

SPECTROSCOPIC PROPERTIES OF MARS-RELEVANT MINERALS: IMPLICATIONS FOR EXOMARS MISSIONS. E. Cloutis¹, C. Caudill¹, S. Potin¹, D. Applin¹, and K. Kubanek¹. ¹ Centre for Terrestrial and Planetary Exploration (C-TAPE), University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, Canada, R3B 2E9; e.cloutis@uwinnipeg.ca.

Introduction: The European Space Agency (ESA) ExoMars Trace Gas Orbiter (TGO) is exploring Mars from orbit, while the ESA ExoMars Rosalind Franklin rover will explore the Martian surface in the near future. Both missions are equipped with a number of optical spectrometers. On ExoMars TGO these include NOMAD (Nadir and Occultation for Mars Discovery) [1] and ACS (Atmospheric Chemistry Suite) [2]. ExoMars TGO can observe Mars in a number of viewing geometries, including nadir, limb, and solar occultation. The Rosalind Franklin spectrometers include ISEM (Infrared Spectrometer for ExoMars) [3], Ma_MISS (Mars Multispectral Imager for Subsurface Studies) [4] and MicrOmega [5]. These instruments have different modes of operation, wavelength coverage, and spectral resolution, some of which are presented in Table 1.

Table 1. Spectral parameters of ExoMars spectrometers.

Instrument	Spectral range (μm)	Spectral resolution
NOMAD	0.2-0.65 2.3-4.3	1.2-1.6 nm 0.15-0.5 cm^{-1}
ACS	0.73-1.6 1.7-17	~ 0.13 -0.8 cm^{-1} $\lambda/\Delta\lambda$: 20,000-50,000
ISEM	1.15-3.3	3.3-28 nm
Ma_MISS	0.4-2.2	~ 20 nm
MicrOmega	0.9-3.5	~ 20 cm^{-1}

To support of spectroscopic investigations of Mars, by these and other missions and instruments, we are investigating the spectroscopic properties of a range of Mars-relevant minerals, focusing on minerals and compounds relevant to Mars habitability and astrobiology, and via a range of spectroscopic techniques, including reflectance and transmittance. Here we report initial results for transmission and reflectance spectra.

Case study: humboldtine. Oxalates, which have been tentatively identified on Mars, are of astrobiological interest because of their association with biological processes [6, 7]. We have measured the spectral reflectance and transmission properties of 99% humboldtine ($(\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O})$ Alfa Aesar) (Figure 1) to facilitate derivation of optical properties, identify absorption features, and to relate them to specific mechanisms.

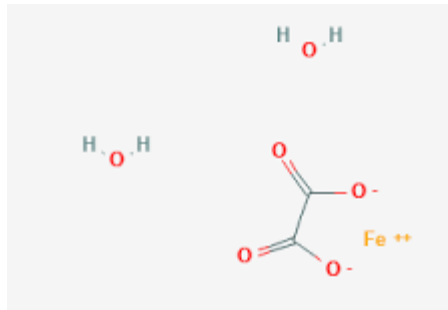


Figure 1. Structure of humboldtine (Fe^{2+} -oxalate) Source: <https://pubchem.ncbi.nlm.nih.gov/compound/Ferrous-oxalate-dihydrate>

The 0.2-2.5 μm reflectance spectrum of a <45 μm powdered sample of humboldtine (our sample ID CRB715) is shown in Figure 2. Its reflectance spectrum is characterized by low reflectance in the UV due to $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ absorptions, a steep absorption edge near 0.5 μm due to the same absorptions, overlapping absorption bands near 1 μm due to Fe^{2+} crystal field splitting, a series of overlapping absorption features due to $\text{H}_2\text{O}/\text{OH}$ at ~ 1.5 and 2.0 μm , and a number of overtones/combination of the C-O, C=O, and O-C=O oxalate molecule vibrations.

At longer wavelengths (Figure 3), there are numerous absorption bands due to various molecular stretches and bends, such as O-H, O-H-O, C-O, C=O, and O-C=O. The complexity of absorption features in this region, including the presence of Reststrahlen bands, both helps and hinders spectral interpretation. Prominent features include OH/ H_2O bands in the 3 and 6 μm regions, carbonate-like overtones in the 4.0 μm region, and saturated oxalate modes at longer wavelengths.

In transmission, humboldtine shows less spectral complexity in the 0.25-1.1 μm region (Figure 4), with a weak minimum in transmittance near 0.38 μm , followed by decreasing transmittance with decreasing wavelength. The differences between reflectance and transmittance is likely due to the methods employed: asperities in the KBr pellets similar to the size of the wavelengths causes scattering proportional to the λ^{-4} , which we have also seen strongly in other pellets. This likely changes the spectral properties of bulk powder reflectance vs. fine-grained powder dispersed in KBr.

In the infrared transmission spectrum (Figure 5), the 3-4 μm range does not present the expected absorptions, likely due to the concentration of the material

chosen to not saturate the oxalates modes near 6-8 μm . Higher concentrations of the material mixed with KBr would yield better results in the 2-4 μm region, but saturated the longer wavelength absorption bands. As with the reflectance spectrum, there are prominent absorption bands in this region. As compared to the reflectance spectrum, these bands are narrower and hence better resolved due to the absence of specular contributions.

Discussion: Spectral reflectance and transmission spectra are expected to, and do, show both similarities and differences. These are largely attributed to the causes of absorption features (e.g., Fresnel peaks), sample preparation (presence/absence of adsorbed water, dehydration of the sample), and scattering differences between bulk powders in reflectance vs. scattered particles in KBr pellets.

Summary and future activities: This spectroscopic study can inform analysis of data from various ExoMars spectrometers. The data are also being used to derive optical constants for future modelling of spectra of Mars and the Martian atmosphere.

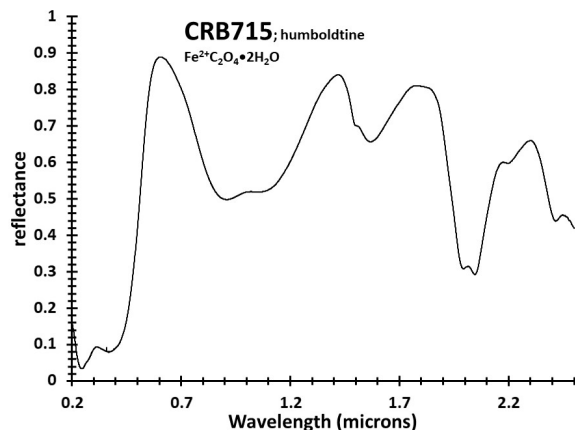


Figure 2. Combined UV-vis-NIR reflectance spectrum of CRB715 (humboldtine; <45 μm powder).

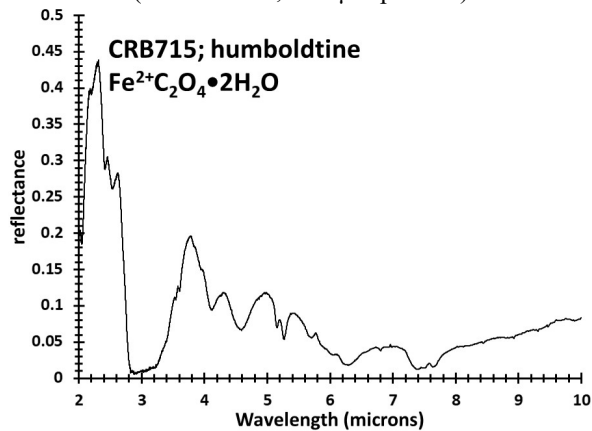


Figure 3. Infrared reflectance spectrum of CRB715 (humboldtine; <45 μm powder).

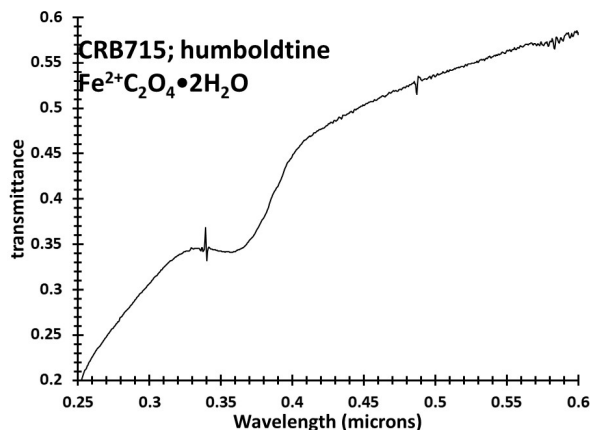


Figure 4. UV-Vis transmission spectrum of CRB715 (humboldtine; <45 μm powder).

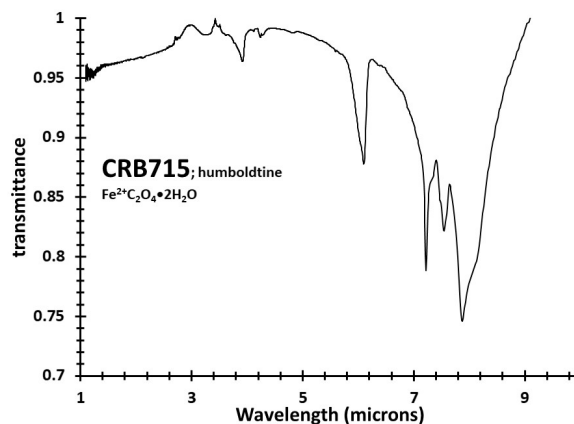


Figure 5. Infrared transmission spectrum of CRB715 (humboldtine; <45 μm powder).

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References: [1] Vandaele A.C., et al. (2018) *Space Sci. Rev.*, 214, 80. [2] Korablev, O.I., et al. (2015) *Solar System Res.*, 49, 529-537. [3] Korablev O.I., et al. (2017) *Astrobiology*, 17, 542-565. [4] De Sanctis M.C. et al. (2017) *Astrobiology*, 17, 612-620. [5] McAdam, A. C., et al. (2020) *JGR: P*, 125.11 [6] Applin D.M. et al. (2016) *Icarus*, 278, 7-30. [7] Applin D.M., et al. (2015) *Earth Planet. Sci. Lett.*, 420, 127-139.