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AN INFRARED SPECTROSCOPY STUDY OF IMPACT SHOCKED CARBONATES AND IMPLICATIONS FOR MARS. L. Pan¹, B. L. Ehlmann^{2,3}, P. D. Asimow², J. Hu², R. N. Greenberger². ¹Laboratoire de Géologie de Lyon, Université Claude Bernard Lyon 1 (2 rue Raphaël Dubois, Bâtiment GEODE, Villeurbanne, 69622. lu.pan@univ-lyon1.fr), ²Division of Geological and Planetary Sciences, California Institute of Technology, ³Jet Propulsion Laboratory, California Institute of Technology.

Introduction: Carbonate minerals have been detected on Mars in various geologic settings using characteristic near-infrared absorptions [e.g., 1-4]. These carbonates can serve as a potential reservoir for CO₂ from an early Martian atmosphere [5-7]. Since most of these carbonate detections are found in craters or associated with ancient cratered Noachian crust, it is important to analyze if impact shock effects on the infrared spectral properties of carbonates affect their detectability on Mars. To improve our understanding of the carbonate reservoir in Martian crust, we compare the spectral variability of carbonate detections on Mars with the spectral variability of carbonate rocks on Earth from (1) a collection from impact craters and other settings and (2) shock recovery experiments on carbonate targets.

Methods: Martian spectra are extracted from CRISM (Compact Reconnaissance Imaging Spectrometer for Mars) data based on the image and location information in the literature with standard data processing [8]. Carbonates from 6 impact craters on Earth with diameters ranging from 6-30 km were collected as well as 11 carbonate samples from other sedimentary settings. Visible and near-infrared spectra of terrestrial carbonate samples were measured with an ASD (Analytical Spectral Devices, Boulder, Colorado) FieldSpec3 spectrometer at the California Institute of Technology.

Two shock-recovery experiments were performed on the 20-mm propellant gun in the Lindhurst Laboratory for Experimental Geophysics at Caltech.

A magnesite sample (Ward's No. 346-4825) was cored and cut into two targets, embedded in steel recovery chambers and impacted by Al-flyer projectiles at velocities of 783.55 m/s and 1284 m/s, respectively, reaching peak shock pressures of ~5 GPa and ~10 GPa. We obtained the spectra of pre- and post-shock magnesite samples using a) an ASD spectrometer with external light source and bare fiber optics on a goniometer and b) a Headwall Photonics Inc. pushbroom imaging spectrometer.

Results: Features of Mars Carbonate IR Spectra.

Detections of Mg and Fe/Ca carbonates on Mars are mostly in the ancient southern highlands near large impact basins (e.g., Isidis and Huygens, Fig. 1A-C). The positions and shapes of the 2.3 and 2.5 μm CO₃-related absorption bands vary with location. Most Martian carbonate detections feature 1.9- μm and sometimes 1.4- μm bands due to H₂O absorption and a positive slope from 1 to 1.7 μm . These features are consistent with non-stoichiometric (water-bearing) carbonate or mixed phases.

Spectral variability of terrestrial carbonates. Like the Martian carbonate spectra, terrestrial carbonates show variations of spectral slope, width and band position of the 2.3 and 2.5 μm absorptions, and 1.4 μm and 1.9 μm water bands (Fig. 1A). Water bands, likely due to aqueous inclusions from water trapped during precipitation [18], are common in both terrestrial and Martian carbonate rocks, though the band strengths are not directly comparable. H₂O absorptions remain unchanged or are enhanced in samples from terrestrial impact craters, suggesting either that inclusions survive the pressure and temperature of the impact or that the carbonates are susceptible to post-impact alteration that re-introduces water. Some Martian spectra fall off the trend of 2.3 and 2.5 μm band positions of terrestrial samples (Fig.

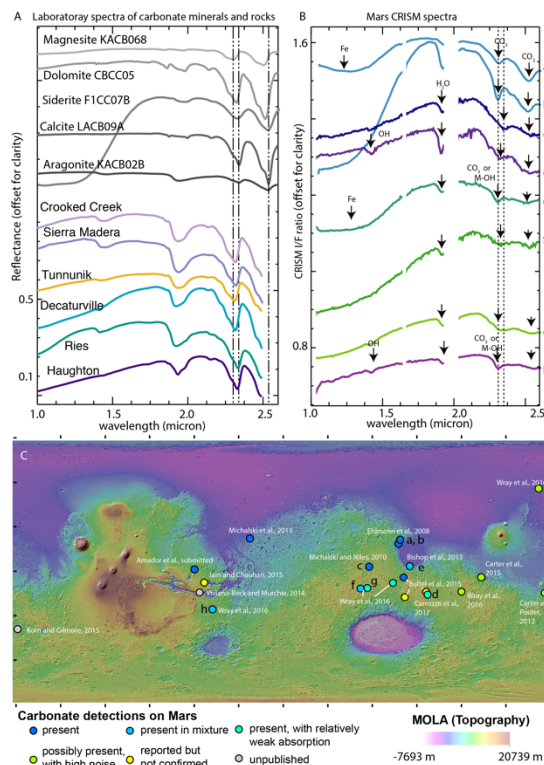


Figure 1: CRISM-based, near-infrared detections of carbonates on Mars: A) Near-infrared spectra of terrestrial carbonate minerals in grey [9] and carbonate rocks from terrestrial impact craters in colors, B) CRISM spectra from the type locations of carbonate detections on Mars [1-4, 10-17]. Arrows showing typical absorption bands and their likely causes in Martian carbonate detections. C) Spatial distribution of carbonate detections on Mars.

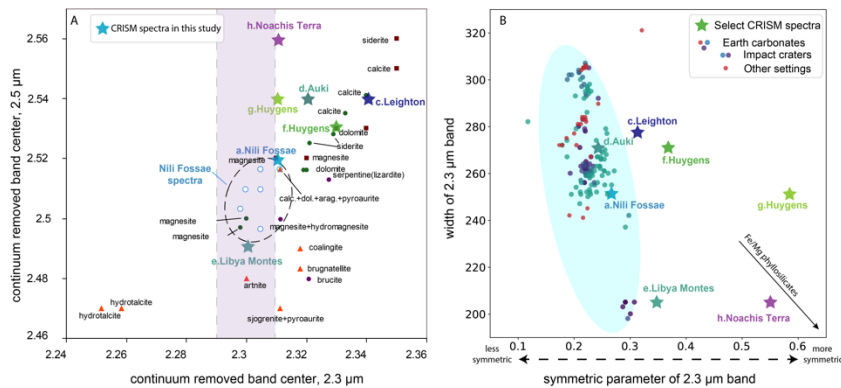


Figure 2: Scatter plot of spectral parameters for Mars data and measurement of terrestrial samples. A) Continuum removed band center of 2.3 and 2.5 μm absorptions (purple area shows the possible range of Fe/Mg phyllosilicate detections); B) Width of 2.3 μm band plotted against the symmetric parameter of the same band calculated as from the following equation: $\text{sym}2300 = (\lambda_{\text{right shoulder}} - \lambda_{\text{band center}}) / (\lambda_{\text{band center}} - \lambda_{\text{left shoulder}})$, so that $\text{sym}2300 = 1$ when the band is perfectly symmetric.

2A). We also observe a rather symmetric behavior of the 2.3 μm band in Mars data compared to terrestrial carbonates (Fig. 2B). Both these features are consistent with an effect of mixing with a different endmember, likely Fe/Mg phyllosilicate, which is widespread on Mars [3].

IR spectra of experimentally shocked carbonates. Near-infrared spectra of the natural magnesite sample before and after the shock recovery experiments show typical C-O bands at 2.316 and 2.515 μm and absorptions due to H₂O and OH in the structure at 1.415 μm and 1.914 μm, the latter forming a doublet with an associated C-O band at 1.968 μm (Fig. 3). The shape of C-O bands remains unchanged, but their strength decreases by 33% after ~10 GPa shock. Both the 1.415 and 1.914 μm absorptions become wider, presumably due to the increase of adsorbed, hydrogen-bonded water molecules relative to structurally bound H₂O. Weak combination absorptions in the carbonates at 1.866

and 2.136 μm are present before the shock and are unchanged at 5 GPa but weakened after the 10 GPa shock. These results suggest that relevant shock pressures induce minor changes associated with structural water in magnesite, but the main CO₃ absorptions persist, exhibiting only minor decrease in band depth at ~10 GPa shock pressure.

Summary and implications: We find absorption features of carbonate are similar in both terrestrial sedimentary carbonate and carbonates in impact structures. Compared to these terrestrial carbonates, Martian spectral detections have more symmetric 2.3 μm bands, consistent with higher clay fractions in the >400 m² footprints of the Mars spectra, unlike the relatively clean carbonate rocks selected to represent Earth. We also observe some weakening of CO₃ bands and broadening of H₂O bands in experimentally shocked samples at ~10 GPa, but the CO₃ bands remain the strongest absorptions in rocks from terrestrial impact craters and impact experiments. Since impacts up to 10 GPa did not alter the carbonate signature significantly, the observed distribution of carbonates may be largely representative of their true distribution on Mars, unless other geologic processes (e.g. burial, volcanic activity, higher shock pressure) masked or altered the spectral signature of carbonates.

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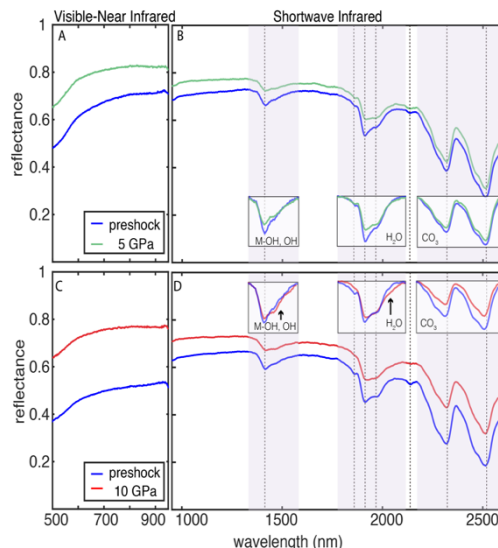


Figure 3: Spectra of magnesite from imaging spectrometer with VNIR and SWIR detectors, before and after shock recovery experiments. A-B) Spectra of Sample A, shocked to ~5 GPa, and C-D) Spectra of Sample B, shocked to ~10 GPa. Zoom windows show the continuum-removed spectra of relevant bands.