THE NATURE OF DIAGENETIC VEIN- AND NODULE-FORMING BRINES IN GLEN TORRIDON, GALE CRATER, MARS.
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Introduction: Within the Glen Torridon region of Gale crater Mars, the NASA *Curiosity* rover discovered the highest clay abundance in its bedrock to date in the crater, as well as chemically diverse diagenesis—including, nodules, veins, and possible cements [1–5]. [3–4] hypothesized that early warm reducing and alkaline groundwater-driven diagenesis altered the bedrock to produce nodules that were Mg-, Fe-, Mn-, or Ca-rich. This warmer groundwater may have been connected to an early hydrothermal process related to the initial impact that occurred to serpentinize rocks beneath Gale (including its central uplift) and bring elements (e.g., F, Ni, Mn, Fe) into fluids that circulated throughout the crater [3].

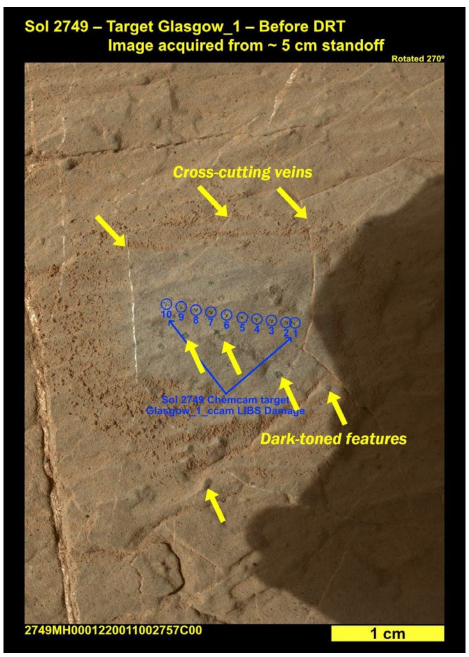

Fig 1: Millimeter-sized dark-toned features revealed within the Glasgow target after ChemCam laser dust-clearing. NASA/JPL/MSSS; [3].

Observations of diagenetic nodules in Glen Torridon show a diverse set of compositions. Of the major element oxides reported by ChemCam, MgO, FeO_T, MnO, and CaO have the greatest variation in nodular targets [3]. MgO and FeO_T are inversely correlated [3]. In nodules observed in the upper member of Glen Torridon (Glasgow member), Fe- and Mg-rich nodules do not contain detectable levels of P, S, F, or Cl; and exhibit high oxide totals, indicating that Mg or Fe is being added without appreciable amounts of other elements [3]. The Mg-rich nodules appear also less hydrated based on their elevated oxide totals [3].

Immediately above the Glasgow nodule-rich bedrock are the Hutton strata, localized diagenetically altered bedrock that sits beneath an unconformity [2]. Hutton hosts three types of veins with chemical compositions that are very different from any previously measured target in Gale crater: Fe/Mn/Ni/Cl dark-toned veins, Mg/F/K/Cl aluminosilicate linear features, and Ca/F/S light-toned veins [3]. Based on their chemistry and probable mineralogy, these veins likely formed at higher temperatures (>90 °C), and the dark-toned veins formed in highly alkaline and reducing conditions [3]. The fluids that precipitated these veins may be related to the fluids that altered underlying Glasgow bedrock, forming the Fe, Mn, Mg-rich 2-3 mm sized nodules were observed in abundance near the Glasgow drill hole [3] (Fig 1).

Notably, no Mg-rich nodules were detected at the Glasgow drill location (Fig 1; either because they were not directly sampled by the laser or the chemistry was not significantly different compared to the surrounding bedrock), but abundant dark-toned nodules were observed in this target. Throughout the Glasgow member, Mg-rich nodules were observed with ChemCam. Hence, the Glasgow drill target, while representative of the bedrock, likely did not contain the nodules of interest in the drill sample.

The mineralogy results from CheMin shows that Glen Torridon clays are mainly dioctahedral Al and Fe^{3+} smectites (nontronite) [4]. Glasgow consists of ~24 wt% clay minerals, the least in Glen Torridon, but still significant in terms of clay compared to the rest of the crater [4]. Lower in the stratigraphy, talc-serpentine group minerals, possibly including minnesotaite, $(Fe^{2+},Mg)_3Si_4O_{10}(OH)_2)$, are likely detected in some drill holes, but not in Glasgow [4].

Here, we use geochemical models (GWB and CHIM-XPT) to explore the nature of the fluids that may have produced the nodules in Glasgow. Our initial hypothesis is that Mg-rich fluids interacted with the clays to also produce mixed-layer clays in Glasgow, but confined to small nodules. Potentially this Mg-rich fluid filled vacancies in the dioctahedral clay structure to produce a mixed-layer clay with smectite-clinochlore (Mg-rich chlorite) layers [e.g. 7].

Other models of clay-groundwater interaction. The hypothesis from [6] discussed brine-driven destruction of clays where this alteration is due to brines percolating from the sulfate unit. A different hypothesis from [4] suggested that burial diagenesis at ~60 °C is responsible for minnesotaite formation in clays (at Glasgow, none of these clays are detected). Thus, while [4,6] hypothesize a range of 0-60 °C temperatures in Glen Torridon materials, we hypothesize that higher temperatures are likely needed to produce observed chemistry and mineralogy within Hutton veins [3].

Methods: We hypothesize that a hydrothermal brine existed that, when cooled, produced Mg/F/K/Cl linear features at the Hutton drill site [3]. To model this brine, we equilibrate, using the code CHIM-XPT, the Mg/F/K/Cl linear feature chemical composition with Gale Portage Water (GPW) [8] at 100 °C, 80 bar (to prevent boiling), and tested pH 10-12 and a large range of water-to-rock ratios (W/R). ChemCam FeO_T was converted to FeO and Fe_2O_3 for pure magnetite to adjust for redox. Primarily igneous minerals and minerals associated with alteration of carbonates by metamorphism or hydrothermal alteration were suppressed. Minerals associated with serpentinization, alteration of basaltic rocks, and those associated with hydrothermal veins were all considered. Quartz represents all silica phases. Li was used for charge balance. After the vein-GPW equilibration step, minerals form in the model, and the resultant fluid at a chosen W/R was analyzed using Geochemist Workbench® (GWB). This fluid will be reacted with Glasgow bedrock in a future work.

Results: CHIM-XPT results suggest that low water to rock ratios log[W/R]<2.5, depending on pH, are needed to form fluorite in the veins, a phase that was likely observed by ChemCam in Hutton veins [3,9]. At pH 11, the other phases that form include lizardite, ferroactinolite, microcline, chlorites, zeolites, hematite, and ilmenite (Fig 2). At pH 11 and log[W/R]=1, a phase diagram calculated in GWB for the fluid resulting from the initial equilibration of the linear feature vein chemistry and GPW and shows that clinochlore and Mg-saponite are both stable (Fig 3).

Discussion: Chloritization of smectite is known to occur in both hydrothermal and burial diagenesis scenarios. Reactions can occur to produce chlorite at temperatures as low as 40 °C during diagenesis, but Mg-rich chlorite formation occurs at 100–120 °C in alkaline conditions to form a mixed-layer clay [10–12]. Mixed layer smectite and serpentine-like phyllosilicates have been observed in Nahklites and are interpreted as hydrothermal products, though at a lower pH and higher temperatures than those tested here [13-14].

Summary: A preliminary model is presented to elucidate the mineral composition and formation conditions of the Hutton veins and Glasgow MgO-rich nodules. While it is possible the Glasgow nodules are a mixed layer chlorite smectite phase, more work is needed to understand its formation conditions. We will expand on this work to a wider range of conditions for pH to better understand its effects on the outcome of the model for the Hutton veins. Resultant fluids from the model will then be used to react with Glasgow bedrock composition to understand nodule formation.

Acknowledgments: NASA Mars Exploration and JPL for operating *Curiosity*.

References: [1] Bennett et al (2022) *JGR:P*, *in press*. [2] Dehouck et al (2022) *JGR:P*, *in press*. [3] Gasda et al (2022) *JGR:P*, *in press*. [4] Thorpe et al (2022) *JGR:P*, *in press*. [5] Lanza et al (2022) LPSC 2689. [6] Bristow et al (2021) *Science*, 373, 198–204. [7] Srodon (1999) *Ann Rev E&P*, 27. [8] Bridges et al (2015) *JGR:P*, 120, 1–19. [9] Forni et al (2021) LPSC 1503. [10] Beaufort et al (2015) *Clay Min*, 50(4), 497–523. [11] Mosser-Ruck et al (2010) *Clay & Clay Min* 8(2), 280–291. [12] Wilson et al (2015) *App Geochem*, 61, 10–28. [13] Changela and Bridges (2011) *MAPS*, 45(12), 1847–1867 [14] Hicks et al (2014) *GCA*, 136, 194–210.

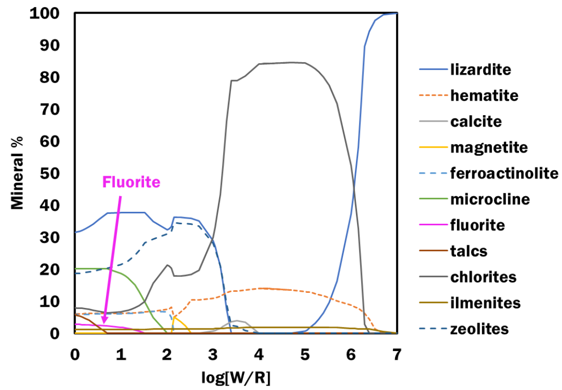

Fig 2: Results after initial equilibration of GPW fluid and linear feature composition at pH 11.

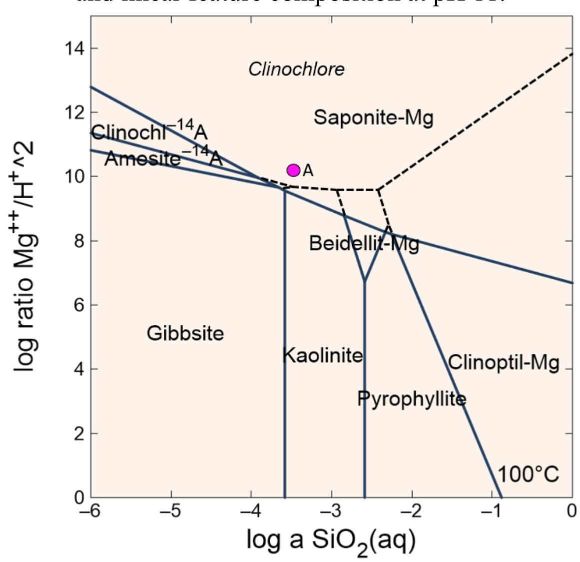

Fig 3: Stability fields for Mg-clays at 100 °C and 80 bar. When saponite is suppressed, clinochlore is stable within the dashed lines. A) Fluid composition after equlibration of GPW and linear feature chemistry at pH 11 and log[W/R]=1.