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**INVESTIGATING THE DETECTABILITY OF ORGANIC COMPOUNDS IN SMECTITE INTERLAYER SITES WITH FLIGHT-LIKE TECHNIQUES.** A. C. McAdam<sup>1</sup>, X. Li<sup>1</sup>, D. M. Bower<sup>1,2</sup>, S. Andrejkovičová<sup>3</sup>, M. Millan<sup>4</sup>, L. Chou<sup>1</sup>, J. M. T. Lewis<sup>1,5</sup>, C. A. Knudson<sup>1,2,6</sup>, J. C. Stern<sup>1</sup>, J. L. Eigenbrode<sup>1</sup>, C. N. Achilles<sup>1</sup>, <sup>1</sup>NASA/GSFC (Amy.McAdam@nasa.gov), <sup>2</sup>Univ. of Maryland, College Park, <sup>3</sup>Aveiro Univ., Portugal, <sup>4</sup>Laboratoire Atmosphères, Observations Spatiales (LATMOS), Guyancourt, France, <sup>5</sup>CRESST, Howard Univ., <sup>6</sup>CRESST, GSFC

**Introduction:** Clay minerals consist of tetrahedral and octahedral sheets, and can have charged surfaces due to cation substitutions or vacancies in these sheets. In smectite clay minerals, this charge is balanced or partially balanced by materials in an interlayer area. These materials can be cations, water and/or organic compounds and when they move into the interlayer space they cause the space to expand.

Smectite clay minerals have been found in martian meteorites [e.g., 1], inferred or identified during in situ analyses [e.g., 2-4], and inferred from orbital spectral investigations, such as near infrared (IR) observations [e.g., 5-7]. Smectites are of particular interest because they can indicate habitable environments [8,9] and possibly facilitate the preservation of organic compounds [e.g., 10-11]. Organic compounds in smectite interlayer sites, specifically, may be especially protected from degradation by radiation and oxidants in the martian environment. Inclusions in martian meteorite igneous minerals that contain organic compounds also commonly contain amorphous materials and smectite clays [12]. Smectite clay minerals were components in samples in which organic compounds have been detected by the *Curiosity* Sample Analysis at Mars (SAM) instrument [e.g., 13-16].

Here we will discuss flight-like analyses of a smectite clay mineral with interlayer glycine (an amino acid) and the implications for in-situ analyses on Mars.

**Methods:** We prepared several samples of the smectite montmorillonite targeting different abundances of interlayer glycine. Amino acids are of interest as they are the building blocks of proteins and glycine is the simplest amino acid. We used the Clay Minerals Society SWy-2 montmorillonite source clay, a well-characterized and relatively pure montmorillonite, with a cation exchange capacity (CEC) of 0.85 mmol/g. Before cation exchange, we reduced the organic content of the natural clay mineral (following Fornaro et al [17]), then performed cation exchange using three concentrations of glycine equivalent to 0.5, 1 and 2 CEC of the SWy-2. One gram of SWy-2 was dispersed in 50 mL of glycine solution and the solution pH was adjusted to 3 with HCl to make glycine into its glycinium cation form to optimize exchange into negatively charged interlayer sites. Mixtures were stirred for 24 hrs, centrifuged (5500 rpm, 20 min.) and dried at 50°C.

Elemental Analysis Isotope Ratio Mass Spectrometry (EA-IRMS) was carried out with a Costech Elemental Analyzer for bulk N analysis via a

Thermo Scientific Delta V isotope ratio mass spectrometer. X-ray diffraction (XRD) was carried out with an Olympus Terra instrument which enables a sample geometry, Co K $\alpha$  radiation, and 2 $\theta$  range similar to the *Curiosity* Chemistry and Mineralogy (CheMin) instrument. These patterns were acquired at ambient and dry (12% relative humidity, N<sub>2</sub> purge) conditions to simulate the conditions that collapse most smectite clay minerals analyzed with CheMin. Raman measurements were done at ambient conditions using a 532 nm EZRaman portable system (50  $\mu$ m spot size) at low power (0.2-0.4 mW). Pyrolysis-GCMS experiments were performed to evaluate glycine extraction and derivatization efficiency. Flash-pyrolysis was used as well as SAM-like pyrolysis conditions. The sample was spiked with the MTBSTFA-DMF derivatization reagent and either (1) heated rapidly at 300°C for one min or (2) at 35°C/min from ambient up to 850°C (SAM-like). Several transfer line temperatures were used: 300°C (optimal), 135°C (SAM), 153°C, and 170°C (maximum SAM temp). LDI-MS analysis was performed with a Bruker matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF)-TOF Autoflex Speed mass spectrometer equipped with a pulsed 355 nm laser (1 kHz), and focal spot up to 100  $\mu$ m.

**Results and Discussion:** EA-IRMS total N indicated that the experiments with glycine concentrations based on 0.5, 1, and 2 CEC glycine resulted in 0.03, 0.05 and 0.1 mmol glycine/gram of montmorillonite; equivalent to 4, 6, and 12 % of the total possible CEC. The full CEC was not reached, but this is more conservative (may be more likely for natural samples on Mars) and this much interlayer glycine was still sufficient to expand the interlayer as assessed by the samples' d<sub>001</sub> spacing under dry XRD conditions.

Raman data of the glycine-clay samples showed spatial variability of detection of glycine/organic features and differences in organics peaks that in an unknown sample may make the glycine difficult to identify (peaks in the lower part of the spectrum indicate organics, but some are not unique to glycine) (Fig. 1). In some samples, the smectite OH bands exhibited a downshift from the typical 3620 cm<sup>-1</sup> position to 3591 cm<sup>-1</sup> and a broadening or disappearance of the glycine bands C-O-O ~889 cm<sup>-1</sup>, CH<sub>2</sub> ~1319 cm<sup>-1</sup>, CH<sub>2</sub> ~1408 cm<sup>-1</sup>, CH<sub>3</sub> ~2950 cm<sup>-1</sup> and CH ~3141 cm<sup>-1</sup>. Some of these variations may indicate bonding of the glycine within interlayer sites of the clay mineral [18].

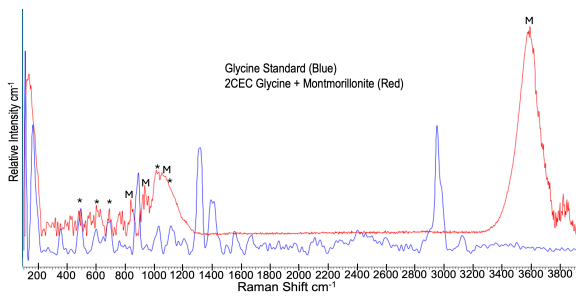


Fig. 1. Raman spectra of glycine (blue) and 2 CEC montmorillonite with interlayer glycine sample (red). Asterisks indicate the definitive glycine peaks in the mixed sample, (M) indicates montmorillonite peaks.

In LDI-MS data, the parent glycine cation ( $m/z$ 75) is detected in positive mode, suggesting the laser is desorbing glycine intact from the interlayer (Fig. 2c and 2d). It is not seen in positive mode if glycine is analyzed directly or mixed with montmorillonite (e.g., Fig. 2b) (i.e., if it is present but not in an interlayer); this is likely because interlayer glycine is a cation. Interlayer glycine is not observed in negative mode, consistent with the glycine being in the smectite interlayers as cations.

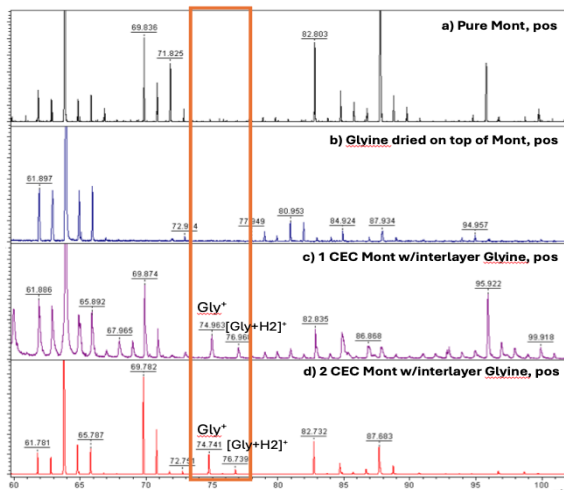


Fig. 2. LDI-MS (positive mode) detects glycine cations in smectite with interlayer glycine (c, d) but not when glycine solution is simply dried down onto smectite (b).

Pyrolysis-GCMS derivatization showed detection of glycine in the 2 CEC glycine-smectite under flash pyrolysis to 300°C and a transfer line temperature of 170°C. However, glycine recovery was only 0.3% under SAM-like conditions (average 35°C/min ramp rate) and transfer lines at 135°C, with better recovery when using 153°C and 170°C. Overall, the extraction/derivatization of glycine was effective in SAM-like pyrolysis but more efficient with flash-pyrolysis.

**Summary:** Our results may suggest that LDI-MS and pyro-GCMS derivatization liberate the glycine from the interlayer bonding and enable at least some of it to

be detected as intact glycine, while Raman was able to assess the glycine in the interlayer but the spectra observed are changed compared to a glycine-only spectrum, likely due to the interlayer bonding environment. CheMin-like XRD of the glycine-smectites under dry conditions indicated collapse compared to ambient lab conditions, but not complete collapse to give  $d_{001} \approx 10$  Å as seen in most CheMin analyses of smectites. It is possible that smectites with less interlayer glycine would collapse to closer to 10 Å.

**Implications:** Our results imply that if glycine were present in the interlayer of smectites investigated by *Curiosity*, SAM may detect the glycine with its pyrolysis-GCMS derivatization, and CheMin XRD from the same sample may show evidence of smectites that are not completely collapsed to 10 Å. The upcoming *Rosalind Franklin* rover, which will sample materials from the smectite clay-rich Oxia Planum region, will include the 532 nm Raman Laser Spectrometer (RLS) instrument, as well as the Mars Organic Molecule Analyzer (MOMA) instrument. MOMA will include LDI-MS in positive mode, as well as pyro-GCMS derivatization with MTBSTFA (in addition to other wet chemistry reagents). If glycine is present in the interlayer of smectites sampled by *Rosalind Franklin*, it is likely to be detected by MOMA's LDI-MS, may also be detected by MOMA's pyro-GCMS derivatization with MTBSTFA, and RLS analyses may give spectral evidence of glycine bound into smectite interlayer sites. *Rosalind Franklin* will also sample materials from up to 2 m in depth; organic incorporation into smectite interlayers may help with preservation against radiation and a location at depth should also mitigate those effects.

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