

Constraining the Hydration of X-ray Amorphous and Clay Mineral Phases in Gale Crater, Mars. S. Czarnecki¹, C. Hardgrove¹, E. B. Rampe², R. J. Smith³, and P. J. Gasda⁴ ¹Arizona State University, Tempe, AZ (sean.czarnecki@asu.edu), ²NASA Johnson Space Center, Houston, TX, ³SUNY Stony Brook, Stony Brook, NY, ⁴LANL, Los Alamos, NM.

Introduction: Clay minerals and salts in the Gale crater stratigraphy investigated by the Mars Science Laboratory (MSL) *Curiosity* rover preserve information about sediment sources, depositional environment, and post-depositional alteration history. The compositions of amorphous components in samples have bearing on the redox potential, pH, and chemistry of alteration fluids, and on the heterogeneity of these conditions [e.g., 1]. Interlayer clay hydration in present-day Gale crater could be an indication of high water/rock ratios of late-stage fluid alteration events, which increases the potential habitability of these post-depositional environments [1]. The MSL Dynamic Albedo of Neutrons instrument (DAN) measures bulk hydration and here we attempt to determine the hydration states of both clay minerals and amorphous components throughout the *Curiosity* traverse to constrain the abundance of individual amorphous phases and determine if clay interlayer water is present today. These implications are also more broadly applicable to similar sedimentary successions outside Gale crater.

In this study, we compare hydration results from DAN to mineralogical results from the MSL Chemistry and Mineralogy instrument (CheMin) for 16 different fluvio-lacustrine sample locations. These samples typically contain one or more hydrated crystalline phases, a hydrated X-ray amorphous fraction composed of multiple amorphous phases, and one or more clay mineral phases which CheMin has consistently measured as collapsed (i.e., no interlayer water). However, Gale samples are known to dehydrate during sample acquisition and handling [2], and because DAN measures hydration to a depth of tens of cm, we can test for the presence of clay interlayer water *in situ* by comparing DAN bulk hydration to CheMin mineralogy. We can also constrain the hydration of the samples' amorphous fractions, and with geochemical data from the ChemCam and APXS instruments, this will allow us to better define the phases which compose this fraction.

Instruments: DAN is an active neutron spectrometer which pulses 14.1 MeV neutrons at 10 Hz and counts thermal (≤ 0.3 eV) and epithermal (0.3 eV $< n < 100$ keV) neutrons returning from the subsurface [3]. Counts are tabulated by time-of-flight in a time-spectrum called a neutron “die-away” curve. The shape of this curve is sensitive to the bulk geochemistry of the top ~50 cm of the subsurface and a few meters laterally. DAN is sensitive to H [e.g., 3], which increases thermal

neutron counts, and neutron absorbers (e.g., Fe, Cl) [4], which reduce thermal neutron counts.

CheMin is an X-ray diffraction instrument which determines mineralogical abundances of powdered samples drilled from depths of a few cm [5]. CheMin results include abundances of well-crystalline minerals as well as clay minerals and amorphous components.

Methods: We compare DAN active data to simulation data using the MCNP6 software package [6]. MCNP6 simulates neutron histories in a 3D environment which models the rover, the atmosphere, and subsurface geochemistry. We independently vary hydrogen abundance and bulk geochemistry (from which we obtain the bulk thermal neutron absorption cross section, Σ_{abs}), creating a ‘grid’ of subsurface models spanning the values observed in Gale crater. We then use a Markov-chain Monte-Carlo analysis to determine a best-fit mean value for each parameter with associated uncertainties [7,8]. Hydrogen abundance results from neutron spectrometers like DAN are typically reported in units of wt.% WEH (water-equivalent hydrogen), which is obtained by converting a best-fit hydrogen abundance into a corresponding water abundance.

We identified DAN active measurements which best correspond to CheMin drill samples. For some sites the DAN measurements were taken directly over the drill hole; for others they were taken within a few meters of the drill hole. Some sites had multiple DAN measurements equidistant from the same drill hole, and for these we have taken the mean value of the DAN results. In a few cases, where multiple samples were obtained within a radius of a few meters of one DAN measurement, we took the mean CheMin mineral abundances for comparison with DAN results.

Crystalline phases are well-constrained by CheMin, which is also typically able to identify the specific clay mineral phase(s), constraining the abundance of structurally-bound hydroxyl. We use the following equation to subtract the WEH due to OH⁻ and H₂O in crystalline phases and structural OH⁻ in clay minerals to calculate the quantity WEH_{aci}, which is the amorphous fraction hydration + clay interlayer water hydration:

$$WEH_{aci} = WEH - \sum WEH_{min_i} [min_i] - WEH_c [clay]$$

where $WEH \equiv$ bulk WEH, $[min_i] \equiv$ abundance of the i th mineral phase.

Results: WEH_{aci} includes both interlayer clay hydration and amorphous component hydration, both of which depend on the composition of the component phases. Several different clay minerals have been identified based on CheMin XRD data, and water retention capability varies among clays. Clay minerals identified include ferrosaponite (Fe-sap) [9,10], ferripyrophyllite (Fe-prl) [11,12], mixtures of Al-montmorillonite and Mg-saponite (Al-mm/Mg-sap) [11], and nontronite [13].

We plotted WEH_{aci} as a function of both amorphous fraction (Fig. 1) and clay fraction (Fig. 2), symbolized by clay mineral. Fe-sap and Fe-prl samples follow similar trends in both plots, whereas Al-mm/Mg-sap samples follow a similar trend to Fe-sap and Fe-prl in the clay plot, but a different trend in the amorphous plot. Similarly, nontronite samples follow a similar trend to Fsap and Fprl in the amorphous plot, but a different trend in the clay plot. Based on these trends, we proceed by grouping Fe-sap and Fe-prl together (Fe-sap/Fe-prl), while keeping separate categories for Al-mm/Mg-sap and nontronite.

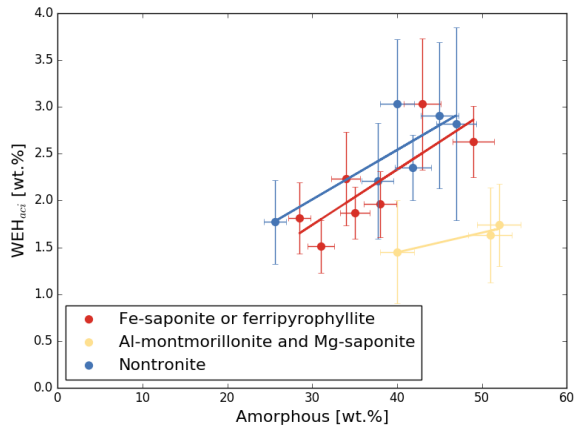


Figure 1: DAN WEH_{aci} plotted as a function of CheMin amorphous fraction for three categories of clay minerals.

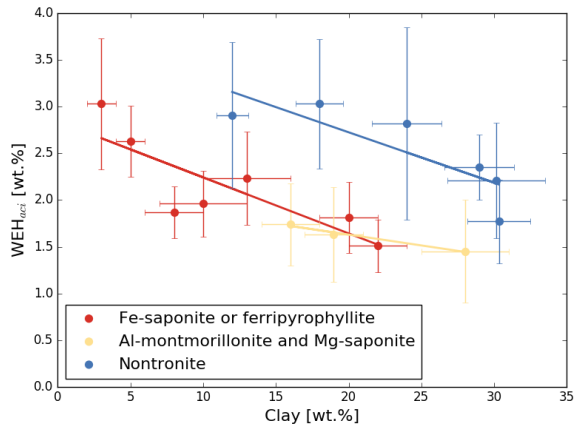


Figure 2: DAN WEH_{aci} plotted as a function of CheMin clay fraction for three categories of clay minerals.

Fig. 2 shows anti-correlation between WEH_{aci} and clay abundances. This may be explained by a positive correlation between WEH_{aci} and amorphous abundance, and that samples with more clay tend to contain less amorphous material. This indicates that amorphous phase hydration is more significant than interlayer clay hydration. However, the significantly greater WEH_{aci} of nontronite samples from the Glen Torridon region in comparison to the other samples [14] could indicate interlayer water remains in these nontronite minerals. Alternatively, the elevated WEH_{aci} of these samples could indicate that the amorphous phases present in nontronite-bearing samples are more hydrated than the amorphous phases in other samples. This can be determined by an amorphous phase analysis which accounts for the chemistry and hydration of the amorphous fraction [8].

Discussion: CheMin XRD results have consistently shown fully dehydrated clay minerals in all clay-bearing samples [9-13]. However, the possibility of remnant interlayer water in a few samples and the known dehydration of other phases in drilled samples allows for the possibility that clay minerals in Gale crater were still hydrated in the subsurface prior to drilling. DAN is uniquely suited to address this question because it measures hydration of *in situ* subsurface material. Although the anti-correlations shown in Fig. 2 suggest that clay minerals are not hydrated in the subsurface, the large abundance of nontronite in Glen Torridon samples [13] and the greater hydration of these samples [14] could indicate that these clay minerals are hydrated.

This work will proceed with an amorphous component analysis which should put constraints on the individual amorphous phases in each sample. This analysis may also support the possibility of nontronite hydration in Glen Torridon samples.

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