**SURVEYING CLAY MINERAL DIVERSITY IN THE MURRAY FORMATION, GALE CRATER, MARS.**

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**Introduction:** One of the primary science goals of Mars Science Laboratory (MSL) is to investigate layered clay mineral-bearing deposits outcropping in the lower NW slopes of Aeolis Mons (Mt. Sharp) detected from orbit [1,2]. Martian clay mineral-bearing layered rocks are of particular interest because they are potential markers of sedimentary deposits formed in habitable aqueous environments.

The CheMin X-ray diffraction (XRD) instrument aboard MSL has documented clay minerals in various drill samples during its traverse of Gale Crater's floor and ascent of Mt. Sharp [3,4]. Previously, the high concentrations of clay minerals (~20 wt.%) detected in drill powders of mudstone (Sheepbed member) at Yellowknife Bay (YKB) allowed their detailed characterization. Drill powders recovered from lacustrine mudstones of the Sheepbed member at YKB contain smectite clay minerals. Based on the position of 02*l* reflections in XRD patterns, which serve as an indicator of octahedral occupancy, the smectites are Fe-bearing, trioctahedral species analogous to ferrian saponites from terrestrial deposits [5,6]. The smectites are thought to have been formed through a process of isochemical aqueous alteration of detrital olivine close to the time of sediment deposition under anoxic to poorly oxidizing conditions [3,5]. The clay minerals are key indicators that the lake waters were benign and habitable at the time [7].

Clay minerals were detected at other locations during MSL's traverse, including samples from the Pahrump Hills [4], but lower abundances and overlapping peaks from crystalline phases in XRD patterns hamper in-depth analysis.

**Murray Buttes drill samples:** A recent strategic drilling campaign sampling the upper Murray Formation at 25 m intervals has revealed a resurgence in clay mineral content [8]. Drill samples named Marimba, Quela and Sebina were acquired in the Murray Buttes region of lower Mt. Sharp. Marimba and Quela sampled from a ~30 m package of finely laminated lacustrine mudstones. Sebina comes from an overlying package of heterolithic mudstone-sandstones [9].

*XRD analysis.* Each sample was analyzed by the CheMin XRD and mineral composition determined using established methods, e.g. [3]. Accurate peak position determination is essential to the interpretation of clay mineralogy and all the patterns discussed here have been calibrated using plagioclase feldspar as an internal standard [10]. Additional modeling of XRD patterns using BGMN, a Rietveld refinement program that can generate XRD patterns of partially disordered smectite clay minerals, was performed to confirm clay mineral peak *hkl* positions [11].

**Results:** The bulk mineralogy of all three samples is similar. Clay minerals make up ~15-25 wt.%, with abundant contributions from plagioclase, hematite, various Ca-sulfate phases and an X–ray amorphous component. Mafic crystalline phases make up <5 wt.% of samples in contrast to the majority of previously analyzed mudstones where abundances were higher [8].

*Clay Mineralogy*. The clay mineral contribution to XRD patterns is similar in all three samples. Clay mineral detections are most evident from broad basal reflections at ~10.4° 2θ CoKα. Peaks at ~15.5° 2θ observed in patterns from Quela and Sebina are contributions from kapton sample cell windows. Kapton contributions do not appear to mask or interfere with basal clay mineral reflections, as shown by the pattern from Marimba which was collected in a cell with mylar windows. Thus, basal reflections indicate the presence of 2:1 group clay minerals. The contribution of the 02*l* clay mineral band at ~22.9° 2θ can be clearly seen because contributions from pigeonite, observed in YKB samples and Pahrump Hills, are minor. The position of the 02*l* band gives an indication of the octahedral occupancy and metal species in the octahedral sites of 2:1 clay minerals. Based on first order observations the 02*l* band is closer in position to dioctahedral 2:1 clay minerals. This is distinct from YKB samples whose 02*l* band position indicates purely trioctahedral 2:1 clay minerals [3]. These differences are confirmed by modeling of XRD patterns (fig. 1). Modeled best fit unit cell parameters are closest to values typically observed for Fe-bearing dioctahedral 2:1 clay minerals like nontronite or Fe-illite.

**Discussion:** XRD patterns from Murray Buttes samples permit a range of possible phases including; illite, Fe-illite, celadonite, dioctahedral smectites such as nontronite and montmorillonite as well as mixed-layer illite/smectite. Under terrestrial conditions smectites, illites and to some extent mixed-layer clay minerals would be distinguished by basal peak position, but the low humidity within CheMin cells promote loss of interlayer $H_2O$ giving similar basal peak positions for all these phases [5].

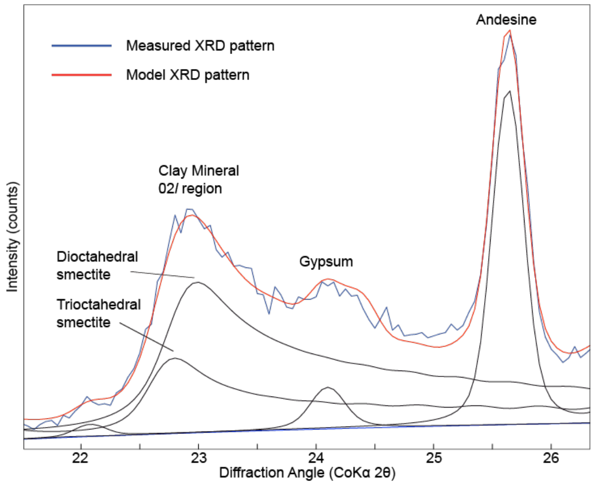


*Figure 1 – Rietveld refinement of Marimba XRD pattern showing modeled contributions from dioctahedral and trioctahedral clay mineral phases to 02l region of the pattern.*

Further constraints on this list of phases can be placed using bulk geochemical data. All three drill samples contain ~0.8 to 0.9 wt.% $K_2O$. Based on typical illite K content of 7.25 wt.% ($K_2O$), illite content of these samples can be as much as 11 wt.% if all K is assumed to be in clay minerals. This equates to about half the total observed clay mineral content. However, we note that clay mineral bearing Murray samples are rather typical in terms of K-content compared with the Murray as a whole, showing no obvious K enrichment over samples with limited clay mineral content such as Oudam. The Murray Buttes samples also contain several wt.% K-feldspar, limiting the possible illite content of samples. In summary, an illitic component, either discrete or as part of a mixed-layer phase is possibly present in these samples, but comprises a few wt.% of the bulk at most.

The SAM instrument performed EGA experiments on a portion of the Marimba sample. Release of $H_2O$ attributed to clay mineral dehydroxylation occurred at 610°C and 780°C [12]. Amongst 2:1 group clay minerals, the temperature of dehydroxylation shows dependence on the metal species and occupancy of octahedral sites. The observed dehydroxylation occurs at temperatures that are too high for nontronites (400-500°C), the less intense release at 610°C appears consistent with a Fe/Al-bearing dioctahedral phase, whereas the peak at 780°C is closer to temperatures at which trioctahedral clay minerals like saponite release $H_2O$ [12].

Combing XRD, EGA and geochemical data indicates the predominance of smectitic clay minerals in Murray Buttes drill samples. However, the simplest interpretation of XRD data which predicts the presence of nontronite is not compatible with the high dehydroxylation temperatures observed by SAM. Instead two dehydroxylation peaks in SAM EGA traces indicate that a mixture of dioctahedral and trioctahedral smectite phases are present. In the correct proportions such a mixture could give a composite 02*l* reflection in the same position as nontronite.

**Implications:** Our interpretation of available data constraining the nature of clay minerals in the upper Murray Formation indicates the presence of a dioctahedral smectite clay mineral not previously observed in Gale. This can be placed in the context of observed changes in bulk mineralogy, including: 1). a transition from magnetite to hematite as the main Fe-oxide, 2). increasing abundances of Ca-sulfates and 3). a reduction in the quantity of reactive mafic minerals [8]. The clay mineralogy is consistent with an increasing degree of aqueous alteration and oxidation of mafic detritus in the upper part of the Murray Formation. In terrestrial settings where alteration sequences of basaltic rocks or sediments are observed, first-stage alteration clay minerals are typically trioctahedral smectite species, as reported from YKB [3,5]. In later alteration stages trioctahedral clay minerals are replaced by dioctahedral clays as a result of removal and/or oxidation of $Fe^{2+}$ and Mg [13]. The abundance of hematite in the upper Murray indicates oxidation of $Fe^{2+}$ making formation of dioctahedral smectites more favorable.

Results from the upper Murray are part of a spectrum of mineralogical facies documented by MSL. Sediment mineralogy indicates a long-lasting, dynamic fluvial-lacustrine system encompassing a range aqueous geochemical proceses under varying redox conditions. Future work is needed to unravel the influence of global and local controls on the range of ancient conditions observed at Gale Crater.

**References:** [1] Grotzinger J. P. et al. *SSR, 170*, 5-56. [2] Milliken R. E. (2010) *GRL, 37(4)*. [3] Vaniman D. T. et al. (2014) *Science, 343(6169)*. [4] Rampe E. B. et al. (in revision) *EPSL.* [5] Bristow T. F. et al. (2015) *Am. Min.*, 100. [6] Treiman A. H. et al. (2014) *Am. Min.*, 99. [7] Grotzinger J. P. et al. (2014) *Science, 343(6169)*. [8] Rampe E. B. et al., *this meeting.* [9] Fedo C. et al., *this meeting*. [10] Morrison, S. M. et al. (in review) *Am. Min*. [11] Ufer, K. et al. (2004) *Zeitschrift fur Kristallographie Sup.,* 219, 519-527. [12] McAdam A. et al., *this meeting.* [13] Meunier, A. (2005) *Clays,* Springer.