DIAGENESIS IN THE MURRAY FORMATION, GALE CRATER, MARS. E. B. Rampe[1], D. W. Ming[2], R. V. Morris[2], D. F. Blake[3], T. F. Bristow[3], S. J. Chipera[4], D. T. Vaniman[5], A. S. Yen[6], J. P. Grotzinger[7], R. T. Downs[8], S. M. Morrison[8], T. Peretyazhko[9], C. N. Achilles[8], D. L. Bish[10], P. D. Cavanagh[10], P. I. Craig[11], J. A. Crisp[6], A. G. Fairén[12], D. J. Des Marais[3], J. D. Farmer[13], K. V. Fendrich[8], J. M. Morookian[6], A. H. Treiman[11] [1]Aerodyne Industries, Jacobs JETS Contract at NASA JSC, elizabeth.b.rampe@nasa.gov, [2]NASA JSC, [3]NASA Ames, [4]CHX Energy, [5]PSI, [6]JPL-Caltech, [7]Caltech, [8]Univ. Arizona, [9]Jacobs NASA JSC, [10]Indiana Univ., [11]LPI, [12]Cornell Univ., [13]Arizona State Univ.

Introduction: The Mars Science Laboratory (MSL) *Curiosity* rover began investigating the rocks of Mt. Sharp in September 2014. The Murray formation is the lowermost unit, which is mostly comprised of finely laminated mudstones, suggesting these sediments were deposited in a lacustrine environment [1]. It is important to characterize the geochemical and mineralogical trends throughout the Murray Fm to interpret the aqueous conditions of the ancient lake, the sources of the lake sediments, and post-depositional alteration processes.

Four samples have been drilled from the Murray Fm so far: Confidence Hills, Mojave 2, and Telegraph Peak were collected from the Pahrump Hills member – the basal portion of the Murray Fm, and Buckskin was collected in the Marias Pass region (Fig. 1). The drill fines were delivered to the instruments inside the rover, including the CheMin instrument, a combination X-ray diffractometer and X-ray fluorescence spectrometer [2]. Rietveld refinements and FULLPAT analyses of 1D CheMin XRD patterns were performed to determine quantitative abundances of minerals and amorphous phases and the unit cell parameters of minerals present in abundances >4-5 wt.% [e.g., 3,4].

Mineral Trends in the Murray Formation: Plagioclase feldspar and X-ray amorphous materials make up ~50-70% of all samples. Pyroxene, phyllosilicate, and hematite are major phases in Confidence Hills, at the base of the Pahrump Hills member, and magnetite, apatite, and jarosite are present in minor amounts. Approx. 1 m stratigraphically above Confidence Hills, the Mojave 2 sample contains similar minerals as Confidence Hills, but has less phyllosilicate, hematite, magnetite, and pyroxene, and more jarosite. Further up section, the Telegraph Peak sample has abundant magnetite, cristobalite and opal-CT, minor amounts of apatite and jarosite, and trace amounts of hematite, but no phyllosilicate. The Buckskin sample, ~6 m stratigraphically above Telegraph Peak, contains magnetite, minor amounts of cristobalite, trace amounts of anhydrite, no phyllosilicate, and abundant tridymite and opal-A (see Morris et al., this meeting, for more information about the Buckskin sample). To summarize the mineral trends in the Murray Fm, hematite, phyllosilicate, and pyroxene are most prevalent at the base of the Pahrump

Hills member; magnetite and silica phases are more prevalent moving up section; and jarosite is present in minor to trace amounts in samples from the Pahrump Hills (Fig. 1).
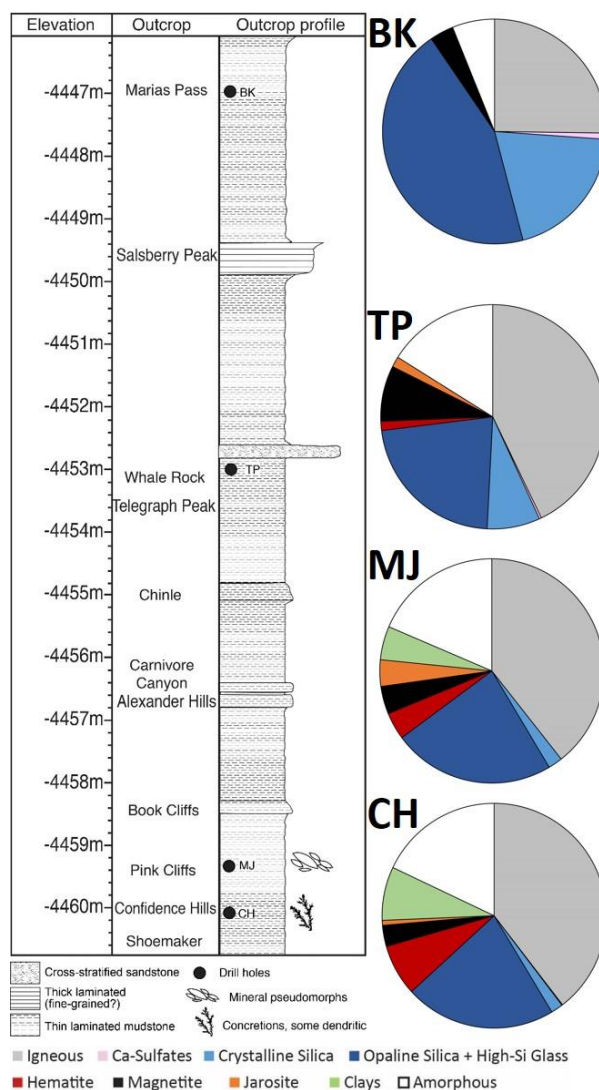

Fig. 1. Murray Fm stratigraphic column [1] and refined mineral and amorphous abundances. Amorphous materials include basaltic glass and ferrihydrite. Black dots represent locations of samples: CH = Confidence Hills, MJ = Mojave 2, TP = Telegraph Peak, BK = Buckskin.

Evidence for Acid-Sulfate Alteration: The main mineralogical evidence for acid-sulfate alteration, at some point in the history of the Murray Fm, is the presence of jarosite in samples collected in the Pahrump Hills. Jarosite is a Fe(III)-sulfate that forms in acidic environments with pH <4. Geochemical and mineral trends also suggest acid-sulfate conditions affected the Murray formation. Geochemical measurements by the Alpha Particle X-ray Spectrometer (APXS) of the dumped samples show that they all have elevated Si and Ti compared to the rocks that *Curiosity* measured on the plains of Gale Crater, which is a common characteristic of acid-sulfate altered materials [5]. There is a paucity of minerals that are susceptible to acid-sulfate alteration (e.g., phyllosilicates and pyroxene), particularly in Telegraph Peak and Buckskin. This lack of minerals that readily dissolve in acid-sulfate fluids further up section may indicate that the acid-sulfate fluids moved downwards through the section.

Acid-Sulfate Experiments in the Laboratory. Some minerals, however, appear inconsistent with the hypothesis that the rocks of the Murray Fm experienced pervasive acid-sulfate alteration. Magnetite and apatite are unstable in oxidative acid-sulfate environments, but magnetite is prevalent in Telegraph Peak and apatite is present in minor amounts in all samples from the Pahrump Hills. To examine the stability of magnetite in acid-sulfate fluids, we performed experiments in which we altered synthetic magnetite gel (synthesis adapted from [6]) in hydrothermal Parr vessels at 148 °C with 0.45 M H_2SO_4. We added H_2O_2 to some experiments to make the solutions more oxidizing. Methods for these experiments are similar to those used by [7].

All acid-sulfate alteration experiments with magnetite produced natrojarosite, hematite, and minor amounts of rhomboclase ($HFe(SO_4)_2 \cdot 4H_2O$) and goethite (FeOOH). The presence of H_2O_2 caused the precipitation of more natrojarosite and less hematite. These experiments may be analogous to the reactions that occurred at the base of the Pahrump Hills member, where oxidative acid-sulfate fluids caused the alteration of magnetite to jarosite and some hematite in Mojave 2, and less oxidative acid-sulfate fluids in Confidence Hills caused the alteration of magnetite to form more hematite and less jarosite. We are continuing our experiments under less oxidizing conditions to further examine the stability of magnetite in acid-sulfate fluids.

Alternative Hypotheses: Processes other than acid-sulfate alteration may explain the formation of minerals observed in the Murray Fm, at some point in the history of the formation. The type of iron oxide may have been controlled by the redox conditions of the lake water, where hematite precipitated under more oxidizing conditions and magnetite precipitated under more reducing conditions. This process may be similar to processes that created iron formations found on Earth [8]. In a different or complementary process, oxidative weathering of detrital iron sulfide minerals would have produced jarosite, perhaps during exhumation of the Murray Fm. This hypothesis is consistent with the presence of apatite throughout the Pahrump Hills and the positive correlation between Ti and P, but it cannot explain the elevated Si and Ti values that are typical of acid-sulfate environments. Alternatively, these sediments may have experienced many different episodes of aqueous alteration pre- and post-lithification, and the minerals in these assemblages may not be in equilibrium.

Multiple Stages of Alteration: We propose the following history for the Murray Fm: (1) Sediments were deposited in a lake. This environment may have been very similar to that of Yellowknife Bay, where authigenic phyllosilicates and magnetite formed from olivine in near-neutral solutions [9,10]. Some hematite and opaline silica may have also formed then [11]. (2) After deposition of the sediments, but before the emplacement of the overlying Stimson formation, acid-sulfate fluids moved from the top of the Murray down. These fluids caused the dissolution of phyllosilicates and mafic minerals and, under more oxic conditions, precipitated jarosite and hematite. This leaching event removed mobile elements, resulting in elevated Si (in the form of opaline silica) and Ti. (3) After lithification and the emplacement of the overlying Stimson Fm, an alkaline diagenetic event occurred in which phosphate, and perhaps Fe-Ti oxides, were mobilized in solution and precipitated apatite, causing the observed correlation between Ti and P. Ti mobility has been recognized in terrestrial sedimentary basins in alkaline fluids and is facilitated by the presence of phosphate in solution [12]. These fluids may have also affected the Stimson Fm, in which light-toned fractures show evidence for P addition. This complex origin, akin to multiple stages of diagenesis in terrestrial sedimentary basins, may be the most parsimonious interpretation of what seem to be contradictory observations.

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