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 diageneric 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).

Methods

Mars surface conditions were simulated using HOSERLab’s mini-ME chamber (12). Atmospheric composition was approximated using CO₂ 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 0.4-2.4 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 4°0 and ε0° using a bifurcated reflectance probe. Reflectance spectra were measured relative to a halon standard located in the sample disk. Spectra from 2.5-5.2 μm were collected with a D&P Model 102F FT infrared spectrometer. Sample illumination was provided by an in-house 100 W QTH light source through an open-air aluminium pipe. Samples were measured at ε=30° and ε=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 CO₂ where oxygen and relative humidity were monitored to be <ε0°.

Reflectance spectra were acquired on BaSO₄ with the QTH at ε=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°, ε=0° with the QTH turned off.

Results

Reflectance spectra from 0.3 to 2.5 μm show potassium oxalate monohydrate (POM) and natrooxalate 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 H₂O 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 in the UV.

Reflectance spectra from 2 to 5.2 μm show natrooxalate, humbolidite, and OA appear to have had no changes to any features. It appears that whewellite may have partially dehydrated and amororhized. The characterstic C-O overtones between 2.4 and 2.5 μm are subdued (~40% band depth loss). C-O overtones/combutions 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 excitation wavelengths of 365 and 405 nm, and none from the excitation wavelength of 332 nm. It is worth noting that the apparent fluorescence of humbolidite is product of the normalization. The reflectance of humbolidite (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. Natrooxalate and POM have increased fluorescence, though much more subdued relative to whewellite and glushinskite. Additionally, whewellite and glushinskite, and to 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 phototoxid 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 μm 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 vs. at typical martian pressures may suggest a way to discern polymict versus nonmonomict CM chondrite parent bodies, though this idea is in its infancy.

Finally, the stability of OA and its salts on Mars has major implications for the identification of endolithic communities, as oxalate is commonly produced by endolithic microbe 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 may oxidize minerals high-value astrobiology targets.

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References