DECARBOXYLATION OF CARBON COMPOUNDS AS A POTENTIAL SOURCE FOR CO_2 and CO OBSERVED BY SAM AT YELLOWKNIFE BAY, GALE CRATER, MARS.

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Introduction: Martian carbon was detected in the Sheepbed mudtsone at Yellowknife Bay, Gale Crater, Mars by the Sample Analysis at Mars (SAM) instrument onboard *Curiosity,* the rover of the Mars Science Laboratory mission [1]. The carbon was detected as CO_2 thermally evolved from drilled and sieved rock powder that was delivered to SAM as a <150-μm-particle-size fraction. Most of the CO_2 observed in the Cumberland (CB) drill hole evolved between 150° and 350° C. In the John Klein (JK) drill hole, the CO_2 evolved up to 500° C. Hypotheses for the source of the the CO_2 include the breakdown of carbonate minerals reacting with HCl released from oxychlorine compounds, combustion of organic matter by O_2 thermally evolved from the same oxychlorine minerals [2], and the decarboxylation of organic molecules indigenous to the martian rock sample [1]. Here we explore the potential for the decarboxylation hypothesis.

Methods: Various compound standards were analyzed in the laboratory using an instrument customized to operate as closely as possible to SAM's analytical conditions for evolved gas analysis (EGA). The sample was added to a preconditioned (pre-combusted) stainless steel cup that was then heated under helium at 30 mb from 50-1050° C at 35° C/min. The evolved gases were then split and 1/100th of the total gas was directed to the quadrupole mass spectrometer. All transfer lines between the oven and mass spectrometer were held at 135° C. The mass spectrometer scanned the 2-300 Da mass range. In a separate set of experiments, the helium carrier gas was exchanged for 99.99% oxygen keeping all other analytical conditions the same.

Carbon compounds. Compound standards chosen for these experiments were selected based on the number of carboxyl groups and differences in the structure of their carbon skeletons. Bicarbonate, oxalates (Figure 1) and acetates (Figure 2) represent the simplest structures. Oxaloacetic and mellitic acid represent slightly larger structures that are also strongly oxidized. Not shown are additional simple aromatic compounds: phthalic acid (one aromatic C-ring with two carboxylic acid groups, benzene tricarboxylic acid, benzene tetra-carboxylic acid, and naphthalene dicarboxylic acid (two aromatic rings) as well as a set of organic-oxalate structures: dimethyl- and diethyl oxalates.

Results: He-EGA pyrograms for *m/z* 44 and 28 reveal the evolution of CO_2 and CO, respectively, at a wide range of temperatures (Figures 1 and 2). CO_2 and CO were the only observed products for oxalates, bicarbonate and mellitic acid. In some cases, CO was the dominant volatile product detected. The oxalates also produced methyl- and ethyl- pyrolysis products (*m/z* 14, 15, 26, and 27). Phthalic acids, having only 2 carboxylic acid groups produced a small amount of CO_2 at 200°-300° C, but the majority of product was the anhydride of phthalic acid. Benzene tri- and tetra-carboxylic acids also produced a small CO_2 peak at 200°-300° C, but the anhydride portions evolved subsequent to the main CO_2 peak and with additional and a continual release of trace CO_2 up to >900° C.
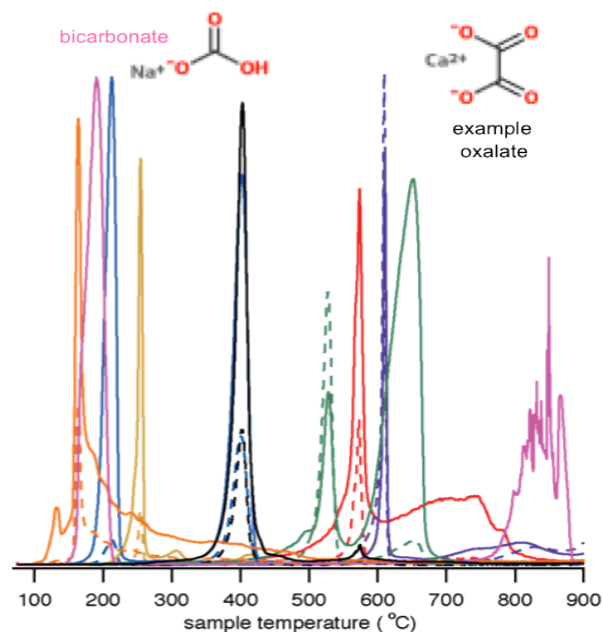

Figure 1. CO_2 (solid lines) and CO (dashed lines) evolved from oxalate ($C_2O_4^{2-}$) minerals. Colors designate different cation moieties of oxalate: orange, H^+; blue, $Fe(III)^+$, hexahydrate; gold, NH_4^+; black, $Fe(II)^{2+}$; green, Ca^{2+}; red, Na^{2+}; purple, K^{2+}. An example oxalate structure is shown. Sodium bicarbonate is shown in pink. Mg-oxalate, not tested, evolves CO_2 between 250° and 300° C [3].

O_2-GA results. In all cases, where oxalates, acetates, and mellitic acid were run under O_2 instead of helium, no volatile products were observed by the mass spectrometer. Benzene and naphthalenic carboxylic acids produced CO_2 between 275° and 1050° C roughly

matching the temperature range of the anhydride products observed under He-EGA. In one case (benzene tetracarboxylc acid), tailing of a CO_2 peak was also observed at 50-80° C. This observation and the absence of any CO_2 detection in all of the oxalate, acetate, and mellitic acid O_2-EGA tests indicates that in the presence of O_2, the temperature of CO_2 evolution was lowered by 150°-200° C and probably reflects oxidation, rather than decarboxylation, of the analyte. In other words, the CO_2 release occurred prior to the start of the mass spectrometer at 50° C.
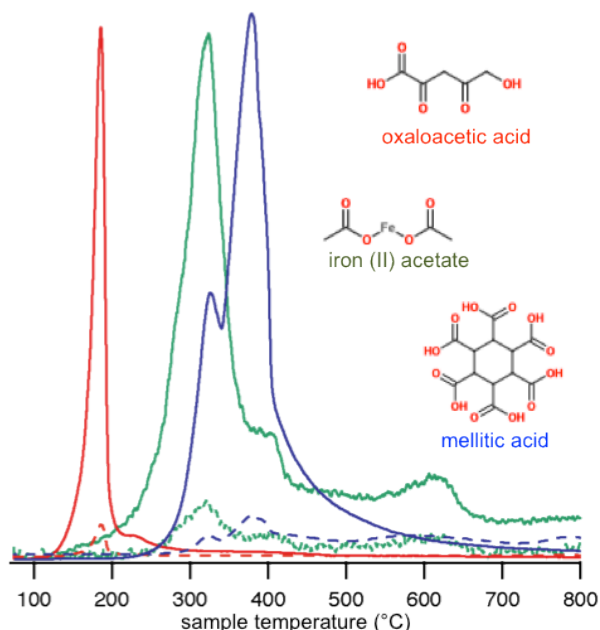

Figure 2. CO_2 (solid lines) and CO (dashed lines) evolved from highly oxidized carbon compounds. Except for m/z 15 (CH_3^+), no other mass products were detected via EGA under SAM-like analytical conditions.

Discussion: The CO_2 released from the Sheepbed mudstone peaked at <300° C, which is distinctly different from the two CO_2 peaks from the Rocknest (RN) material (~400° and ~512° C)[2]. An additional shoulder of the CO_2 release from the JK drill fines of the Sheepbed mudstone occurred at 400-450° C. A similar shoulder was not observed in the CB drill fines. The onset of O_2 release in samples differed: ~150° C in JK, ~230° C in CB, and ~300° C in RN [1] and the onset of CO_2 release always preceeded O_2 release: <50° C in JK, ~180° C in CB [1], and ~125° C in RN [2,4].

The temperatures of the CO_2 and CO thermally evolved from the Sheepbed mudstone and Rocknest aeolian material are consistent with decarboxylation of simple carbon compounds. Further, O_2 evolved from other minerals suggests the possibility of complete oxidation of oxalate, acetate, and other carbonyl- and carboxyl-bearing molecules—if such molecules were present. This oxidation would occur at the onset of O_2 release and limited by reactant availability.

Oxalates have not been directly detected by the CheMin X-ray diffraction instrument or SAM on *Curiosity*. If present, they may have escaped CheMin detection due to low abundance or their presence in an X-ray amorphous state that can result from dehydration [5]. On Earth, oxalates are formed in diagenetic and hydrothermal settings [6]. More broadly, partial oxidation products, such as oxalates, acetates, and benzene-carboxylic acids may be Fenton-reaction products formed by UV radiation [7]. Extrapolating from this hypothesis, these compounds are expected metastable products formed as a result of other cosmic ray radiolysis in the presence of oxidants within near-surface rocks. Assuming martian sedimentary deposits contain a macromolecular component—the most common form of natural organic matter—from a geological, exogenous, or biological source, macromolecules might weather to the carbon compounds discussed above [7] before being destroyed by further radiolysis and oxidation. The detection of partially oxidized carbon compounds may depend on the rates of weathering macromolecular organics relative to rates of destruction of small carbon compounds in the surface environment of Mars. Preservation mechanisms, such as mineral encapsulation, limited oxidant exposure, and limited cumulative radiation dose [8,9], may limit the rate of weathering of macromolecular organics.

Conclusion: Simple carbon compounds that are oxidized, such as oxalates, acetates, and mellitic acid, will undergo decarboxylation to produce CO_2 at temperatures as low as 150° C under inert conditions (i.e., He), but in the presence of 99.99% oxygen, the CO_2 evolution can be shifted to lower temperatures. It is possible that the CO_2 peaks evolved from the Sheepbed mudstone reflect decarboxylation and/or further oxidation of already partially oxidized carbon compounds, organic or inorganic. Such small carbon compounds are consistent with diagenetic and hydrothermal formation processes as well as oxidative radiolytic weathering of more complex organic molecules in surface materials on Mars.

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