EVOLUTION OF HYDROGEN DURING SAM ANALYSES OF THE SHEEPBED MUDSTONE, GALE CRATER, MARS.

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Introduction: The Mars Science Laboratory (MSL) Curiosity drilled at two locations (John Klein, JK, and Cumberland, CB) within the Sheepbed mudstone member of Yellowknife Bay, Gale Crater. Both the Sample Analysis at Mars (SAM) instrument suite and the Chemistry & Mineralogy X-Ray Diffraction/X-ray Fluorescence (CheMin) instrument analyzed several portions of the JK and CB drill samples. SAM detected hydrogen gas (H_2) during solid sample evolved gas analyses (EGA) of the samples.

Methods: For SAM EGA quadrupole mass spectrometer (QMS) analyses, the delivered sample fines were initially heated from ambient conditions in SAM (~30 °C) to ~835 °C at 35 °C/min [3]. For some SAM analyses, the sample heating approach involved a low temperature hold (termed a "boil-off") followed by heating at a steady rate to ~835 °C in order to mitigate the contributions of MTBSTFA (a derivatizing agent) to the SAM instrument background [1-3]. Evolved gases were carried through manifold lines to the QMS by a He carrier gas. The pressure of He in the oven was ~30 mb and the flow rate was ~0.8 mL/min [3]. The SAM-like EGA-MS laboratory analog systems–including the high fidelity SAM testbed–were used to analyze several milligrams of <150 μm phyllosilicate reference material under SAM-like conditions (flight SAM-like carrier gas, gas flow and pressure conditions, temperature range, and heating ramp rate).

Smectite: Smectite has been detected at abundances of ~20 wt% by CheMin analyses in the <150 μm fraction of Sheepbed Mudstone [4-6]. This detection is confirmed by SAM EGA data [8]. Laboratory and testbed EGA experiments confirm that evolution temperatures for water and hydrogen measured by SAM are consistent with thermal decomposition of smectite (Fig. 4).

There are many distinct sites where smectite can store water or hydrogen (Fig. 1). Phyllosilicate minerals incorporate hydroxyl groups into their octahedral layer within the chemical structure (Fig. 1). Smectite also stores water in an expandable interlayer layer between the 2:1 sheets either in association with solvation cations or as free H_2O molecules [e.g., 7]. In addition, atmospheric water is likely adsorbed to

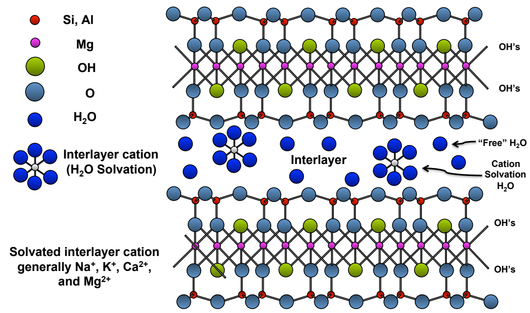

Figure 1. Smectite structure, showing interlayer and structural sites of H-bearing phases (OH, H_2O).

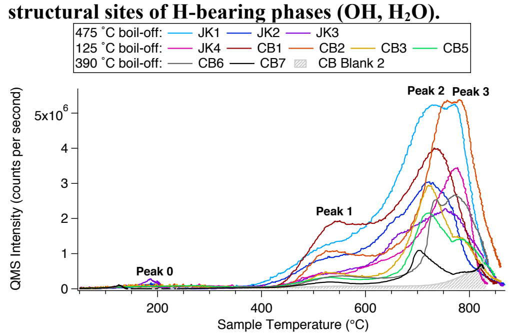

Figure 2. H_2 evolution from SAM analyses of JK and CB.

mineral surfaces [8]. Adsorbed and interlayer H_2O evolves at low temperatures (<250 °C), whereas structural OH groups remain bound until higher temperatures, generally >400 °C [7,9].

SAM observations of evolved hydrogen: Three blank cups and ten JK/CB subsample portions were analyzed by the SAM EGA. A high temperature H_2 peak (>750 °C) was detected in all of the blanks. Hydrogen deuteride (HD, *m/z* 3) was observed in the blanks above 750 °C, but it was barely above the detection limit.

Each JK and CB sample evolved two to four distinct high temperature H_2 peaks (Fig. 2). Some of the runs with a 475 °C boiloff evolved a small H_2 peak below 200 °C (Peak 0). All JK and CB samples evolved an H_2 peak starting at 400 °C (Peak 1), followed by a larger peak (Peak 2) that starts at 600 °C. Another large peak (Peak 3) often evolves between 750-850 °C, though the peak maximum varies in temperature, sometimes overlapping with the Peak 2 evolution completely. Peak 2 usually trends with both H_2O and HD, indicating a common source for these volatiles (Fig. 3). Most H_2 evolved above 400 °C is likely derived from structural dehydroxylation of clay minerals [9].

The HD (m/z 3) evolution trends closely with H_2, except at very high temperatures (>~750 °C, Peak 3) where H_2 has a peak and HD does not (Fig. 3). This behavior is also seen in the blanks (H_2 peak >750 °C with very little accompanying HD), so Peak 3 could be interpreted as an instrument background effect.

After subtracting the possible instrument background, including the Peak 3 contribution, the JK single-portion samples (JK1-2, and JK4) evolved an average of 3.5 ± 0.6 nmol of H_2 above 400 °C, and CB single-portion samples (CB1-3, and CB5) evolved 3.5 ± 2.0 nmol of H_2 above 400 °C.

Variability in hydrogen data: Although the samples are theoretically homogenized by the MSL sample processing system, the observed variability of H_2 evolution temperature, abundance, and peak shape suggests the sample is not completely homogeneous. It is also surprising to see differences between two nearby (~3 m apart) drill sites from within the same rock unit, however the presence of veins in the drill hole wall suggests that the JK site has likely undergone more post-formation alteration than CB [e.g., 4].

High-fidelity rover testbed work has constrained the sample portion size delivered to SAM to 45 ± 18 mg [9], so portion size may provide a significant source of variability between subsamples. However, the H_2 abundance does not trend with abundance changes of other major volatiles [9]. Therefore, variations in subsample size cannot explain the differences entirely so the possibilities of non-homogeneous mixing, variable background levels of H_2, or complex chemistry within the SAM oven during pyrolysis must be considered.

There is evidence for reactions between H_2 and the other evolved volatiles, such as O_2 and SO_2, in the SAM oven. For example, it is likely that some of the H_2S evolved from JK and CB samples results from the reaction of SO_2 and H_2 [9-10].

Hydrogen evolution from smectite during laboratory SAM-like EGA: SAM-like EGA setups, including the high-fidelity SAM testbed, are being used to analyze Mars analog minerals. On these systems, the smectite minerals also evolve H_2 at high temperatures (Fig. 4), generally coincident with the evolution of H_2O from dehydroxylation. The Fe-saponite griffithite appears the most consistent with JK and CB data in terms of evolution temperature and peak shape of H_2O [11] and H_2 (Fig. 4).

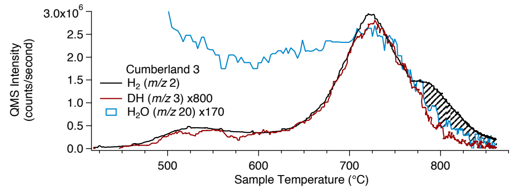

Figure 3. SAM EGA data showing associations between H_2O, H_2, and HD. The H_2 peak above 750 °C (shaded) does not correlate to an H_2O release and has a much lower δD than the smectite dehydroxylation peaks, so this H_2 may come from another source.

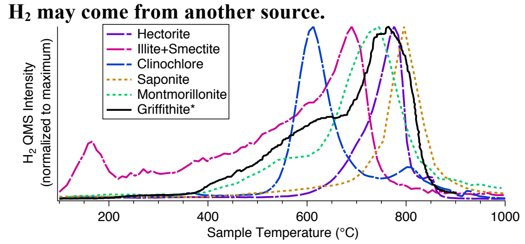

Figure 4. SAM-like evolved gas analyses of selected phyllosilicates on GSFC laboratory instruments (dashed) and SAM testbed (solid).

Conclusion and Implications: Though the H_2 EGA data from SAM exhibits variability likely due to factors such as sample heterogeneity, variable background contributions (which are still being studied), and complex reactions between compounds in the SAM oven during heating, it seems very likely that a portion is related to H_2O from dehydroxylation of the ~20 wt% smectite clays present in the subsamples.

The SAM TLS and QMS independently measure δD in H_2O, and QMS data can also determine δD in H_2 [12]. The δD in the >400° C H_2 and H_2O show important differences from the δD in the lower temperature evolved H_2O. These differences may record information about past and present environments on Mars [12-14].

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References: [1] Glavin D.P. et al. (2013) *JGR*, 20144. [2] Leshin L.A. et al. (2013) *Science*, 1238937. [3] Mahaffy P. R. et al. (2012) *Space Sci. Res.*, **170**, 401-478. [4] Vaniman D.T. et al. (2013) *Science,* 1243480. [5] Rampe E.B. et al. (2014) *LPSC XLV*. [6] Morris R.V. et al. (2014) *LPSC XLV*. [7] Sheppard S.M.F. et al. (1996) *Clay Minerals*, **31**, 1-24. [8] Savin S.M. et al. (1970) *Geochim. Cosmochim. Acta*, **34**, 25-42. [9] Ming D.W. et al. (2013) *Science,* 1245267. [10] McAdam A.C. et al. (2014) *LPSC XLV*, #2257. [11] McAdam A.C. et al. (2014) *LPSC XLV*, #2337. [12] Mahaffy P.R. et al. (2014) *LPSC XLV*. [13] Morad S. et al. (2003) *Int. Assoc. Sedimentol. Spec. Publ.*, **34,** 63–91. [14] Meunier A. et al. (2012) *Nature Geoscience*, **5**, 739–743.