MEASURING SULFUR ISOTOPE RATIOS FROM SOLID SAMPLES WITH THE SAMPLE ANALYSIS AT MARS INSTRUMENT AND THE EFFECTS OF DEAD TIME CORRECTIONS.

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Introduction: The Sample Analysis at Mars (SAM) instrument suite comprises the largest science payload on the Mars Science Laboratory (MSL) "Curiosity" rover [1, 2]. SAM will perform chemical and isotopic analysis of volatile compounds from atmospheric and solid samples to address questions pertaining to habitability and geochemical processes on Mars. Sulfur is a key element of interest in this regard, as sulfur compounds have been detected on the Martian surface by both *in situ* and remote sensing techniques [3-8]. Their chemical and isotopic composition can help constrain environmental conditions and mechanisms at the time of formation.

A previous study examined the capability of the SAM quadrupole mass spectrometer (QMS) to determine sulfur isotope ratios of SO_2 gas from a statistical perspective [9]. Here we discuss the development of a method for determining sulfur isotope ratios with the QMS by sampling SO_2 generated from heating of solid sulfate samples in SAM's pyrolysis oven. This analysis, which was performed with the SAM breadboard system, also required development of a novel treatment of the QMS dead time to accommodate the characteristics of an aging detector.

The SAM Instrument: The SAM analytical suite consists of the QMS, two pyrolysis ovens, six gas chromatograph (GC) columns, and a tunable laser spectrometer (TLS). Volatiles may be introduced into the QMS and TLS either directly from the atmosphere or by heating solid samples acquired at the Martian surface in the pyrolysis ovens. While the TLS can measure isotope ratios of carbon, oxygen, and hydrogen in certain compounds, it has no channel capable of measuring sulfur isotopes, so the QMS must perform this function.

Experimental Methods: In evolved gas analysis (EGA) experiments, powdered solid samples are heated in one of SAM's pyrolysis ovens and sampled directly by the QMS without passing through a GC column. This is the most fundamental type of experiment that SAM will perform with solid samples, yielding clues pertaining to mineralogy and the presence of organics. During a nominal EGA run, the pyrolysis oven is heated from ambient temperature to ~1000 °C at a constant ramp rate. The experiments described here utilized a ramp rate of 40°C/min. As volatiles are released from the sample, they are swept through the gas manifold by helium carrier gas. The QMS continuously samples the outflow from the pyrolysis oven, scanning over the m/z range of interest. Different types of compounds thermally decompose at different temperatures, so the variation in QMS signal with temperature provides information on the sample's contents. Integration of signal over time allows quantitative estimates of chemical and isotopic abundance.

Testing and calibration of the SAM flight model's EGA functionality was performed with synthetic calcite ($CaCO_3$) and melanterite ($FeSO_4 \cdot 7H_2O$), which evolve CO_2 and SO_2, respectively, at characteristic temperatures. Note that melanterite also evolves H_2O. Sulfur isotope ratios were computed from breadboard EGA experiments with these same materials. The melanterite sulfur isotopic composition was independently measured with high precision by chemical extraction/mass spectrometry in the stable isotope laboratory at the University of Maryland using standard techniques [10].

Dead Time Determination: The SAM breadboard includes a laboratory analog of SAM's pyrolysis ovens and the SAM prototype QMS, controlled by flight-like electronics and software. The system has been designed to mimic the performance of the flight model as closely as possible. The SAM QMS contains a single-channel electron multiplier detector, operated in pulse counting mode. Typically in these types of detectors, there is a minimum length of time that must separate two events for them to be recorded as two separate pulses, known as the "dead time" [11]. If multiple events occur within the time required for a single output pulse, some events may be lost, leading to erroneously low measurements at high count rates. Accurate quantitative analysis requires a correction to the raw QMS data to account for this phenomenon. A standard form for this correction for paralyzable detector systems is $o = ne^{-n\tau}$, where o = observed count rate, n = the true count rate, and τ = the dead time [11]. Usually τ is represented by a constant value, typically between 20-80 ns for these types of detectors. While other components of the system, such as the electronics, can also contribute to the dead time, the dead time of the SAM QMS is overwhelmingly dominated by detector performance.

The QMS dead time was determined from calibration of pure Kr and SO_2 by two different methods. The

first method assumed linearity of the signal at a given m/z with pressure. However, possible non-linear behavior of the pressure gauge introduces a potential source of error into this measurement. The second method, which was used for the sulfur isotope analysis, assumed a constant ratio of two isotopes with increasing count rate. Initially it was assumed that the dead time was constant for the system. However, no single value for the dead time could be found that would fit the breadboard calibration data across the full range of pressures and count rates.

At the time of this study, the breadboard QMS had been operated for several years with its original detector, thus greatly exceeding the normal expected detector lifetime. By assuming that the aging detector was displaying non-ideal behavior in which the dead time increased with observed count rate, it was possible to obtain good fits for the calibration data for both Kr and SO_2. The mathematical form $\tau = ae^{bo}$, where a and b are constants and o = observed count rate, was used for the variable dead time correction. The dead times obtained with this formula for SO_2, obtained by assuming a constant ratio of m/z 66 to 64 for the SO_2 tank gas, ranged from approximately 2 to 66 ns. Note that the detector begins to saturate shortly above 2E+06 counts/s, and the correction given here is valid only up to the point where the detector output begins to decrease with increasing ion current.

Calculation of Sulfur Isotope Ratios: Sulfur isotope ratios were computed first for the SO_2 tank gas to validate the dead time correction procedure. Vienna Standard Mean Ocean Water (V-SMOW) composition was assumed for the oxygen isotopes. The ratio of $^{36}S/^{32}S$ was assumed to be constant, matching that of Vienna Cañon Diablo Troilite (V-CDT). The ratios of $^{33}S/^{32}S$ and $^{34}S/^{32}S$ were then determined iteratively as constrained by the observed count rates at each SO_2 isotopologue.

Figure 1 illustrates the importance of applying the dead time correction in the computation of the sulfur isotope ratios. Open symbols in the figure represent the uncorrected raw data, while closed symbols show the data after correction for the dead time. Dotted lines represent V-CDT composition. While the isotopic composition of the tank has not been independently measured, it is not expected to deviate significantly from V-CDT. Note that isotope ratios computed from the uncorrected raw data deviate dramatically from V-CDT as the count rate increases.

Sulfur isotope ratios were computed for the SO_2 evolved during melanterite pyrolysis by integrating the total counts under the dead time-corrected, background-subtracted EGA curve for each isotopologue of SO_2. As described before, V-SMOW composition was assumed for the oxygen isotopes, the $^{36}S/^{32}S$ ratio was assumed to match V-CDT, and the ratios of $^{33}S/^{32}S$ and $^{34}S/^{32}S$ were then determined iteratively as constrained by the observed peak areas. Results were compared to the high-precision measurements after chemical extraction. For six separate EGA runs, the difference in the $^{34}S/^{32}S$ QMS ratio from the high-precision ratio was -0.2 ± 8.6‰. The $^{34}S/^{32}S$ ratio was also computed using the standard method that applies an oxygen correction to the ratio of m/z 66 to 64. For the same six EGA runs, the average deviation of QMS from high-precision results was -15.0 ± 6.1‰. Errors in the $^{33}S/^{32}S$ ratio were several percent.

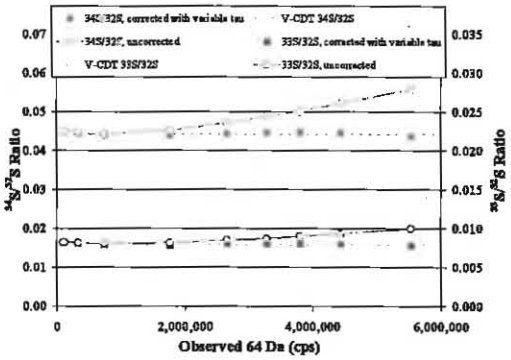

Figure 1. Effect of dead time correction on sulfur isotope ratios.

Future Work: Calibration of the SAM flight model (FM) is being performed with the same dead time formulation devised for the breadboard. The dead time computed from FM tests shows a much less pronounced variation with increasing count rate, although use of the variable dead time still produces the best fit to the data. The breadboard QMS has recently been refurbished with a new detector. The sulfur isotope study described here will be repeated with this new detector, which is expected to perform in a more flight-like manner. If resources permit, the sulfur isotope ratios of the SO_2 tank gas may also be measured independently to validate those obtained from QMS calibration data.

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