

**HYDROTHERMAL AMMONIATION OF CHONDRITES: IMPLICATIONS FOR CERES.**

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**Introduction:** Ceres is the largest object in the main asteroid belt and the only dwarf planet in the inner solar system. Ceres shows evidence of current geological activity including transient emissions of water vapour [1], cryovolcanism [2] and extensional tectonics related to upwelling [3]. Ceres is a transitional object between the volatile-poor, silicate-dominant inner solar system and the ice-rich outer solar system. Telescopic observations of Ceres [4] and later measurements by the visible-and-infrared spectrometer (VIR) on the Dawn mission [5] have shown a feature near 3.06  $\mu\text{m}$ , interpreted as a fundamental N-H stretching vibration in ammonium-bearing clay minerals [4,5]. Because ammonia is not expected to have condensed at Ceres' current heliocentric distance [5] suggested that Ceres might have formed at a much greater heliocentric distance and subsequently migrated inward. The formation of ammonium-bearing phyllosilicates on Ceres is proposed to have been due to the low-temperature interaction between  $\text{NH}_3$ -bearing solution and a silicate assemblage similar to aqueously-altered carbonaceous chondrites [4-6]. In a recent study, [6] investigated the interaction of aqueously-altered carbonaceous chondrites and terrestrial phyllosilicates with ammonia (using ammonium acetate solutions) at ambient conditions, finding no significant spectral or mineral changes in their carbonaceous chondrite samples. We have investigated the interaction between ammonia-water solutions and aqueously-altered carbonaceous chondrites, as well as a Rumuruti (R) chondrite, and terrestrial analogue minerals (saponite and serpentine) under hydrothermal conditions to better constrain the formation of ammoniated phyllosilicates on asteroids.

**Methods:** Solutions of 10%, 5%, and 0%  $\text{NH}_3$  were created with ultra-pure water and ammonium hydroxide solution (28%). Aliquots of ~1 mg of homogenized meteorite powder (Mukundpura CM2, Northwest Africa (NWA) 801 CR2, Tagish Lake C2 ungrouped; NWA 753 R3.9) were sealed in Au capsules with ~10  $\mu\text{l}$  of solution. The capsules were placed in Teflon pressure vessels along with additional  $\text{NH}_3$  solution identical to that within the capsule. The Teflon vessels were loaded in sealed autoclaves and placed in a 200  $^\circ\text{C}$  muffle furnace for 72 hours. The internal pressure lies along the liquid-vapour stability curve, ~15 bar at 200  $^\circ\text{C}$ . The vessels were cooled in air, then the capsules removed, opened, and dried in a vacuum desiccator overnight. Additional experiments using larger volumes ~1 g of pure

natural saponite and serpentine were conducted by placing rock powder and ammonia-water solution in the Teflon vessels without use of an Au capsule. Fourier-transform infrared (FTIR) spectroscopy (transmission geometry) was used to investigate the fundamental bending and stretching vibration regions. Pre- and post-reaction materials were analyzed using micro-focus X-ray diffraction using  $\text{Cu K}\alpha$  radiation. For serpentine and saponite, additional powder X-ray diffraction data were collected with  $\text{Cu K}\alpha$  radiation. For selected samples, Raman spectroscopy was conducted (532 nm excitation) to confirm mineralogical changes.

**Results:** Terrestrial saponite showed clear evidence of ammoniation, in the form of new FTIR spectral features at ~7.1  $\mu\text{m}$  (1400  $\text{cm}^{-1}$ ), attributable to NH bending, and near ~3.3  $\mu\text{m}$  and ~3.5  $\mu\text{m}$  (3050  $\text{cm}^{-1}$  and 2860  $\text{cm}^{-1}$ ), attributable to NH stretching (Fig. 1A). In addition, the position of the (001) X-ray diffraction peak at ~13.05  $\text{Å}$  in untreated saponite was observed at ~12.89  $\text{Å}$  in ammonia-treated samples. Saponite samples reacted for 24, 72, and 240 hours with 10% ammonia showed no significant differences in X-ray diffraction patterns, indicating that the system had reached equilibrium. Serpentine, in contrast, showed no evidence of ammoniation (Fig 1B). Carbonaceous chondrites did not show spectral changes consistent with silicate ammoniation. The hydrous mineralogy of Mukundpura (CM2) and NWA 801 (CR2) are dominated by serpentine. Consistent with our results for terrestrial serpentine, post-reaction FTIR spectra of NWA 801 and Mukundpura show no signs of NH-related spectral features (Fig. 1C,D). Surprisingly, the Tagish Lake meteorite, despite containing ~60% saponite [7], showed no spectral features due to NH following reaction (Fig 2). Pre- and post-reaction Tagish Lake spectra contain a feature near 3.06  $\mu\text{m}$ , similar to that reported by [6] in their unreacted, ambient-temperature Tagish Lake samples. Tagish Lake did not, however, show clear evidence for the longer-wavelength N-H stretching features near ~3.3  $\mu\text{m}$  and ~3.5  $\mu\text{m}$ , nor an unambiguous signature of NH bending near ~7.1  $\mu\text{m}$ . Intriguingly, the R3.9 chondrite NWA 753 showed a clear spectral signature of ammoniation, with features at ~3.3  $\mu\text{m}$ , ~3.5  $\mu\text{m}$  and ~7.1  $\mu\text{m}$ , similar to those observed in ammoniated saponite (Fig. 3). X-ray diffrac-

tion showed that diffraction peaks of olivine and orthopyroxene present in the pre-reaction sample were not present in the experimental products; and a new peak near  $1.54 \text{ \AA}$  consistent with the (060) peak of a clay mineral was observed. Raman spectroscopy revealed the disappearance of features at  $820$  and  $852 \text{ cm}^{-1}$  consistent with olivine dissolution.

**Discussion and Conclusions:** Our results show that aqueously-altered carbonaceous chondrites do not react with ammonia to produce  $\text{NH}_4$ -clays similar to those that have been suggested on Ceres. Both the hydrothermal experiments conducted here, and ambient-condition experiments reported previously [6] did not generate ammoniated clay minerals. Rather, a spectral and mineral signature of ammoniated clays was detected in the R chondrite experiment. One interpretation of these results is that Ceres did not accrete from materials similar to known aqueously-altered carbonaceous chondrites alone, but also required a significant fraction of nominally-anhydrous, olivine- and- pyroxene-rich material possibly with elevated silicate Fe/Mg ratios similar to R chondrites. Therefore, the current surface of Ceres may retain evidence of early, globally-extensive hydrothermal alteration involving water-ammonia solutions and Fe-rich olivine and pyroxene. Another notable finding here is that the saponite-rich Tagish Lake meteorite did not develop spectral characteristics diagnostic of ammoniation during reaction with ammonia-water under hydrothermal conditions. In both this study, and the ambient-condition study of [6], untreated Tagish Lake samples show a spectral feature near  $\sim 3.06 \mu\text{m}$  that was unchanged by interaction with the ammonia-bearing solution. One possibility, suggested by [6] is that Tagish Lake already contained ammoniated phyllosilicates. The presence of a  $\sim 3.06 \mu\text{m}$  feature in pre-reaction saponite FTIR spectra, combined with previous studies of the vibrational features in this spectral region [8] may indicate that this feature is ascribable mainly to OH stretching vibrations in structurally-bound  $\text{H}_2\text{O}$ . It is possible, therefore, that the presence of a  $\sim 3.06 \mu\text{m}$  feature is not uniquely diagnostic of ammoniated clays.

**References:** [1] Nathues et al., *Nature* 528:237–240 (2015); [2] Ruesch et al., 2016 *Science* 353:6303; [3] (2018); [3] Scully et al., *GRL* 44:19 9564–9572 (2017); [4] King et al., *Science* 255: 1551–1553 (1992); [5] De Sanctis et al., *Nature* 528:241–244 (2015); [6] Ehlmann et al., *Met. Pl. Sci.* 1–18; (2016); [7] Izawa et al., 2010 *Met. Pl. Sci.* 45:675–698; [8] Klopogge et al., 1999 *J. Mat. Sci. Lett.* 18: 1401–1403

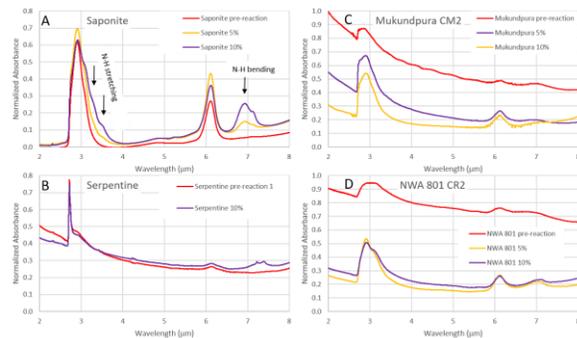


Figure 1: Results of ammoniation experiments on terrestrial reference phyllosilicates saponite (A) and serpentine (B); and serpentine-bearing CM2 chondrites Mukundpura (C) and CR2 chondrite NWA 801 (D). Saponite shows clear evidence of ammoniation, serpentine does not, as expected from their crystal structures. Consistent with their mineralogy, neither meteorite shows evidence of ammonia incorporation.

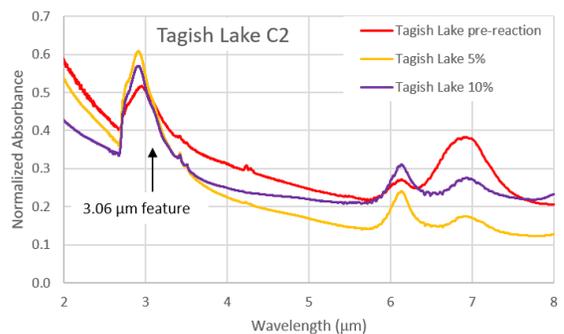


Figure 2: Results of ammoniation experiments on Tagish Lake (C2 ungrouped), a very saponite-rich chondrite. Unexpectedly, Tagish Lake shows no evidence for ammoniation.

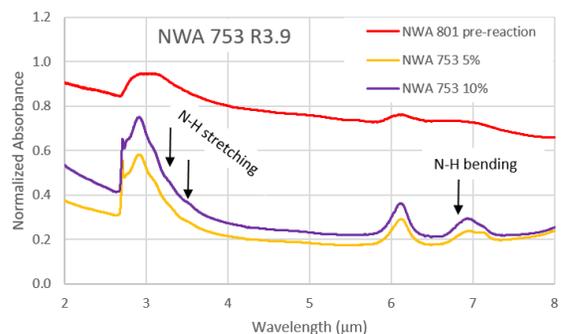


Figure 3: Results of ammoniation experiments R3.9 chondrite NWA 753. Despite a lack of pre-existing phyllosilicates, this olivine-dominant meteorite showed clear spectral signatures of ammoniation.