CEMENTATION AND AQUEOUS ALTERATION OF A SANDSTONE UNIT UNDER ACIDIC CONDITIONS IN GALE CRATER, MARS.

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Introduction: The Curiosity rover landed on Mars in August 2012 to explore the sedimentary history and to assess the habitability of Gale Crater. After 1200 sols of surface operations and over 12 km of traverse distance, the mineralogy of 10 samples has been determined by the CheMin X-ray diffractometer (XRD) and the chemical composition of nearly 300 targets has been established by the Alpha Particle X-ray Spectrometer (APXS).

Light-toned fracture zones (Fig. 1) containing elevated concentrations of silica have been studied by Curiosity's instruments to determine the nature of the fluids that resulted in the enrichment of SiO_2. Multiple fluid exposures are evident, and the chemistry and mineralogy data indicate at least two aqueous episodes may have occurred under acidic conditions.
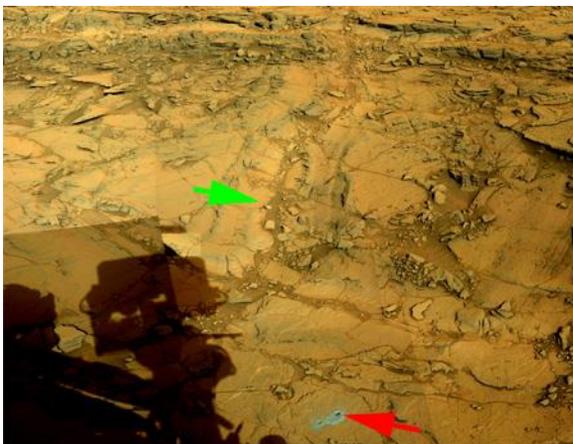

Fig 1: "Big Sky" (red arrow) and "Greenhorn" (green arrow) targets are found outside and inside an altered fracture zone, respectively.

Cementation: The light-toned alteration features occur within a cross-bedded sandstone ("Stimson" unit) which, in its unaltered form, is nearly chemically identical to young aeolian deposits analyzed by the APXS instruments at Gusev Crater, Meridiani Planum and Gale Crater. This is an indication that the crustal composition of Mars does not deviate significantly from an average basaltic value in many exposed geologic units.

Given the chemical similarities across multiple landing sites and that Mars is largely a basaltic planet, we consider the possibility that prior to cementation the sandstones of the Stimson unit were once also *mineralogically* comparable to modern aeolian fines. XRD results from a loose, scooped bedform, "Rocknest," and the drilled sandstone sample outside the fracture zone, "Big Sky," are shown in Figure 2 along with the Si-enriched sample in the fracture zone ("Greenhorn").

As expected for a collection of basaltic fines, the Rocknest sample is dominated by plagioclase feldspar, olivine, pyroxenes and an X-ray amorphous component consistent with basaltic glass. Minor amounts of magnetite and anhydrite are also found in this sample. In comparison, the Big Sky sandstone has strikingly similar abundances of feldspar, pyroxene, amorphous constituents, anhydrite and other phases. The only significant difference is the absence of olivine and the more abundant iron oxides (magnetite and hematite) in Big Sky.

We suggest that the sandstone formation involved nearly isochemical cementation of ancient sands initially chemically and mineralogically similar to modern deposits. This occurred through exposure to liquid water where olivine alteration resulted in the formation of magnetite and hematite, possibly through intermediate iron-oxyhydroxide phases which are no longer expressed. These iron oxides may currently serve as the cementing agent in the sandstone. The suggestion that this fluid exposure was under acidic conditions is based on the preservation of the amorphous component attributed to basaltic glass. Hydrolytic alteration of basaltic glass and olivine typically occur at comparable rates [1], but enhanced dissolution of olivine relative to basaltic glass is observed under low pH, hydrothermal conditions [2].
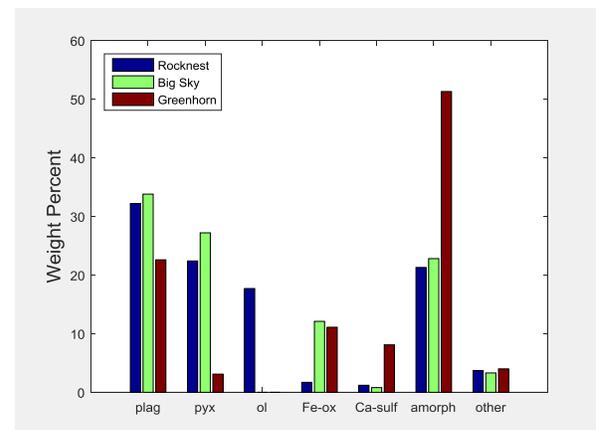

Fig 2: CheMin-derived mineralogy for a scooped aeolian deposit ("Rocknest") and the drilled "Big Sky" and "Greenhorn" targets.

Sulfur Addition: The concentration of SO_3 in the ~10 cm scale, light-toned, altered fractures exceeds 13 wt%. Sulfur is correlated with calcium in the APXS data, and the CheMin mineralogy from Greenhorn indicates ~2 wt% bassanite and 7 wt% anhydrite. Not all of the Ca, however, is in sulfate, given the abundance of plagioclase (~20 wt% An35-40) and minor pigeonite in Greenhorn. In fact, after accounting for the known crystalline phases there are not enough Na, Mg, Al, K and Ca cations to account for the sulfur anions in the fracture zone targets, suggesting that Fe-sulfates may be involved. Any sulfate present in Greenhorn other than bassanite and anhydrite is either below the detection limit of CheMin (~1 wt%) or attributed to the non-crystalline fraction of the sample. The roughly 50 wt% X-ray amorphous material in Greenhorn is where much of the sulfur resides. One straightforward mechanism for creating mixed-cation, amorphous sulfates is to add sulfuric acid, e.g. from a volcanic source, to a sediment and evaporate or quickly freeze the fluid before equilibrium crystal growth and long range order can be achieved [3]. While this scenario is not necessarily unique, a low pH origin is also implicated by the likely presence of Fe-sulfates.

A similar process occurs at the gas-solid interface for martian dust and soil grains, where non-specific sulfates are formed through condensation of volcanic volatiles. The fixed ratio of sulfur to chlorine in multiple in-situ analyses across the planet indicates a consistent volcanogenic source of sulfuric and hydrochloric acid. Sulfur concentrations in soils vary by a factor of two, largely correlated with grain surface area, but no clear cation associations are evident.

Laboratory experiments have shown that the chemistry and mineralogy of rocks at Meridiani Planum could have resulted from the percolation of sulfuric acid through basaltic sediments forming a variety of sulfates and other alteration products [4]. Similar to the case of the light-toned fractures at Gale Crater, weak cation correlations with SO_3 for the Meridiani rocks do not account for the total abundance of sulfate, which varies from ~10 to ~30 wt%. The addition of sulfur through volcanic fluids rich in sulfuric acid is a plausible process for forming mixed sulfates at Greenhorn.

Silica: The most significant difference between Greenhorn and its unaltered counterpart, Big Sky, is the abundance of amorphous silica in Greenhorn (largely present as Opal-A). This increase in amorphous silica is balanced by reductions in plagioclase feldspar and pyroxenes (Fig. 2). As discussed in the previous section, the Greenhorn target also contains Ca-sulfate. The dissolution of plagioclase and pyroxene and the development of amorphous silica could have occurred over a wide range of pH. Silica could

have been carried in and deposited by neutral to alkaline pH fluids or other elements could have been leached away by acidic fluids resulting in a passive enrichment of silica.

One argument in support of an intermediate pH scenario is that a number of element ratios remain the same across the alteration zone. The dilution effect from the simple addition of silica and Ca-sulfate can account for many of the elemental concentrations. On the other hand, the observed correlation between Si and Ti (Fig. 3) is a characteristic signature of acidic alteration as both of these elements are difficult to mobilize in low pH fluids. Furthermore, if cementation of the sandstone and addition of the abundant sulfur occurred under low pH conditions, it seems unnecessary to invoke a separate moderate pH episode for the silica addition, especially when passive silica enrichment could have occurred in close association with the sulfur addition.
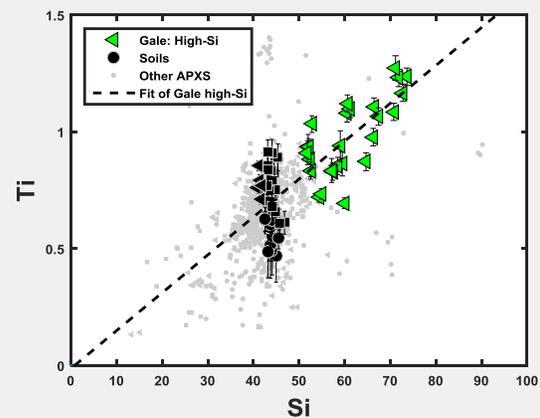

Fig 3: Ti-Si correlation (molar values) for high silica targets at Gale, a signature of passive enrichment in a low pH environment.

Future studies: This proposed scenario of sandstone cementation, sulfur addition and silica enrichment through episodes of acidic, possibly hydrothermal, alteration will continue to be tested as Curiosity continues its traverse. "Hematite ridge" may be a region of deposition for the Fe, Mg and Al mobilized during the passive enrichment of silica. Further chemical and mineralogical studies may provide additional information on the cementation and sulfur addition processes as well as provide insight into the apparent retention of magnetite through an episode of acidic alteration.

References: [1] Eggleton et al. (1987) *Clays and Clay Min. 35(3)*, 161-169. [2] Hausrath and Tschauner (2013) *Astrobiology, 13,* 1049-1064. [3] Morris et al. (2015) *46th* LPSC, 2434. [4] Golden et al. (2005) *JGR, 110*, E12S07.