

**NH<sub>4</sub>-SMECTITE, A POTENTIAL SOURCE OF N COMPOUNDS (NO) IN SAM ANALYSES.** S. Andrejčkovičová<sup>1,2</sup>, A. C. McAdam<sup>1</sup>, J. C. Stern<sup>1</sup>, C. A. Knudson<sup>1,2</sup>, R. Navarro-González<sup>3</sup>, M. Millan<sup>1,4</sup>, S. T. Wieman<sup>1,5</sup>, J. A. Seabee<sup>6</sup>, N. M. Bishop<sup>6</sup>, E. B. Rampe<sup>7</sup>, P. R. Mahaffy<sup>1</sup>, <sup>1</sup>NASA GSFC, Greenbelt, MD, USA, slava.carvalhoandrejckovicova@nasa.gov, <sup>2</sup>CRESST, Univ. of Maryland, College Park, MD, USA, <sup>3</sup>Univ. Nacional Autónoma de México, Mexico City, Mexico, <sup>4</sup>Georgetown Univ., Washington, DC, USA, <sup>5</sup>CRESST, Univ. of Maryland, Baltimore, MD, USA, <sup>6</sup>Univ. of Northern Iowa, Cedar Falls, IA, USA, <sup>7</sup>NASA JSC, Houston, TX, USA

**Introduction:** Recent detection of nitrate by Curiosity's Sample Analysis at Mars (SAM) instrument suite in Gale Crater sediments on Mars at abundances up to ~600 mg/kg [1,2] indicates that nitrogen fixation processes occurred in early martian history. But little is known about other possible N reservoirs on Mars, including those that may contain reduced forms of fixed N (i.e., NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>) in the mantle, crust and sediments. Specifically, fixed nitrogen (i.e. NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>, NO<sub>x</sub> or N that is chemically bound to either inorganic or organic molecules and can be released by hydrolysis to form NH<sub>3</sub> or NH<sub>4</sub><sup>+</sup>) is useful to terrestrial living organisms [3]. Therefore, understanding whether reduced N compounds such as NH<sub>4</sub><sup>+</sup> are present in surface materials is important to assess habitability in the martian environment. While these species generally have short photochemical lifetimes, nitrogen in this form may be sequestered and stabilized in the soil by inclusion of NH<sub>4</sub><sup>+</sup> in certain phyllosilicates [3-5].

Oxychlorine phases, such as perchlorates, have also been detected in most samples analyzed by SAM [6-8] and at other sites on Mars [9-10], and when heated they evolve oxygen. The main aim of this laboratory study is to determine if reduced N in the form of NH<sub>4</sub><sup>+</sup> sequestered in the interlayer space of the smectite clay mineral montmorillonite when heated with perchlorate salts, produce N compounds (NO) during heating comparable to those observed during heating in SAM.

**Materials and Methods:** The smectite sample used for this study was the Clay Minerals Society Source Clay SWy-2 montmorillonite (natural Na<sup>+</sup> form). To prepare the monoionic NH<sub>4</sub><sup>+</sup> form of SWy-2 (NH<sub>4</sub>SWy-2), NH<sub>4</sub>Cl was used. 2 g of SWy-2 was dispersed in 50 ml solution of 1M NH<sub>4</sub>Cl for 24 hrs, centrifuged at 5500 rpm for 20 min, supernatant chloride solution was removed and replaced by fresh 50 ml solution of 1M NH<sub>4</sub>Cl (repeated 5×). Sample was introduced to dialysis tubes, placed in distilled water to remove chloride ions (AgNO<sub>3</sub> test) and dried at 50 °C. For mixtures with perchlorate, 5 wt.% of Mg(ClO<sub>4</sub>)<sub>2</sub>\*6H<sub>2</sub>O was added to smectite samples to provide a relevant oxidizing agent (O<sub>2</sub>) during heating. FTIR spectra were performed on a Thermo Scientific (Nicolet iS50) FT-IR (Fourier Transform Infrared) spectrometer equipped with a diamond attenuated total reflectance (ATR) at room temperature in the range of 4000-500 cm<sup>-1</sup>. X-ray diffraction (XRD) patterns were

acquired both under ambient conditions and in a N<sub>2</sub>-purged glove box (~22°C, 12 % relative humidity) purged overnight, to simulate dry, Mars-like surface conditions. XRD patterns were acquired with an Olympus Terra field portable XRD, which is similar in geometry and operation to Curiosity's Chemistry and Mineralogy (CheMin) instrument. XRD patterns were acquired for 400 exposures (Co K $\alpha$  radiation). For SAM evolved gas analysis mass spectrometry (EGA-MS), sample fines were heated to ~860°C at 35°C/min. Evolved gases were detected by the mass-to-charge ratio (m/z) of the molecule (e.g., NO is shown by m/z 30). The pressure in the oven was ~25 mb and the flow rate was ~0.8 sccm. EGA-MS laboratory analyses were done on a Setaram LabSys Evo Thermogravimeter/Differential Scanning Calorimeter coupled to a Pfeiffer OmniStar QMS set up to operate with a SAM-like temperature range, heating rate, He flow rate and gas pressure condition.

#### Results and Discussion:

**FTIR.** NH<sub>4</sub><sup>+</sup> in the interlayer space of NH<sub>4</sub>SWy-2 was verified by the presence of the characteristic bending vibration of NH<sub>4</sub><sup>+</sup> at 1434 cm<sup>-1</sup> (Fig. 1), not observed in the starting SWy-2 material. Identification of N-H stretching bands (3300–2800 cm<sup>-1</sup>) is complicated due to overlap with OH stretching vibration bands of water. More detailed description of FTIR bands of SWy-2 can be found, e.g. in work of [11].

**XRD.** XRD patterns of both materials, acquired under ambient conditions, are shown in Fig. 2. The characteristic basal *d*<sub>001</sub> reflection is ~12 Å for both original and NH<sub>4</sub>SWy-2 due to the same hydration state of interlayer cations in both materials. However, the NH<sub>4</sub>SWy-2 sample shows a broad *d*<sub>002</sub> band (missing in SWy-2) at 17 °2 $\theta$  (5.9 Å), and shifts and changes in relative intensities of several reflections towards lower °2 $\theta$  values are expected when the interlayer is occupied by NH<sub>4</sub><sup>+</sup> (also observed in [12]). CheMin XRD data from most drilled samples containing clay minerals show a broad 10 Å 001 peak which is indicative of the presence of a collapsed 2:1 smectite [13,14]. Exposure of NH<sub>4</sub>SWy-2 to simulated (dry) martian conditions changes the *d*<sub>001</sub> spacing from 12 to 10.7 Å (Fig. 3), closer to martian samples, but not reaching a totally collapsed structure (10 Å) as observed, for example, in the smectite clay-bearing Marimba sample [13,14].

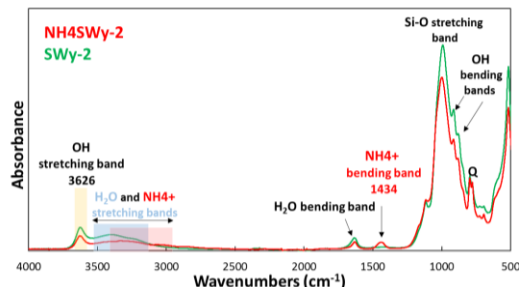


Fig. 1. FTIR-ATR analysis of natural SWy-2 and NH<sub>4</sub>SWy-2. (Q-quartz admixture).

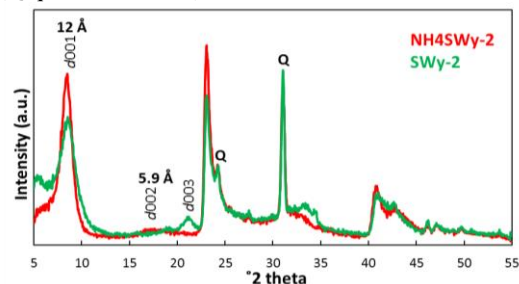


Fig. 2. XRD patterns of natural SWy-2 and NH<sub>4</sub>SWy-2. (Q-quartz admixture).

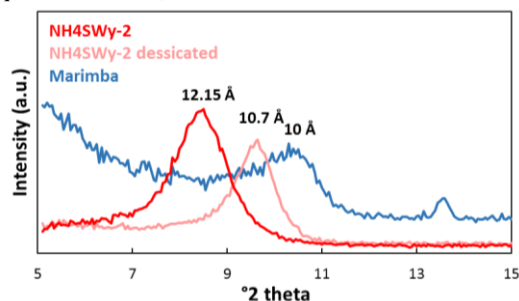


Fig. 3. Low angle NH<sub>4</sub>SWy-2 XRD patterns under ambient (red) and simulated martian (pink) conditions, compared to the CheMin XRD pattern of Marimba (blue) [XRD pattern obtained from <https://odr.io/CheMin>].

**EGA.** Fig. 4 shows  $m/z$  30 (NO) evolutions from the laboratory synthesized samples and compared with two example martian drill samples Confidence Hills (CH) and Mojave (MJ), fluvial/lacustrine mudstones of the Murray Formation [e.g. 8], which contain 10 Å 2:1 phyllosilicates [15]. It is obvious that the only laboratory sample evolving significant NO is NH<sub>4</sub><sup>+</sup> exchanged montmorillonite containing 5 wt.% of perchlorate (black trace in Fig. 4). The evolution between ~200-550°C is similar to the NO evolutions observed in CH and MJ, consistent with the idea that oxidized interlayer N could contribute to the NO evolved from martian smectite-bearing samples. Both the laboratory sample and CH and MJ also show  $m/z$  30 evolutions at higher temperatures, though in the laboratory sample this evolution is more intense. This intense peak coincides with H<sub>2</sub>O evolution due to dehydroxylation of the

montmorillonite, and interestingly suggests that though some N is clearly released at lower temperatures more consistent with evolution from the smectite interlayer, some N remains to higher temperatures.

It is likely that some of the NO evolved from martian samples from ~200-550°C results from the decomposition of nitrate salts. Several different nitrate salts decompose in that temperature range. But, oxidation of interlayer NH<sub>4</sub><sup>+</sup> could contribute part of this evolution in addition to contributing to the low intensity evolution at high temperature. It is also important to consider that for our initial study we have investigated an end-member in which all or most of the interlayer sites are filled with NH<sub>4</sub><sup>+</sup>. In a natural system there would likely be a mixture of interlayer cations, resulting in less N per amount of sample smectite. Also, our initial work with one smectite has shown that dehydroxylation temperature may affect the  $m/z$  30 trace. Therefore, next, we will investigate a smectite clay mineral with a different (lower) dehydroxylation temperature and compare to N compound evolution from martian samples.

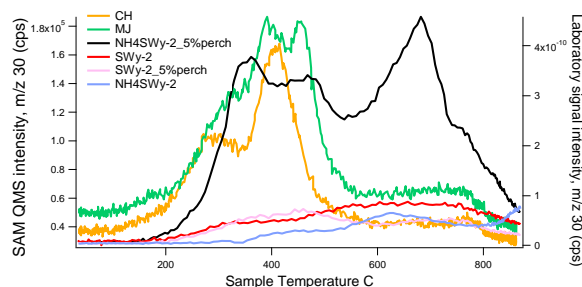


Fig. 4. The SAM-like EGA NO ( $m/z$  30) traces from laboratory analog samples compared with Confidence Hills (CH) and Mojave (MJ) SAM experiments.

**Conclusions:** Laboratory EGA of NH<sub>4</sub>SWy-2 mixtures with Mg perchlorate salt suggests that interlayer NH<sub>4</sub><sup>+</sup> could contribute to  $m/z$  30 (NO) observed in SAM EGA analyses of martian samples. Future work will investigate additional interlayer NH<sub>4</sub><sup>+</sup> concentrations and additional smectite clay minerals. The potential detection of these reduced N compounds on Mars has important implications for the development of a nitrogen cycle on Mars, and therefore Mars' potential habitability.

**References:** [1] Stern et al. (2015) *PNAS*, 112(14), 4245. [2] Stern et al. (2017) *GRL*, 44, 2643. [3] Mancinelli and Banin (2003) *IJA*, 2, 217. [4] Mancinelli et al. (1997) *LPS XXVIII*, 1815. [5] Bishop et al. (2002) *PSS*, 50, 11. [6] Leshin et al. (2013) *Science*, 341(6153). [7] Ming et al. (2014) *Science*, 343(6169). [8] Sutter et al. (2017) *JGR*, 122, 1. [9] Hecht et al. (2009) *Science*, 325(5936). [10] Navarro-González et al. (2010) *JGR*, 115, E12010. [11] Madejová and Komadel (2001) *CCM*, 49, 410. [12] Gautier et al. (2010) *ACS*, 49, 247. [13] Bristow et al. (2017) *LPS XLVIII*, 2462. [14] Rampe et al. (2017) *LPS XLVIII*, 2821. [15] Rampe et al. (2017) *EPSL*, 471, 172.