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Introduction

Reflectance spectra of several carbonates with variable Ca, Mg and Fe concentrations are presented here. Shifts in the NIR band centers near 2.3, 2.5, 3.4 and 4 μm and the mid-IR fundamental vibrations near 750, 900, 1550 cm^{-1} ($\sim 14, 11, 6.5 \mu\text{m}$) are observed as a function of the type of cation present. This study builds on earlier analyses of the spectral properties of carbonates [1,2,3] and seeks to provide spectral data that will enable determination of carbonate chemistry through remote sensing on Mars.

VNIR Spectral Analyses

Continuum-removed spectra of several carbonates are shown in Figure 1 highlighting the four bands near 2.3, 2.5, 3.4 and 4 μm most useful for detecting carbonates on Mars with CRISM. These data show distinct variations in band center and shape depending on the carbonate composition. Sample purity may be affecting the band strengths of the ankerite and siderite spectra in Figure 1.

VNIR spectra of the 3 synthetic samples are shown in Figure 2 where the strong effect of a small amount of Fe (0.3%) can be seen to contribute to a band centered at 1.14 μm in the spectrum of Mg carbonate. This band is similar in shape and intensity for Synth-2 (65% Fe) and Synth-3 (91% Fe). Multiple vibrational absorptions due to CO_3^{2-} are observed from 1.5-5 μm . Gaffey [1] found that the ~ 2.3 and 2.5 μm band centers are coordinated and that these are correlated with the mass of the cation. Band centers for our data are plotted in Figure 3.

Band depths typically increase for increasing particle sizes in the NIR region (Figure 4), except for the band near 4 μm , likely due to saturation. Particle size also influences the band shape and changes the spectral properties sufficiently in some cases that it could influence detection of these minerals.

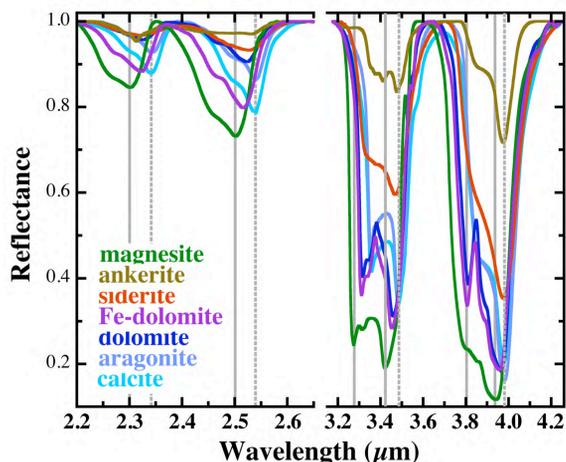


Figure 1 Continuum-removed spectra of several carbonates with different compositions. Gray lines are drawn at 2.30, 2.34, 2.5, 2.54, 3.27, 3.42, 3.48, 3.80, 3.93, and 3.97 μm to facilitate comparison of the data.

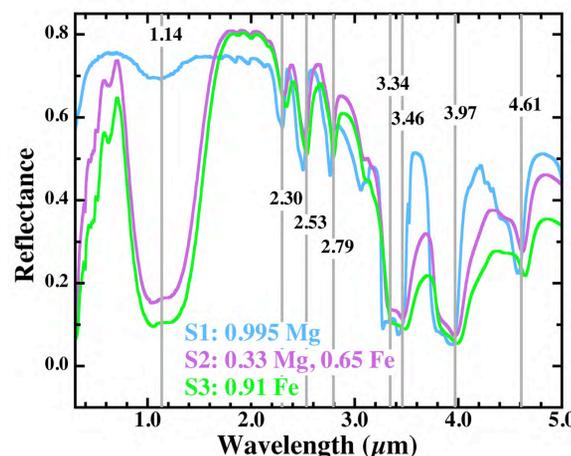


Figure 2 VNIR spectra of the 45-125 μm size fraction of three synthetic carbonates. Band centers of the dominant carbonate bands and the Fe band are labeled. In addition to Mg and Fe, minor Mn is present.

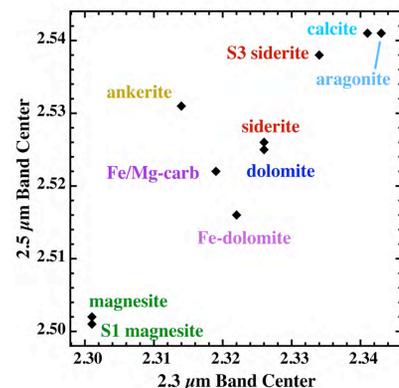


Figure 3 Carbonate band center comparison for the 2.3 and 2.5 μm bands. Values determined from the continuum-removed spectra.

Summary of Key Spectral Features

VNIR spectra of carbonates -- band centers shift with cation and structure, some dependence on grain size:

- ~2.3 μm band -- for Mg it occurs at 2.30 μm , for Mg/Fe at 2.32 μm , for Fe at 2.33 μm , and for Ca at 2.34 μm .
- ~2.5 μm band -- for Mg it occurs at 2.50 μm , for Mg/Fe at 2.51-2.52 μm , for Fe at 2.53 μm , and for Ca at 2.54 μm .
- ~3.4 μm doublet -- for Mg it occurs at 3.26 & 3.42 μm , for Mg/Fe at 3.33 & 3.46 μm , for Fe at 3.4 & 3.48 μm , for Ca at 3.36 & 3.49 μm .
- ~3.9 μm band -- for Mg it occurs at 3.93 μm , for Mg/Fe at 3.96 μm , for Fe at 3.99 μm , for Ca at 3.98 μm .

Mid-IR spectra of carbonates -- bands flip direction depending on grain size:

- ν_2 band ($\sim 11 \mu\text{m}$, $\sim 885 \text{cm}^{-1}$) and ν_4 band ($\sim 14 \mu\text{m}$, 710cm^{-1}) occur as emissivity minimum (reflectance maximum) for coarse grains and as emissivity maximum (reflectance minimum) for fine grains.

Mid-IR spectra of carbonates -- band centers shift with cation, structure, and grain size:

- ν_3 band: for Mg it occurs at 1590 cm^{-1} , for Mg/Fe at 1560 cm^{-1} , for Fe at 1540 cm^{-1} , for coarse-grained Ca at 1525 cm^{-1} , and for fine-grained Ca at 1550 cm^{-1} .
- ν_2 band: for Mg it occurs at 905 cm^{-1} , for Mg/Fe at 890 cm^{-1} , for Fe at 880 cm^{-1} , and for Ca at 870-885 cm^{-1} .
- ν_4 band: for Mg it occurs at 755 cm^{-1} , for Mg/Fe at 745 cm^{-1} , for Fe at 745 cm^{-1} , and for Ca at 710-715 cm^{-1} .

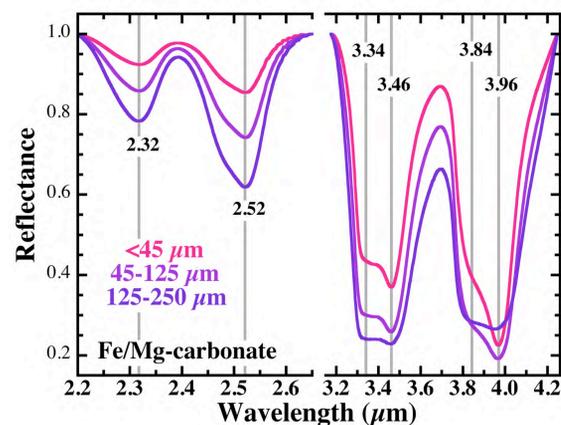


Figure 4 Continuum-removed spectra of 3 grain sizes of Synth-2, containing 0.33 Mg and 0.65 Fe cations.

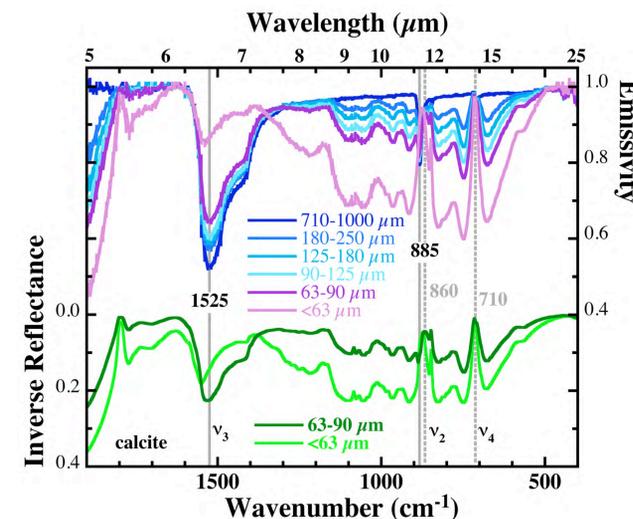


Figure 5 Emissivity and reflectance spectra of multiple size fractions of calcite.

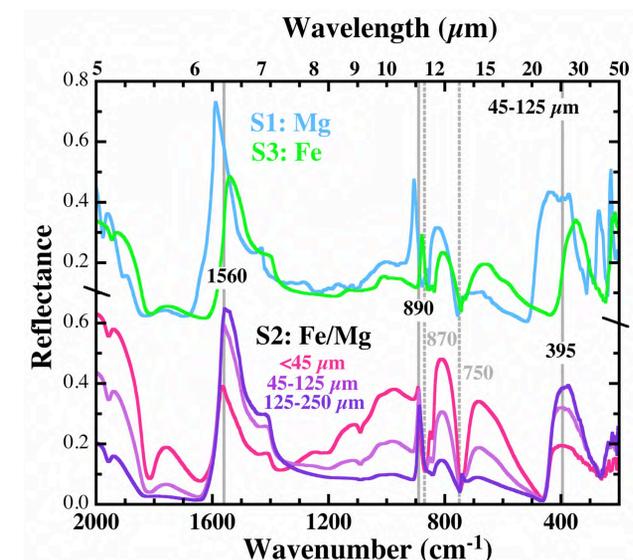


Figure 6 Mid-IR reflectance spectra of the synthetic carbonates. The dominant carbonate bands are labeled for the Fe/Mg-carbonate.

Mid-IR Spectral Analyses

Three dominant bands are observed for carbonates in the mid-IR region. These include the asymmetric stretching vibration (ν_3), the out-of-plane bending vibration (ν_2) and the in-plane bending vibration (ν_4) [3,8]. These are observed near 1525, 885 and 710 cm^{-1} for calcite (Figure 5) and near 1560, 890 and 750 cm^{-1} for Fe/Mg-carbonate (Figure 6). The bending vibrations for carbonates are particularly sensitive to grain size and flip from bands to peaks for smaller particles [9-10].

Applications to Mars

Fe/Mg-carbonate has been proposed as a type of carbonate on Mars [e.g. 11-12]. Other studies using CRISM data have proposed Mg- and Ca-bearing carbonates [e.g. 13-17] and potentially talc-carbonation of serpentine [14,17]. Studying the spectral properties of carbonates as a function of cation composition and grain size will facilitate characterization of carbonates on Mars. Another motivation for characterizing Fe/Mg-carbonates is that they are thought to be a host mineral of carbon in the Earth's mantle [4].

Samples

Carbonates were collected from several sources for this study: calcite ML-C2 (CaCO_3) from Durango, Mexico, aragonite (CaCO_3) from Somerset, England, dolomite ($(\text{Ca,Mg})\text{CO}_3$) from Selasvann, Norway, Fe-dolomite ($(\text{Ca,Mg,Fe})\text{CO}_3$) from Angels, Calif., ankerite ($(\text{Ca,Mg,Fe})\text{CO}_3$), magnesite (MgCO_3) from Brumado, Brazil, siderite (FeCO_3) from Nova Scotia, Canada. Some carbonates were also synthesized that contain specific amounts of Mg, Fe and Mn cations [4], including: Synth-1 (Mg 0.995, Fe 0.003, Mn 0.002), Synth-2 (Mg 0.33, Fe 0.65, Mn 0.02), and Synth-3 (Mg 0.06, Fe 0.91, Mn 0.03). When sufficient sample material was available, multiple grain sizes were prepared.

Methods

Bidirectional reflectance spectra were measured of particulate samples from 0.3-2.5 μm under ambient conditions. FTIR reflectance spectra were measured of particulate samples from 1-25 μm or 1-50 μm . Some of these data were reported earlier [5,6]. The near-infrared (NIR) data were processed using a continuum removal procedure [7] to enable comparison of the band centers with changes in compositions. Emissivity spectra were measured from 5-25 μm or 5-50 μm for some carbonates in this study as well as related samples [3].

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