

RESTSTRAHLEN BANDS NEAR 3 MICRONS IN CARBON-BEARING COMPOUNDS AND APPLICATIONS TO ASTEROID SPECTROSCOPY. D. M. Applin^{1*}, and E. A. Cloutis¹, M. R. M. Izawa²,
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Introduction: Thermal treatment, oxidation, hydrolysis, and photochemical decomposition of carbonaceous materials and volatiles (such as kerogens, bitumens, coals, and many cometary materials like HCN, etc.) often form major amounts of carboxylic acids, carboxylates, and carbonates through a very large number of reaction mechanisms, with concentrations typically increasing with processing [1-5]. Given the high number of pathways that can form these compounds, it might be expected that they would be spectrally significant components of carbonaceous asteroid surfaces through mechanisms such as space weathering, aqueous alteration, or low-temperature metamorphism. Carboxylic acids are strongly stable as solid dimers in the absence of high humidity and significant water activity, while many carboxylates and carbonates are highly resistant to radiolytic decomposition [5,6]. Given possible underreporting of these compounds in various planetary materials, we investigated the infrared spectral reflectance properties of solid oxalic acid and various volumetrically minimal (at least terrestrially) carbonate minerals and compared these spectra to those of asteroids.

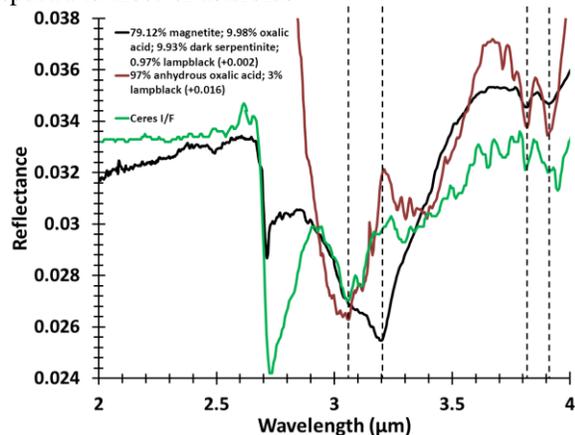


Figure 1. Reflectance spectra of oxalic acid mixtures compared to recent observations of Ceres by DAWN. Ceres I/F was modified from [8].

Methods: All intimate mixtures of particulate samples were measured by weight, and subsequently pulverized together with a mortar and pestle. Starting grain sizes were as follows: MAG103 (magnetite) <45 μm; ASB267 (dark serpentine) <45 μm; LCA101 (lampblack) <0.023 μm; ART002 (anhydrous oxalic acid) <100 μm. M1, a mixture of ART002 and LCA101 was pulverized together for less than 1 mi-

nute. M2, a mixture of all starting materials was pulverized together for over 5 minutes. Both mixtures were baked in air at 110°C, and cooled in dry N₂ prior to spectral measurements.

Diffuse reflectance spectra from 2.0-25.0 μm were collected with a Bruker (Billerica, MA) Vertex 70 Fourier Transform Infrared spectrometer equipped with an infrared Globar light source, mercury cadmium telluride detector, and KBr broadband beamsplitter. Spectra were acquired relative to a Labsphere Infragold[®] 100% reflectance standard measured at $i=30^\circ$ and $e=0^\circ$ using a SpecAc Monolayer grazing angle specular reflectance accessory. Up to 200 000 spectra were collected at a scanner velocity of 20 kHz, and averaged to improve SNR.

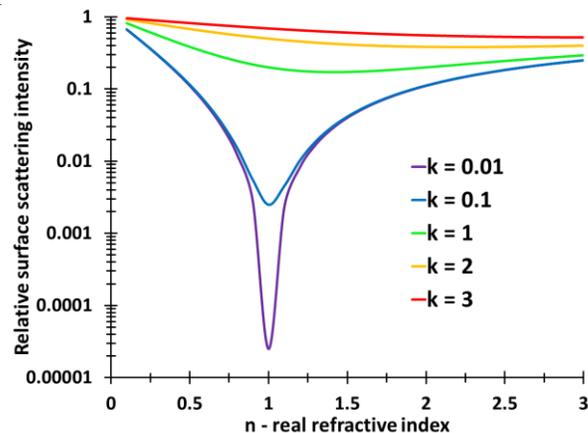


Figure 2. Simplified relationship between surface scattering intensity and optical constants. k = imaginary refractive index.

Results and discussion: Carboxylic acid dimers are known to have very intense OH stretching absorption bands centered near ~3.2 μm [7]. As seen in **Fig. 1**, the absorption appears as a ‘Reststrahlen band’ in M1. These Reststrahlen bands are phenomena that occur in reflectance where the centre of an absorption band appears as a peak due to strong surface scattering caused by high absorption (k) and a large deviation from a refractive index (n) of the surrounding (air or vacuum) (**Fig. 2**), which commonly occurs in mineral spectra >6 μm. Below this, typically only water ice, at 3.14 μm, is reported to exhibit such a feature. A competing process is that of volume scattering (where reflected photons have made some penetration into a grain), and where intensity is roughly a function of the absorption coefficient, grain size, and wavelength (**Fig. 3**). When grain size is large and wavelengths are small,

volume scattering is small to non-existent, and reflected photons are due to surface scattering only. The opposite occurs as grain size decreases. This is observed in M2 [Fig. 1, black], where the peak becomes a transmission-like absorption band due to what is likely submicroscopic grain sizes caused by the long grinding time.

These spectra appear qualitatively similar to those of Ceres collected by DAWN [Fig. 1]. So much so that if oxalic acid in M2 were of sufficient grain size, the spectra would likely be strongly replicated near 3 μm , including the positions of the ~ 3.8 and ~ 3.9 μm features, which are only known to occur in carbonates and carboxylic acids.

The reflectance spectra of asteroid 24 Themis exhibit similar reflectance spectra, with absorption features somewhat shifted consistently longward [Fig. 4]. Features at ~ 3.87 and ~ 3.94 μm are present but were not discussed by [9]. These features are indicative of carboxylic acids or carbonates, as no other compounds are known to show this spectral behaviour.

Also of significance is a relatively strong Reststrahlen band exhibited by dawsonite ($\text{NaAlCO}_3(\text{OH})_2$) at 3.05 μm (Fig. 4). Other carbonate minerals exhibit OH stretching at this wavelength, although they are typically quite broad [10]. Collection of reflectance spectra of these minerals stripped of adsorbed water may provide better insights into their spectral behaviour.

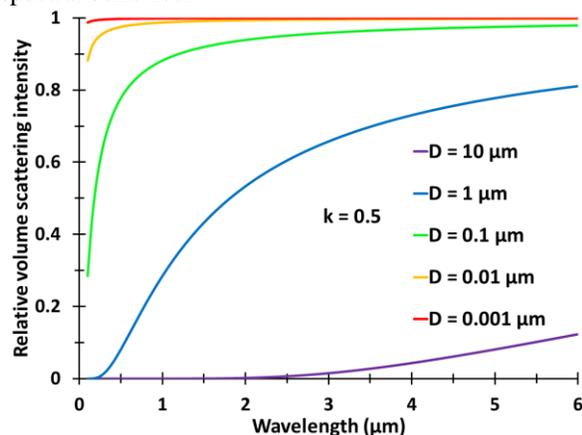


Figure 3. Simplified demonstration of the dependence on grain size and wavelength by volume scattering intensity. D = grain size

Conclusions: Minerals and compounds other than water ice are shown to exhibit Reststrahlen bands near 3 μm . The presence of absorption bands at ~ 3.05 μm and at ~ 3.8 and ~ 3.9 μm by carboxylic acids and carbonates, as well as the presence of quite a few other asteroids bearing similar spectra indicates that such a feature at ~ 3.05 μm does not necessarily need to be assigned to NH_4 phases. Consequently, this implies that Ceres does not require an outer solar system origin.

What may perhaps be occurring is the formation of radiolytically stable carboxylic acids, carboxylates, and carbonates by space weathering and/or aqueous alteration.

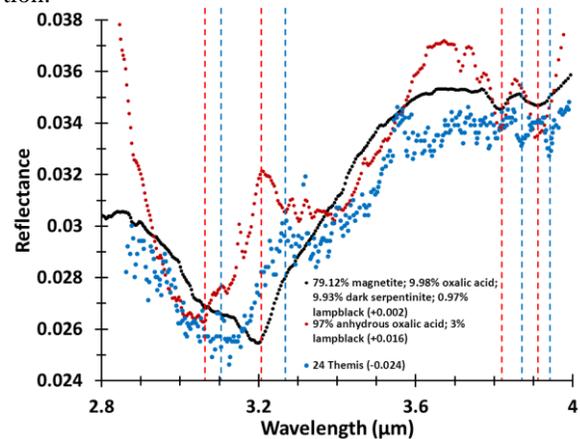


Figure 4. Reflectance spectra of oxalic acid mixtures compared to telescopic observation of asteroid 24 Themis. Spectra of 24 Themis were modified from [9], where error bars can be viewed.

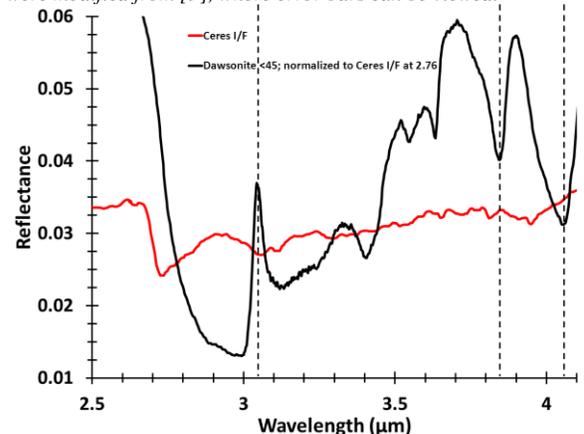


Figure 5. Reflectance spectra of the carbonate mineral dawsonite compared to recent observations of Ceres by DAWN.

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