

**UV-VIS-NIR REFLECTANCE SPECTRA OF INTIMATE MIXTURES OF SYNTHETIC  $\text{CaCO}_3$  AND AMORPHOUS  $\text{SiO}_2$ : 0.35 – 2.5  $\mu\text{m}$ ; IMPLICATIONS FOR THE SPECTRAL IDENTIFICATION OF SHOCKED ASSEMBLAGES ON MARS.** M. A. Craig<sup>1</sup>, R. L. Flemming<sup>1</sup>, G. R. Osinski<sup>1</sup> and E. A. Cloutis<sup>2</sup>,  
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**Introduction:** Carbonates are important rock-forming minerals on Earth. They have been detected on Mars from both landed and orbital spacecraft as well as in Martian meteorites and also occur in many classes of meteorites. Many of these carbonates share the common theme of being shocked due to meteorite impact. It is notable that the effects of shock on carbonates are still poorly understood [1]. As illustrated in [2], the shock and melting produced by hypervelocity impact events has a measurable effect on the reflectance spectrum of carbonates. The reflectance spectra of these shocked/melted assemblages are so altered by the impact event they appear spectrally to be free of carbonate despite the clear presence of the crystalline carbonate calcite, as revealed by micro X-Ray diffraction ( $\mu\text{XRD}$ ) [2]. In order to quantify these spectral changes a number of analytical techniques have been used to explore the alterations in gross mineralogy and the resultant spectra. Here we investigate the spectral features of a calcite + amorphous quartz mixture suite produced in an attempt to isolate the  $\sim 2.2 \mu\text{m}$  feature that would seem to be replacing the  $\sim 2.33 \mu\text{m}$  C-O stretching fundamental overtone of calcite in the spectrum of the highly shocked oolitic limestone from the Haughton crater, HMP99-052, as shown in Figure 1.

**Experimental Procedure:** The two synthetically produced samples of 99.999% pure calcium carbonate ( $\text{CaCO}_3$ ) and amorphous silica ( $\text{aSiO}_2$ ) were gently dry sieved to produce a  $<45 \mu\text{m}$  fraction. They were then mixed at 10 wt% fractions using a 4 decimal place metric balance.

The carbonate samples from Haughton were gently crushed with an alumina mortar and pestle and dry sieved by hand to produce  $<45$  and  $45\text{--}90 \mu\text{m}$  powdered splits. Absolute reflectance spectra were collected with an Analytical Spectral Devices (ASD) FieldSpec Pro HR spectrophotometer at the University of Winnipeg Planetary Spectroscopy Facility (PSF), from  $0.35\text{--}2.5 \mu\text{m}$  at phase angles of  $i=30^\circ$ ,  $e=0^\circ$  using a PSF-built 50 watt quartz-tungsten-halogen collimated light source for illumination. Spectra were acquired relative to Spectralon<sup>®</sup> and corrected for minor irregularities in Spectralon's<sup>®</sup> absolute reflectance in the  $2\text{--}2.5 \mu\text{m}$  range. Spectral calibration was monitored via periodic measurement of a holmium oxide-doped Spectralon<sup>®</sup> reflectance standard. The field-of-view (FOV) of the spectrometer was  $\sim 5 \text{ mm}$ .

The ASD instrument has a fixed spectral resolution between  $2\text{--}7 \text{ nm}$  and the spectra are interpolated to 1 nm resolution internally by the spectrometer prior to output. Each output spectrum is the sum of 1000 spectra to increase the SNR. The spectra were corrected in post-processing for breaks that occur at the  $1.0$  and  $1.83 \mu\text{m}$  junctions of the three detectors used by the ASD instrument and FOV is given as approximate as the fibre-optic bundle which feeds the spectrometer has a random distribution of fibres at the pick-up end.

Each of the samples was loaded into aluminium sample cups for spectral measurement with sample well diameters of  $10 \text{ mm}$ , and depths of  $5 \text{ mm}$ . Sample loading was performed by lightly tamping the powders into the wells then “cutting” across the top surface with a glass slide.

$\mu\text{XRD}$  patterns were acquired with the Bruker D8 Discover micro X-ray diffractometer at the University of Western Ontario using  $\text{Cu K}\alpha$  radiation,  $\lambda = 1.54056 \text{ \AA}$ , at  $40 \text{ kV}$ ,  $40 \text{ mA}$ , with a  $500 \mu\text{m}$  nominal beam diameter and a 3 frame coupled scan with the sample oscillating continuously about an  $\sim 2$  by  $2 \text{ mm}$  area with a scan time of 16 minutes per frame [3].

Curve fits of absorption band minima were computed with GFit<sup>®</sup> using a  $12^{\text{th}}$  degree polynomial.

**Results:** The results are presented in Figures 1 and 2. Figure 2 shows the acquired absolute reflectance spectra of the 11  $\text{CaCO}_3/\text{aSiO}_2$  mixtures normalized to 1 at  $2.05 \mu\text{m}$ . Looking at the  $2.33 \mu\text{m}$  feature, following a vertical line from bottommost to topmost spectrum shown in Figure 2 we have calcite content beginning at 100% and falling by 10% per step until we reach 100%  $\text{aSiO}_2$ . Within this set, the  $2.337 \mu\text{m}$  absorption indicative of  $\text{CaCO}_3$  remains consistently resolvable with band minima within  $\pm 1 \text{ nm}$  of  $2337 \text{ nm}$  until there is no calcite remaining in the mixture. The  $2.155 \mu\text{m}$  calcite absorption remains clearly resolvable until the level of calcite falls below 50% with band minima shifting some 5 nm to longer wavelengths in the 60/40 and 50/50  $\text{CaCO}_3/\text{SiO}_2$  mixtures.

The  $2.2 \mu\text{m}$  feature of interest, indicative of amorphous silica is clearly resolvable as a shoulder on the  $2.337 \mu\text{m}$  calcite absorption band until the  $\text{aSiO}_2$  content reaches 20% by weight. There is however some movement in the band minima,  $\pm 12 \text{ nm}$ , which is most likely due to the broad nature of the  $2.2 \mu\text{m}$  feature as a result of the combination of overtones which create it and the difficulty which arises in attempting curve fits

on a shallow feature on the sloping shoulder of the relatively deep 2.337  $\mu\text{m}$  band.

Figure 1 compares the spectra of the <45  $\mu\text{m}$  splits of unshocked **HMP99-097A**, with the highly shocked **HMP99-052** normalized to 1 at 2.15  $\mu\text{m}$ . Of note here are the features at  $\sim 2.1 \mu\text{m}$  in both spectra indicative of calcite, the 2.2  $\mu\text{m}$  aSiO<sub>2</sub> feature in **HMP99-052** and the  $\sim 2.33 \mu\text{m}$  calcite feature in **HMP99-097A**.

**Discussion:** It is clear that the 2.2  $\mu\text{m}$  absorption feature in the spectrum of HMP99-052 is caused by the presence of a spectrally significantly amount of aSiO<sub>2</sub> which was confirmed by  $\mu\text{XRD}$ . There are, however, some differences worthy of note between the 2.2  $\mu\text{m}$  feature seen in the manufactured aSiO<sub>2</sub> and that in the sample from Haughton. In both the absorption band is a result of a combination of the fundamentals of the vibrational modes of Si-O and Si-O-Si oxygen bridging bonds between adjacent SiO<sub>2</sub> or SiO<sub>4</sub> tetrahedra observed in vitreous quartz/silica [4–6]. The minima of the band falls at approximately  $2216 \pm 10 \text{ nm}$  and the feature itself can be either symmetric/asymmetric or broad/narrow and vary significantly in wavelength space. The possible variance in band minima position is a consequence of the combination of a set of overtones which arise from the possible stretching and bending modes of the Si-O/Si-O-Si bridging oxygen and can vary widely as a result of the 60° variance, 120–180°, of the bond angle near the bridging oxygen [5]. With the preferred bond angle of 144° and the resultant set of ordering, the feature would be a result of the  $2.22_{v_2}$ ,  $2.38_{v_2}$  and  $2.27_{v_2}$  overtones of the 8.91, 9.52 and 9.09  $\mu\text{m}$  Si-O/Si-O-Si stretching/bending fundamentals and the  $2.27_{v_3}$  overtone of the 18.18  $\mu\text{m}$  fundamental which is a combination of a bending mode perpendicular to the bond plane and a stretching mode of Si-O-Si [5, 6]. In the synthetic aSiO<sub>2</sub> the 2.2  $\mu\text{m}$  band is symmetric and broad indicating no preferential distribution of Si-O bond angles, while it is asymmetric toward longer wavelengths in HMP99-052. Given the range of possible bond angles the band minima of the  $\sim 2.2 \mu\text{m}$  feature could fall anywhere between 2.08 and 2.38  $\mu\text{m}$  [6].

Another distinct difference is notable regarding the  $\sim 2.1 \mu\text{m}$  overtone of calcite. In the synthetic CaCO<sub>3</sub> it falls at 2155 nm, while in the Haughton sample the feature's band minima is at  $\sim 2090 \text{ nm}$ . There is the possibility this is a result of the likely minute amounts of Si-OH present in the Haughton sample [7]. Though, it is also plausible it is indicative of calcite, so position aside, its band depth may be of use to compute a rough measure of calcite content even though the 2.33  $\mu\text{m}$  feature is obscured. Based simply on relative peak heights using the  $\mu\text{XRD}$  data for HMP99-052, the calcite makes up approximately 25% of the crystalline

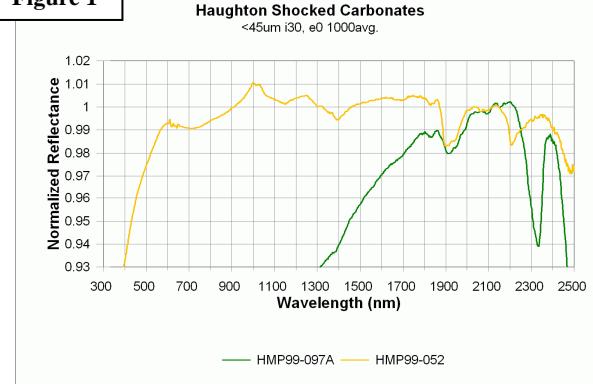
content. This suggests it may be a resolvable band well below the detection limits indicated by its disappearance in the spectra of synthetic mixtures shown in Figure 2.

**Conclusion:** The shocked/melted samples from Haughton, as well as those from several other craters (unpublished data), all share the  $\sim 2.2 \mu\text{m}$  feature which can be attributed to overtones of the vibrational modes of Si-O-Si in vitreous silica/quartz. This feature may prove to be quite useful in identifying impactites spectrally on the Martian surface as well as terrestrially. Future work will leverage the results from further analytical studies to fully elucidate the origin of each of the spectral absorptions observed in the Haughton impactites.

**References:** [1] Osinski et al. (2008) *Geo. Soc. Amer. SPE347*, 1-18. [2] Craig M. A. et al. (2009) *LPS XXXX*, Abstract #1643. [3] Flemming R. L. (2007) *CJES*, 44, 1333-1346. [4] Šimon L. and McMahon H. O. (1953) *Jour. Chem. Phys.*, 21, 1, 23-30. [5] Kukšenka K. N. et al. (1975) *Zhur. Prikladot Spektr.*, 22, 6, 1048-1051. [6] Bell R. J. and Dean P. (1970) *Discuss. Farady Soc.*, 50, 55-61. [7] Kamitsos et al. (1993) *Phys. Rev.*, 48, 17, 499-505.

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**Figure 1**



**Figure 2**

