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Detection of reduced sulfur and other S-bearing species evolved from Rocknest sample in the Sample Analysis at Mars (SAM) experiment

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The SAM instrument suite onboard the Mars Science Laboratory (MSL) Curiosity Rover detected sulfur-bearing compounds during pyrolysis of soil fines obtained from aeolian material at Rocknest in Gale Crater. SO_2 and H2S were identified by the quadrupole mass spectrometer (QMS) both in direct evolved gas analysis mass spectrometry (EGA-MS) and after gas chromatograph separation (GC-MS) [1].
In EGA-MS, the 34 Da trace shows at least 3 peaks. The first peak is evolved at relatively low temperature (T), near 400°C, and the other peaks evolved as part of a "hump" at higher T, between ~500°C and ~800°C. The higher T releases at 34 Da occur at T close to, but not at exactly the same, as an evolution of SO_2 from the samples. We hypothesize that these 34 Da releases are due to H2S. This assertion is supported by peaks in 35 and 36 Da traces at the same T. The lower T release of 34 Da species corresponds to a large O_2 release from the Rocknest samples, and can be attributed for the most part to an isotopologue of O_2. However, the GCMS analysis of the temperature cut involving this first evolved peak displays evidence of H2S based on a comparison of the mass spectrum to a NIST library. Therefore, we propose that H2S must be contributing to the 400ºC peak. The quantification of H2S from GCMS shows an amount of this species of less than 1 nmol. It is unclear what the source of this lower T H2S is and how sulfur remains in its reduced form instead of undergoing oxidation to SO_2 at the temperature where O_2 is evolved; laboratory work with relevant analogs to inform these questions is ongoing. An initial hypothesis for the low temperature H2S source is the product of a reaction between an S-bearing phase and a hydrogen-bearing phase, such as the abundant water evolved at less than 500ºC from the sample. Potential sources of this water are adsorbed water or mineral structural water.
There is also EGA-MS evidence of reaction of reduced S with CO_2 in the pyrolysis oven to form OCS (main mass 60 Da) and possibly CS2 (main mass 76 Da). Sulfur in all detected compounds is highly likely to have a Martian origin, as from the analysis of SAM background, the S-bearing species are quantitatively very limited and no known chemical process enables the formation of H2S from the background. Pyrolysis experiments on SNC meteorites and most recently the Tissint meteorite show a large SO_2 peak evolved at temperatures above 600ºC, which was not observed at lower temperature, and may be from sulfate thermal degradation. GC shows that a large quantity of CO_2 is evolved along with OCS and CS2. However, the absence of H2S confirms a high oxidation of the molecules in the sample. This Tissint meteorite is believed to have resemblances with Rocknest soil, and a cross-analysis of these results, in addition to the lab work, are essential steps for a complete understanding of these Martian sulfur-bearing compounds.