

**HEMATITE FORMATION IN GALE CRATER.** J. C. Bridges<sup>1</sup>, S. P. Schwenzer<sup>2</sup>, R. Leveille<sup>3</sup>, R.C. Wiens<sup>4</sup>, A. McAdam<sup>5</sup>, P. Conrad<sup>5</sup>, S. P. Kelley<sup>2</sup>, <sup>1</sup>Space Research Centre, University of Leicester, UK, LE1 7RH j.bridges@le.ac.uk, <sup>2</sup>Dept. of Physical Sciences, Open University, UK MK7 6AA s.p.schwenzer@open.ac.uk, <sup>3</sup>McGill University, Montreal, Quebec, Canada, <sup>4</sup>Space Remote Sensing, Los Alamos National Laboratory, Los Alamos, NM 87544, USA. <sup>5</sup>NASA Goddard Space Flight Center, Greenbelt, MD, USA.

**Introduction:** Secondary minerals identified by Mars Science Laboratory (MSL), together with their sedimentological and stratigraphic context, provide an unprecedented opportunity to constrain the nature of martian fluids and habitability. One of the main targets for the MSL mission within the new Extended Mission is the Hematite Ridge on the north, lower slopes of Mt. Sharp (Aeolis Mons). This was identified by CRISM, with clay and sulfate-rich mineralogy in other parts of Mt Sharp [1,2] and is a 200 m wide layer extending 6.5 km northeast-southwest [3].

After landing in August 2012, Curiosity has identified clay and Fe oxides within fine-grained sediments along the traverse to Hematite Ridge. ChemCam analyses show the overall basaltic composition of the sediments (Fig. 1). The Sheepbed member is a mudstone of basaltic chemical composition with ~15% smectite, ~50% igneous minerals, and ~35% X-ray amorphous material [4]. The observed magnetite is considered to be of authigenic origin [5]. In previous work we showed that dissolution of approximately 70:20:10 % amorphous material, olivine and whole rock in an open system within the Sheepbed Member mudstone can explain the smectite and magnetite abundances identified by ChemMin XRD at the John Klein and Cumberland sites [6]. More recently, at the Kimberley drill site, ChemMin has identified ~10% magnetite with some hematite [7].

Here we show thermochemical models for the formation of Fe oxide enrichments, and the ferric oxide hematite in particular, within Gale sediments. This provides an insight into the formation conditions of the Hematite Ridge layer during diagenesis or other alteration stages. This model will be tested once we have a full mineral assemblage from Hematite Ridge.

**Method:** We use ChemCam (PLS1), APXS and ChemMin analyses and sedimentological observations of the Gale sediments [4,8,9] to guide the input parameters of our thermochemical model. We have used CHIM-XPT [10] to perform the model runs for a variety of compositional, T, W/R values and initial fluid compositions. The bulk composition is assumed to be basaltic (Fig. 1). Here Water/Rock ratio W/R is the ratio of incoming fluid to reacted rock.

**Results:** 1. *The Effect of Water/Rock Ratio.* In general, the model based on dissolution of 70% amorphous phase, 20 % olivine and 10 % whole rock [6], produces precipitates that are enriched in Fe, Al, and S

compared to the original rock. This effect can be more pronounced at higher W/R (Fig. 2). High W/R runs e.g. >1000 also predict the precipitation of ferric oxide at the expense of ferric silicates or other Fe oxides. Repeated weathering/leaching cycles such as can occur at the surface or along fluid conduits, will increase the effect. For example, if the alteration assemblage formed by incongruent dissolution of Portage soil (with 70 % amorphous phase, 20 % olivine and 10 % whole rock), is subject to another fluid event, the newly precipitated assemblage (at W/R 1000) contains 27 % goethite, 44 % serpentine, and 22 % clay with minor pyrite and apatite (Fig. 3).

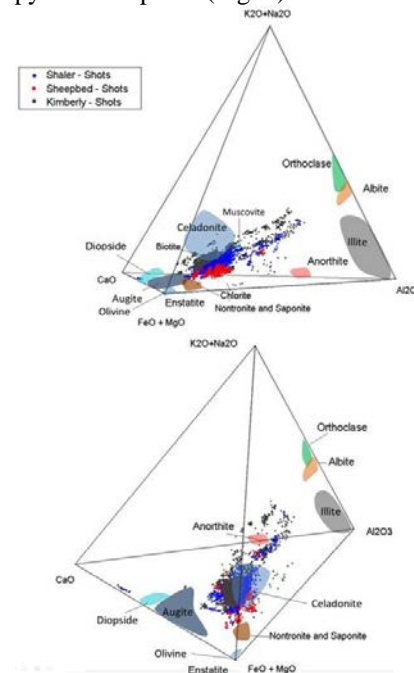


Fig.1. ChemCam Shots data (PLS1) of the Sheepbed Member mudstones from Yellowknife Bay. The sedimentary horizons show an overall basaltic mixing trend between pyroxene and feldspar, with a relatively tight clustering of analyses. The more alkali-rich Kimberley and Shaler units are shown for comparison.

2. *The effect of carbonate dissolution:* If Hematite Ridge represents rocks that were initially altered in the presence of CO<sub>2</sub>, carbonate formation could have resulted, which would have been accompanied by quartz, kaolinite and potentially zeolites. The carbonate would have been predominantly sideritic or ankeritic compo-

sition. Dissolution of such carbonates can lead to iron oxide formation - magnetite in the presence of low oxygen fugacity and hematite under more oxidizing conditions [11].

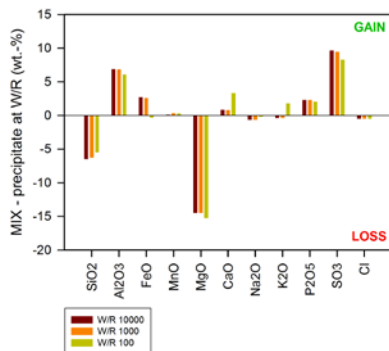


Fig. 2. Element gain/loss in precipitate relative to the dissolving host rock (incongruent dissolution of Portage soil, see [6])

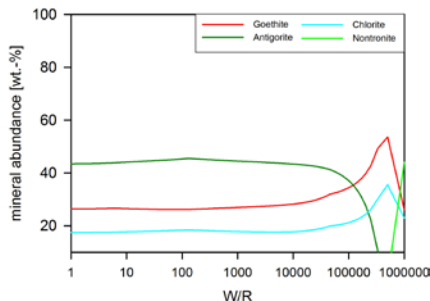


Fig.3. Re-dissolution of an alteration mineral assemblage at W/R 100 from the model runs for the 70:20:10 amorphous:olivine:bulk rock mixture. The original weathering products were dissolved in a new batch of the dilute diagenetic brine (see [6]). This shows that repeated weathering cycles will lead to enrichment of ferric oxide (goethite here, though this can readily transition to hematite).

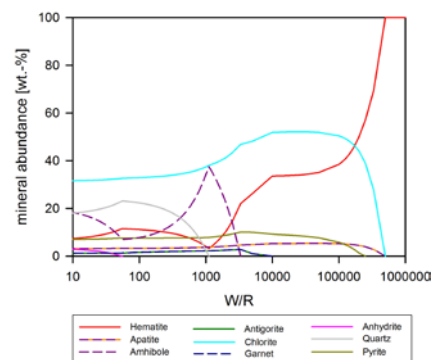


Fig.4. The effect of temperature on ferric oxide abundance. Higher T, here 150 °C, is associated with a greater abundance of hematite relative to magnetite and other ferric oxides; and the effect is especially prominent at the very highest W/R. From [6].

3. *The Effect of Temperature.* The diagenetic assemblage in Yellowknife Bay is low T, 10–50 °C. However, increasing temperature favours the precipitation of hematite (Fig. 4).

**Discussion:** A likely origin consistent with our model and the mineralogical evidence, is from the in-place weathering of precursor silicate materials under oxidizing conditions: Hematite Ridge might represent an ancient sub aerially exposed horizon. High W/R associated with FeMg mineral alteration and hematite enrichment is envisaged within a near surface aquifer located. In a variation on this model, higher temperatures would have enhanced hematite precipitation, and this could have been associated with pore water from within the Mt. Sharp sediment pile. An alternative model has been suggested by [3] who suggested exposure of anoxic  $\text{Fe}^{2+}$  rich groundwater to an oxidizing environment, leading to precipitation of hematite or its precursors. This type of scenario is a subject of our ongoing modelling.

**Conclusions:** Fe oxides analysed by Curiosity and CRISM show the effects of extensive alteration of predominantly basaltic sediments. High W/R, such as that associated with exposed weathering profiles would strongly favour Fe enrichment in precipitates, the formation of ferric oxides including hematite and goethite (which transition between each other), and Fe carbonate if alteration occurred with a  $\text{CO}_2$ -rich surface fluid. However, while hematite formation is possible at low temperatures, higher T e.g. >50–150 °C associated with hydrothermal processes in Gale would also enhance solubility and element mobility and thus favour the production of hematite. Our model suggests that Hematite Ridge is a relict layer of high W/R in an open fluid system and although we favour a low T weathering scenario, perhaps associated with a near surface aquifer, the temperature remains uncertain. This will become testable through MSL analyses of co-existing mineral phases at Hematite Ridge.

**References:** [1] Milliken A.B. et al. (2010) *GRL*, 37, doi: 10.1029/2009gl041870. [2] Thomson B.J. et al. (2011) *Icarus*, 214, 413. [3] Fraeman A.A. et al. (2014) *Geology*, doi:10.1130/G34613.1. [4] Vaniman D. T. et al. (2014) *Science*, 343: 10.1126/science.1243480. [5] McLennan, S. M. et al. (2014) *Science*, 343, doi:10.1126/science.1244734. [6] Bridges J.C. et al. (2014) *JGR*, 10.1002/2014JE004757. [7] Treiman A.H. et al. (2015) *LPSC*. 46 [8] Gellert R. et al. (2013), *LPSC*, 44, #1432. [9] Grotzinger J.P. et al. (2014) *Science*, doi:10.1126/science.1242777. [10] Reed, M.H. et al. (2010) User Guide for CHIM-XPT. Univ. of Oregon. [11] Kopp, R. E., Humayun, M. (2003) *GCA*, 67: 3247–3256.