

MODELING WATER-ROCK REACTIONS BENEATH THE GREENHEUGH PEDIMENT, GALE CRATER, MARS. S.M.R. Turner¹, S.P. Schwenzer¹, J.C. Bridges², B. Sutter³, and C.C. Bedford⁴, ¹AstrobiologyOU, School of Environment, Earth and Ecosystem Sciences, The Open University, UK, (stuart.turner@open.ac.uk). ²School of Physics and Astronomy, University of Leicester, UK. ³Jacobs, NASA Johnson Space Center, USA. ⁴Lunar and Planetary Institute, URSA, USA.

Introduction: The Mars Science Laboratory *Curiosity* rover has been exploring the clay rich Glen Torridon unit in Gale crater since sol 2300 of the mission [1]. As identified in orbital data [2], this clay rich area [3] in the Murray formation is overlain with the Greenheugh Pediment unit to the south, which is part of the Stimson Formation [4]. *Curiosity* acquired the drill sample Hutton in the Upper Murray formation 2 – 3 meters below the Greenheugh Pediment [5,6].

This study uses thermochemical modelling to investigate the hypothesis for alteration in the Murray formation below the Greenheugh Pediment. Specifically, if the contact between the Greenheugh Pediment and Murray sediments was a conduit for diagenetic fluids (a low water/rock scenario) or if subaerial weathering altered the Murray sediments before cementation began (a high water/rock scenario) [6]. Here, we report on preliminary modeling where we have reacted the chemical composition for the Hutton drill sample with Gale Portage Water (GPW) at 25 °C, 50 °C and 200 °C, for 10% $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ of the host rock.

Modeling: Thermochemical modeling was carried out using CHIM-XPT, which is a program for computing multicomponent heterogeneous chemical equilibria in aqueous-mineral gas systems [7], and has been used extensively in water-rock reaction studies for Gale crater [8-11]. In CHIM-XPT, each water / rock reaction step calculates equilibrium between a user-defined fluid and dissolved chemical reactant list (the rock), meaning that each step can be interpreted independently. The water/rock ratio (W/R) in CHIM-XPT is the ratio of incoming fluid to reacted rock. In this abstract, we focus on 1 – 100,000 W/R.

The Starting Fluid. GPW has been used extensively in thermochemical modeling studies for Gale Crater [8-10]. GPW is a dilute brine that was derived from the equilibrium mediation of a brine and rocks of the Gale area [8]. The solution is initially oxidizing (all S species as SO_4^{2-}), and the $\text{SO}_4^{2-}/\text{HS}^-$ pair in the fluid controls the redox of the fluid. The $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratio of the host rock controls the redox of the system throughout each model.

The Reactant Rock. For the preliminary modeling shown here, the APXS composition for the Hutton drill sample, as posted on the NASA PDS, was used as the reactant rock. Two versions of this composition were used: the APXS composition (Hutton_dump_corrected, sol 2684) and the APXS composition minus the

contribution of anhydrite wt.% as determined by CheMin (NASA PDS).

Results: Preliminary thermochemical modeling at 25 °C, 50 °C and 200 °C are shown in Figs. 1-3. The pressure for each model was selected to prevent the fluid from boiling. The removal of 0.6 wt.% anhydrite, as per the CheMin wt.% detection [5], showed minimal impact on the thermochemical modeling results. Therefore, here we focus on the thermochemical models using the APXS composition with anhydrite included.

The models show goethite, a potential hematite precursor [12], formed at 25 °C (Fig. 1) and 50 °C (Fig. 2) with a peak wt.% occurred at 100 W/R. At 200 °C (Fig. 3) hematite forms instead, and at higher W/R than at 25 °C and 50 °C. ~1 wt.% magnetite formed at 15 W/R at 50 °C. Nontronite clays form between 100 – 100000 W/R at >30 wt.% abundance at 25 °C (Fig. 1) and 50 °C (Fig. 2). At 200 °C (Fig. 3) formation of prehnite and pumpellyite occurs between 10 – 10000 W/R, with amphiboles and feldspar between 1 – 1000 W/R. An SiO_2 phase formed from 1 – 1000 W/R, with a peak wt.% of ~8 at 330 W/R.

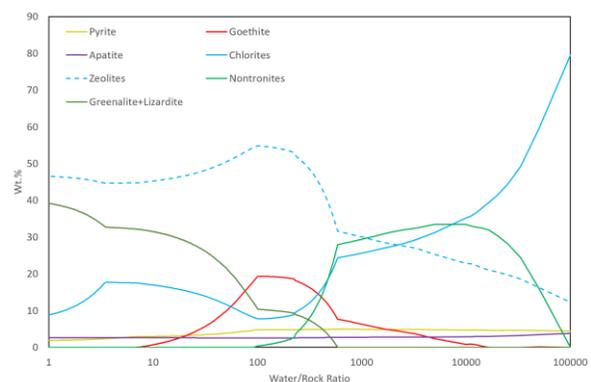


Fig 1: CHIM-XPT thermochemical model for Hutton APXS composition reacted with GPW APXS at 25 °C and 10 % $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$. Trace wt.% of calcite and troilite are not shown on the plot.

Discussion: To consider the accuracy of the preliminary thermochemical modeling shown in Figs.1-3, we must consider the mineralogy of the Hutton drill. CheMin has shown the Hutton drill sample to contain a significant amount of feldspar and pyroxene (~35 wt.% bulk), with 6.3 wt.% bulk magnetite and 2.4 wt.% bulk hematite. Only 6.3 wt.% of Hutton was reported as phyllosilicate,

with an amorphous component at 37.5 wt.%. Various SiO₂ phases (quartz, cristobalite and opal-CT) make up ~10 wt.%.

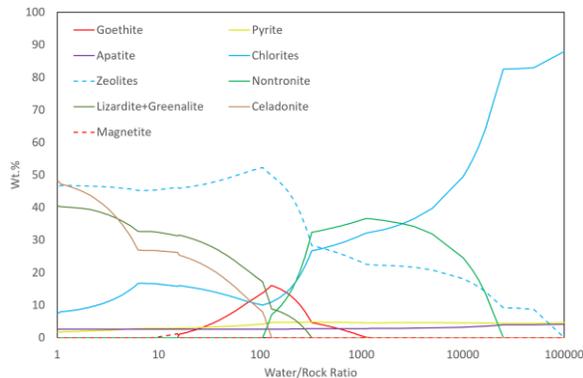


Fig 2: CHIM-XPT thermochemical model for Hutton APXS composition reacted with GPW APXS at 50 °C and 10 % Fe³⁺/Fe_{tot}. Trace wt.% of pyrrhotite, calcite and kaolinite are not shown on the plot.

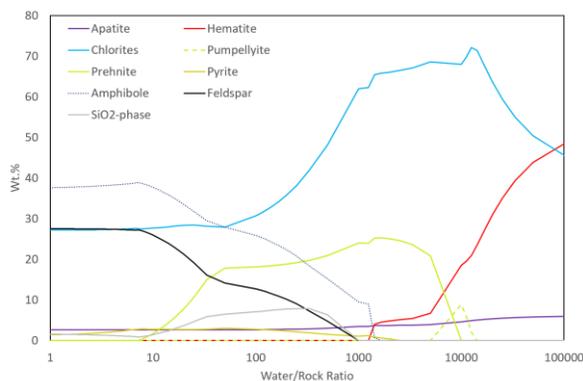


Fig 3: CHIM-XPT thermochemical model for Hutton APXS composition reacted with GPW APXS at 200 °C and 10 % Fe³⁺/Fe_{tot}. Trace wt.% of pyrrhotite is not shown on the plot.

Comparing the mineralogy of Hutton to the preliminary modeling suggests further refinement is required. Considering the comparable abundances of Fe-oxides and phyllosilicates as detected by CheMin, this could indicate W/R between 100 – 1000 for 25 °C (Fig. 1) and 50 °C (Fig. 2), with later transformation of Fe-oxide. Fig. 3 indicates that if alteration occurred at 200 °C a higher W/R (>1000) needs to be considered, as this is the region in which hematite formed, which is directly comparable to the detection of hematite in Hutton by CheMin. However, the presence of zeolites and amphiboles in Figs. 1-3 is not consistent with what has been observed in the Hutton sample [5].

Previous thermochemical modelling has suggested 100 – 10000 W/R for diagenetic alteration in Gale crater

[7,8], which is comparable to the W/R ratios indicated by the preliminary modeling shown in Figs 1-3. However, previous thermochemical modeling indicated temperatures <100 °C [8,9].

Thermochemical modeling using data for the Telegraph Peak sample, located in the lower Murray formation [13], as shown by [14] shows how >30 wt.% abundance of an SiO₂ phase can be formed when considering the amorphous component between 1 and 10000 W/R. Considering the comparability of the Telegraph Peak APXS sample to Hutton, this suggests a potential source for the SiO₂ phases observed in Hutton, and will be explored further.

Summary: Preliminary modeling shown in this abstract has indicated that a reaction pathway where GPW reacted with the Hutton host rock is a possibility for the secondary mineral assemblage observed by *Curiosity* in the Upper Murray immediately below the Greenheugh Pediment. Further thermochemical modeling will investigate the dependence on temperature, the reactant host rock chemical composition, and refine the phases prevented from forming during the modeling process. With the detection of carbonates we will also explore the addition of varying amounts of CO₂ to the model fluid.

The scope of the thermochemical modeling will also be expanded to investigate additional hypotheses [4] such as alteration by fluids originating below Hutton and subsequent evaporation through the Greenheugh Pediment, and groundwater flow through the Greenheugh Pediment.

References: [1] Fox, V.K. et al. (2020). LPSC Vol. 51, No.2833. [2] Fraeman, A.A. et al. (2016). JGR: Planets, 121, 1713-1736. [3] Thorpe, M.T. et al. (2020). LPSC Vol 51. No.1524. [4] Bedford, C.C. et al. (2021). LPSC this conference. [5] Thorpe, M.T. et al. (2021) LPSC this conference. [6] Sutter, B. et al. (2020) AGU. [7] Reed M.H. et al. (2010). User Guide for CHIM-XPT: A Program for Computing Reaction Processes in Aqueous-Mineral-Gas Systems and MINTAB Guide. 71p., University of Oregon, Eugene. [8] Turner, S.M.R. et al. (2021). In prep. [9] Bridges J.C. et al. (2015). JGR: Planets, 120, 1-19. [10] Schwenzer S.P. et al. (2016). MAPS, 51(11), 2175-2202. [11] Schieber J. et al. (2017). Sedimentology, 64, 311-358. [12] Cornell R.M. and Schwertmann U. (2003). *The Iron Oxides*. Wiley and Sons. [13] Rampe, E.B. et al. (2017) *EPSL*, 471, 172-185. [14] Turner, S.M.R. et al. (2019). LPSC Vol. 51, No.1897.