DETECTION LIMITS OF SOME CARBOXYLATES BY X-RAY DIFFRACTION AND REFLECTANCE SPECTROSCOPY. D. M. Applin[1*], M. R. M. Izawa[2], E.A. Cloutis[1]. [1]Centre for Terrestrial and Planetary Exploration, 515 Portage Avenue, R3B 2E9, Winnipeg, Manitoba, Canada, *daniel.m.applin@gmail.com. [2] Institute for Planetary Materials, Okayama University – Misasa 827 Yamada, Misasa, Tottori 682-0193 Japan

Introduction: Both endogenous and exogenous inputs of solid abiotic carbon phases to the surface of Mars exist [1-3]. Martian meteorites contain endogenous abiotic carbon, where numerous plausible formation scenarios have been posited [3,4]. The estimated concentration of accumulated meteoritic carbon within the regolith has a wide range of between 1 and 500 ppm [5-7]. The SAM instrument on Curiosity has identified organic compounds [8], and has repeatedly shown gas evolution profiles to be consistent with a carboxylate component, which includes carbonates [9]. These data, in combination with X-ray diffraction (XRD) patterns from the CheMin instrument have also shown multiple detections of siderite near the detection limits of CheMin [10]. The SHERLOC instrument on the Perseverance rover has identified organic compounds based on laser-induced fluorescence spectra [11]. These fluorescence spectra are also consistent with some of the carboxylates that are thought to contribute to the gas evolution profiles observed in SAM data [12]. Here, we aim to quantitatively determine the detection limits of solid carboxylates with XRD and reflectance spectroscopy, in order to provide insight to finding these materials with CheMin and Supercam [13] measurements on Mars.

Experimental details: Powders of Ca, Mg, and Fe carbonates, oxalates, acetates, and formates (carboxylates) were dry-sieved to less than 45 microns. These powders were intimately mixed with aliquots of the JSC Mars-1a palagonite Mars analogue material. This JSC Mars-1a sample was heated to 130°C in order to remove ~11 wt.% of mostly water.

Visible and near-infrared reflectance spectra of the mixtures were collected with an ASD LabSpec4 Hi-Res® spectrometer (350-2500 nm) at a viewing geometry of i=30°, e=0°. A Bruker Vertex 70 FTIR spectrometer equipped with the SpecAc reflectance accessory and an InSb detector was used to collected reflectance spectra from 1.1 to 5.0 microns. These data were collected at a viewing geometry of i = 30° and e = 0°, and relative to InfraGold at a resolution of 6 cm^{-1}, and spectra were average over 500 scans.

X-ray diffraction patterns were collected with an Olympus Terra, a commercial version of the CheMin instrument on Mars. The instrument also uses a Co tube, and processes the collected 2D X-ray images to produce patterns from 5 to 55° 2θ with a 0.25° FWHM angular resolution and 0.05° angular sampling interval. The XRD patterns were all normalized relative to total counts on the CCD.

Results: Examples of the resulting data are shown in Figures 1 to 6. Figures 1 to 3 show the XRD patterns collected on the mixtures with the Fe oxalate humboldtine, how the data were processed, and the resulting calibration curves that were used to calculate the limits of detection (LODs). Similarly, Figures 4 to 6 show the reflectance spectra, continuum removal, and calibrations curves for siderite at MIR wavelengths.

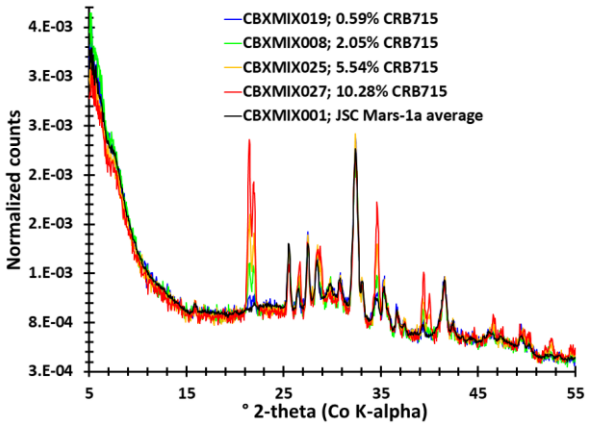

Figure 1: X-ray diffraction of humboldtine (Fe oxalate) intimately mixed with the JSC Mars-1a palagonite.

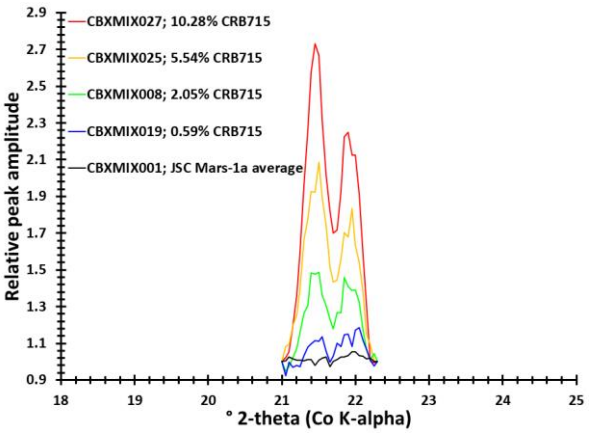

Figure 2: Continuum-removed X-ray diffraction peak amplitude of the strongest humboldtine (Fe oxalate) reflection from the data shown in Figure 1.

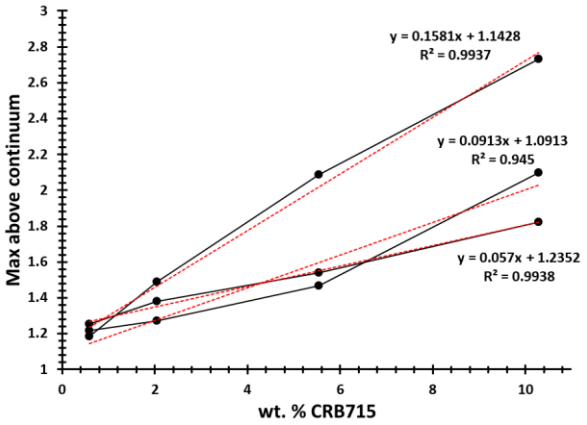

Figure 3: Calibration curves for the three strong humboldtine reflections when intimately mixed with the JSC Mars-1a palagonite. The top most curve is represented in Figures 1 and 2.

Discussion and Conclusions: The LODs of these fine-grained carboxylates in palagonite with the Terra XRD instrument was found to be roughly 1.0 wt.%. In particular, siderite and magnesite were found to have LODs of 0.65 and 0.56 wt. %, respectively, whereas the formates studied have LODs >2 wt.%. In contrast, the formates and acetates studied show LODs <0.5 wt.% in reflectance at NIR wavelengths, whereas very fine grained carbonates and oxalates are not detectable at concentrations lower than 10 wt.% at these wavelengths. Reflectance at the 4.0 micron band in carbonates shows very low LODs of <0.3 wt.%. These results will be used as information in the processing of CheMin and Supercam data to look for traces of these carboxylates.

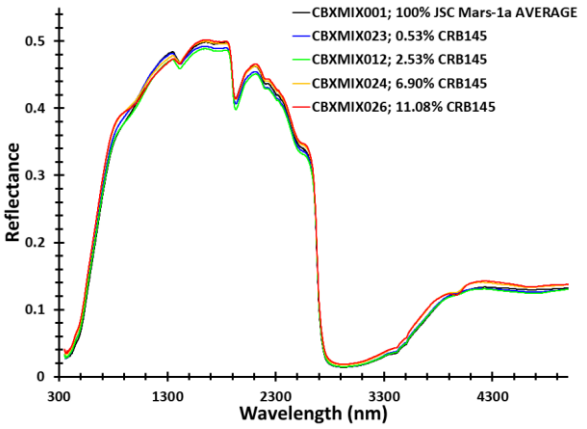

Figure 4: Reflectance spectra of siderite intimately mixed with the JSC Mars-1a palagonite.

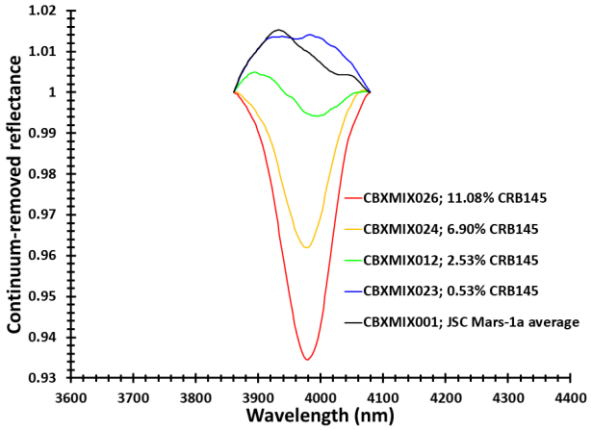

Figure 5: Continuum-removed reflectance spectra of the 4.0 micron absorption band from the data shown in Figure 1.

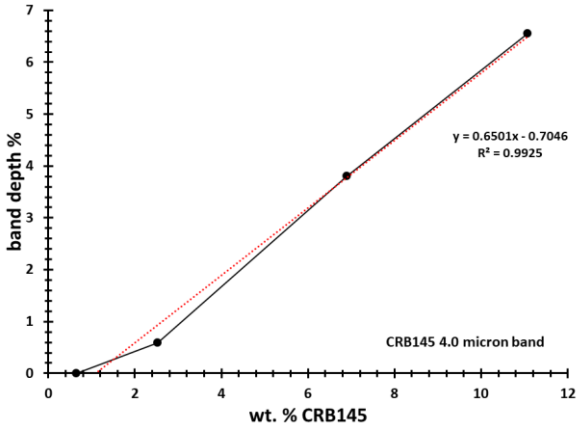

Figure 6: Calibration curves for the 4.0 micron siderite absorption band. The top most curve is represented in Figures 4 and 5.

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References: [1] Flynn, G. (1996) *Worlds in Interaction*, 469-474 [2] Grady, M., et al. (2004) *IJAB* 3, 117-124 [3] Steele, A., et al. (2016) *MAPS* 51, 2203-2225 [4] Steele., A., et al. (2018) *Science Advances* 4, 5518 [5] Benner, S. A., et al. (2000) *PNAS* 97, 2425-2430 [6] Fries, M., et al. (2017) LPSC, #2570 [7] Carillo-Sanchez, J. D., et al., *Icarus* 335, 113395 [8] Eigenbrode, J. L., et al. (2018) *Science* 260, 1096-1101 [9] Lewis, J. M. T., et al. (2021) *JGR:P* 126, JE006803 [10] Thorpe, M.T., et al. (2022) *JGR:P* 127, JE007099 [11] Scheller, E. L., et al. (2022) Science, v 378 [12] Applin, D. M., et al. (2016) *Icarus* 278, 7-30 [13] Wiens, R. C., et al. (2021) *SSR* 217, 1-87