SULFIDE MINERALS NOT NECESSARY FOR HYDROGEN SULFIDE EVOLUTION IN LABORATORY SAM-LIKE EGA. G. M. Wong[1], J. L. Eigenbrode[2], A. C. McAdam[2], C. H. House[1], [1]Department of Geosciences, Pennsylvania State University, University Park, PA 16802, gkw5061@psu.edu, [2]NASA Goddard Space Flight Center, Greenbelt, MD, 20818

Introduction: One of the main goals of the Sample Analysis at Mars (SAM) instrument suite on board the Mars Science Laboratory (MSL) rover is to assess the past habitability of Gale Crater [1]. SAM has observed both oxidized and reduced sulfur compounds during evolved gas analysis-mass spectrometry (EGA-MS) of martian rock samples, which may indicate differences in the oxidation state of sulfur in the rocks [2]. The coevolution of SO_2 and H_2S in EGA may indicate the presence of nonequilibrium mineral assemblages [3]. However, the source of the observed H_2S is not well constrained. Here, we present the results of ongoing laboratory experiments under SAM-like conditions and explore possible sources of reduced sulfur on Mars with mineral mixtures involving sulfur.

Methods: We mixed kieserite, ferric sulfate hydrate, jarosite, or pyrite with NaCl, $MgCl_2$, $CaCl_2$, or $Ca(ClO_4)_2$ in 10:1 mass ratios to test the effects of HCl-evolving minerals on H_2S production. We also prepared mixtures of nontronite and magnetite with each of the sulfur minerals in 1:1:1 mass ratios to determine possible effects on H_2S evolution. EGA-MS was conducted on each mixture using a Frontier PY-3030 pyrolyzer attached to a 5975C inert XL MS set up to operate under SAM-like conditions [4]. Several evolved gases were detected from each mixture; here we focus on SO_2 and H_2S evolution. Data were background subtracted and m/z 34 data were corrected to remove O_2 isotopologues and SO_2 fragments. Areas under SO_2 (m/z 64) and H_2S (m/z 34, corrected) peak curves were calculated to determine abundances of these volatiles evolved.

Results: We analyzed sulfur mineral controls for H_2S and SO_2. We calculated the fractional percentage of H_2S for the primary peak evolutions of H_2S and SO_2. The H_2S percentages ranged from 0.91% to 1.19% with a mean of 1.01% (Fig. 1). Ferric sulfate hydrate had the greatest fractional percentage of H_2S, followed by jarosite, pyrite, and kieserite.

The mineral mixtures were analyzed by comparisons to their respective sulfur controls. Most (17/20) mixtures demonstrated H_2S/SO_2 ratios that were at least as reduced as the controls. The NaCl mixtures were similar to controls. The $CaCl_2$ and $MgCl_2$ mixtures exhibited similar H_2S/SO_2 ratios and were higher than respective controls. The nontronite/magnetite mixture was the next most reduced/least oxidized. The $Ca(ClO_4)_2$ mixtures were the most reduced/least oxidized (Fig. 2). The $Ca(ClO_4)_2$ mixtures had H_2S/SO_2 ratios 17-50% greater than the other mixtures.

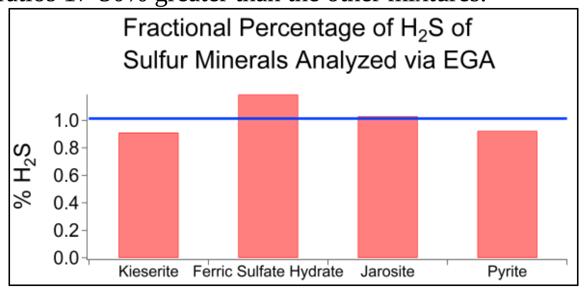

*Fig. 1. Fractional percentage (100*$H_2S/(H_2S+SO_2)$) of H_2S for sulfur mineral controls. Blue line is the mean percentage.*

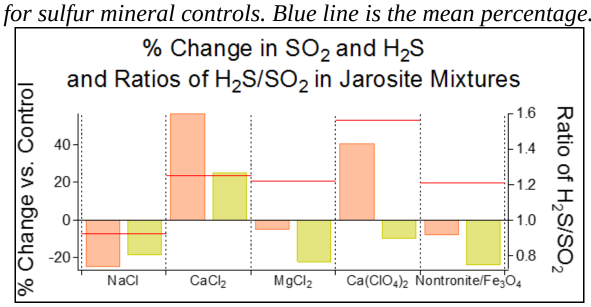

Fig. 2. % change in H_2S (orange) and SO_2 (yellow) of jarosite mixtures vs. control. Red lines are H_2S/SO_2 of mixtures vs. control. Note increased H_2S, decreased SO_2, and high comparative H_2S/SO_2 ratio for $Ca(ClO_4)_2$ vs. control.

Conclusions: The H_2S evolved from our sulfur mineral controls suggests that evolution of H_2S is not dependent on reactions with other minerals or gases. H_2S was produced in all samples. Interestingly, ferric sulfate hydrate produced the most H_2S while pyrite produced the third least H_2S in our analyses. Hence, our results suggest that observations of H_2S in EGA-MS are not necessarily evidence of sulfide minerals.

Further, our mineral mixture data indicate that the minerals available to interact with the sulfur species can have a relatively strong effect on H_2S and SO_2 evolution. Calcium perchlorate, in particular, has an especially strong effect on the relative peak evolutions of H_2S and SO_2, which may explain some of the H_2S evolved from martian samples during EGA-MS.

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