THE STABILITY OF OXALIC ACID AND ITS SALTS ON THE SURFACE OF MARS

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Introduction

Abiogenic formation of oxalate minerals on Earth include low-temperature hydrothermal and diagenetic deposits (1), and possibly atmospheric hydrocarbon interaction with carbonate (2). Oxalates are widespread in soil and endolithic environments due to the production of oxalic acid (OA) by soil and endolithic microbes (3).

Abiotic conditions for OA and oxalate formation include PAH degradation and diagenesis (4), possible CO_2 ice-hydrocarbon mixtures exposed to solar radiation (5), CO_2 hydrate radiolysis (6) and possibly Fe-rich clay sequestration of CO_2 (7). The most significant abiotic source is from meteorite aqueous alteration. Analysis of insoluble organic matter (IOM) of the Murchison meteorite has shown that ~30% is ether groups containing molecules with aliphatic carbon chains, dominated by OA (8). OA has also been identified in Yamato-791198 (9). This is significant, as we have putatively identified OA-like bands in Murchison IOM (Fig. 1).

Oxalates are the most geological stable salt of any organic acid (10), and their absence from widespread occurrence in the rock record may be due the biologically produced oxalate decarboxylase enzyme which creates the oxalate-carbonate pathway (11). In the absence of this enzyme, which is likely on Mars, oxalates could have accumulated through meteorite introduction and the formation conditions we have outlined. In order to evaluate this, we need to constrain their stability when exposed to the conditions present on the surface of Mars.

Methods

Mars surface conditions were simulated using HOSERLab's mini-ME chamber (12). Atmospheric composition was approximated using CO_2 passed through Drierite®. Pressure of 600 Pa was achieved by a continuously running scroll pump and monitored by two digital pressure gauges. Ultraviolet irradiation was provided by a 25W deuterium lamp where one day of irradiation roughly equals the irradiation of 6 martian years. Sample surfaces were kept <10°C.

In situ reflectance spectra from 04-2.4 µm were collected with an ASD FieldSpec Pro HR spectrometer. Incident light was provided by an in-house 100 W quartz-tungsten-halogen (QTH) light source. Spectra were acquired at i=0° and e=0° using a bifurcated reflectance probe. Reflectance spectra were measured relative to a halon standard located in the sample disk. Spectra from 2-5.2 µm were collected with a D&P Model 102F FT infrared spectrometer. Sample illumination was provided by an in-house 100W QTH light source through an open-air aluminum pipe. Samples were measured at i=30° and e=0°. Reflectance spectra were acquired relative to an Infragold® diffuse gold-coated standard. After exposure to simulated Mars-surface conditions for 38 days, the chamber was closed off and opened in a glove box purged with CO_2, where oxygen and relative humidity were monitored to be <<1%. We measured reflectance (200-2500 nm), Raman, fluorescence, and XRD/XRF (we only present in situ reflectance and pre/post-exposure fluorescence here).

Fluorescence was measured from 370 to 1100 nm with an Ocean Optics Maya2000 Pro spectrometer. Spectra were acquired with an in-house 50W QTH light source and three different induction wavelength light sources (364, 405, and 532 nm). Reference spectra were acquired on $BaSO_4$ with the QTH at i=30° and induction light source directed into one end of a bifurcated probe, with the other end directed into the detector. Sample spectra were acquired at i=0°, e=0° with the QTH turned off.
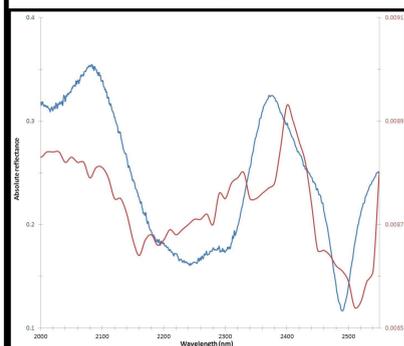

Figure 1. NIR reflectance of OA (**blue**) and the 120-150 um fraction of Murchison meteorite insoluble organic matter (**red**) without continua removed.
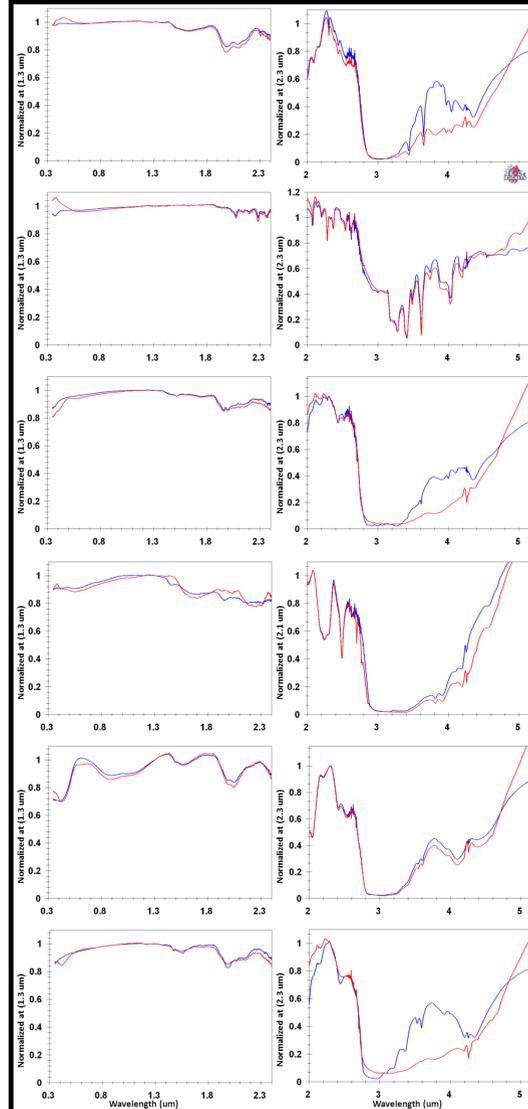
Results

Figure 2. In situ spectral monitoring: **blue** spectra are before exposure, **red** are post. From top to bottom: POM, natroxalate, whewellite, OA, humboldtine, and glushinskite.

Reflectance spectra from 0.3 to 2.5 µm show potassium oxalate monohydrate (POM) and natroxalate appear mostly unchanged with the exception of an increase in reflectance at the highest energies measured (Fig. 2). Whewellite shows no decrease in intensity of the OH and H_2O absorption bands at 1.4 and 1.9 µm. The only observable change is the development of a significant colour center at 0.58 µm and a slight reddening of the slope into the UV. OA had taken on water prior to data acquisition. During the monitoring we observe that OA monohydrate has reverted back to anhydrous, which occurred within minutes of dropping pressure. Humboldtine has also developed a colour center at 0.62 µm, and is otherwise unchanged. Glushinskite appears to have partially dehydrated, observed as a decrease in intensity of the water bands, and also developed a sharp reddening into the UV.

Reflectance spectra from 2 to 5.2 µm show nnatroxalate, humboldtine, and OA appear to have had no changes to any features. It appears that whewellite may have partially dehydrated and amorphized. The characteristic C-O overtones between 2.4 and 2.5 µm are subdued (~40% band depth loss). C-O overtones/combinations between 3 and 4 µm, and the O-C=O bending overtone near 4.4 µm are very subdued. We see very similar results with glushinskite.

These oxalates exhibit very little fluorescence prior to exposure (Fig. 3). There is some blue broadband fluorescence with excitations wavelengths of 365 and 405 nm, and none from the excitation wavelength of 532 nm. It is worth noting that the apparent fluorescence of humboldtine is product of the normalization. The reflectance of humboldtine (Fig. 2) is markedly different to the other oxalates due to the charge transfer of the Fe. This causes a gross exaggeration of the residual lamp output ~750 nm. After exposure to simulated Mars-surface conditions, whewellite and glushinskite show very strong broadband fluorescence in the blue region when excited with the 365 and 405 nm light sources. Natroxalate and POM have increased fluorescence, though much more subdued relative to whewellite and glushinskite. Additionally, whewellite and glushinskite, and to a lesser extent the other oxalates exhibit very small amounts of fluorescence when excited with 532 nm.
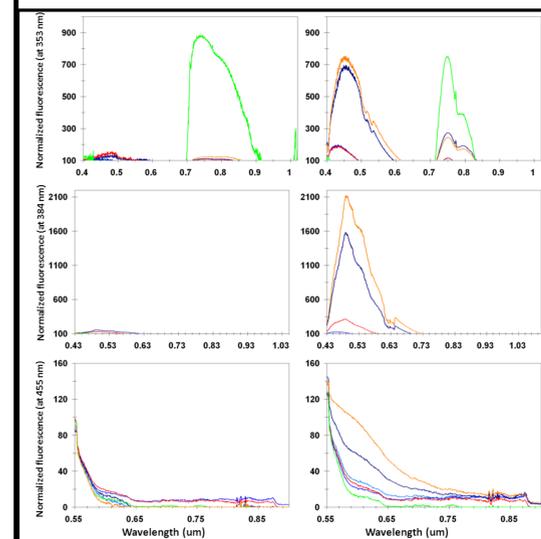
Discussion and Conclusion

Contrary to previous reports (13), OA compounds may be stable on the surface of Mars. This questions the applicability low-pressure and low Earth orbit experiments to the stability of oxalates, and perhaps other carboxylic acids on the surface of Mars. Interestingly, the fluorescence produced by these oxalates post-exposure to Mars surface conditions may be from the development of phototolerant compounds, as was observed to have occurred on mellitic acid in the previously mentioned experiments.

Our results suggest that oxalates maybe be a source for carbonates on Mars, and may play a significant role in the martian carbon cycle as a minor constituent of the martian regolith. Interestingly, OA itself has two C-O absorption bands at 4 um that are closer to those observed in huntite than any other candidate mineral for the bands observed by the Planetary Fourier Spectrometer (14), with an almost identical band depth. OA also has C-O overtones in very similar positions as magnesite and those observed by the CRISM (15), albeit with different band shapes and with inflections of additional combination bands.

Additionally, the dichotomous distribution of carboxylic acids (particularly dicarboxylic acids including OA) in CM chondrites, coupled with their instability in vacuo versus at typical martian pressures may suggest a way to discern polymict versus monomict CM chondrite parent bodies, though this idea is in its infancy.

Finally, he stability of OA and its salts on Mars has major implications for the identification of endolithic communities, as oxalate is commonly produced by endolithic microbes and plays important metabolic roles (e.g., as a chelating agent for trace metal nutrients and in ligand-promoted mineral dissolution). The stability of oxalate compounds on the martian surface combined with their potential link with biological processes make oxalate minerals high-value astrobiology targets.

Figure 3. Fluorescence: left column is before exposure, right column is post-exposure. Induction light sources from top to bottom: 365 nm, 405 nm, and 532 nm. POM: blue, natroxalate: red, whewellite: dark blue, OAA: cyan, humboldtine: green, glushinskite: orange.

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