EVIDENCE OF MULTIPLE FLUID EVENTS IN ELEVATED-MN CHEMCAM TARGETS IN THE BRADBURY RISE, GALE CRATER, MARS.
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Introduction: High concentrations of manganese in rocks on Mars could provide clues to the ancient climatic and atmospheric conditions of the planet. On Earth, it is well understood that elevated amounts of Mn oxides may be evidence of highly oxidizing conditions, because in most cases, Mn is only sensitive to high potential oxidants [1]. E.g., Mn is only recorded in the terrestrial rock record after the Great Oxidation Event, when microbial photosynthesis began to produce oxygen, causing a highly oxidizing environment conducive to Mn oxide precipitation [1, 2]. Mn^{2+} is a relatively mobile species, especially in more acidic and reducing water lacking CO_2 [1].

Our analysis of rocks with MnO content greater than the mean bedrock value for MnO in Gale crater (0.2 wt.%) shows evidence of multiple early- to late-stage fluid events. We have observed that elevated Mn is often associated with diagenetic materials and typically decoupled from the initial stages of aqueous alteration [3].

Methods: In the first 600 sols of the NASA *Curiosity* rover's traverse across Gale crater, we identified 201 elevated-Mn targets in ChemCam data [4] and sorted them into 16 unique facies using the classification system developed by [4].

We created 576 binary oxide plots, one for every pair of major oxides within each facies. Due to the complexity of this dataset, we developed a technique using correlation heatmaps to determine the most interesting patterns in the data (Fig. 1) [5]. The patterns revealed in this approach guided the subsequent analysis.

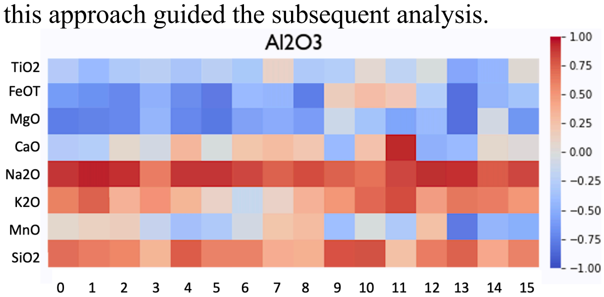

Fig. 1: Correlation Heatmap between Al_2O_3 and the other major oxide compositions of the targets in facies 0 – 15 [5]. Facies are labeled on the x-axis. Degree of correlation is represented by the shade of each square (darker = stronger correlation), and the type of correlation is represented by the color (blue = negative; red = positive) [5].

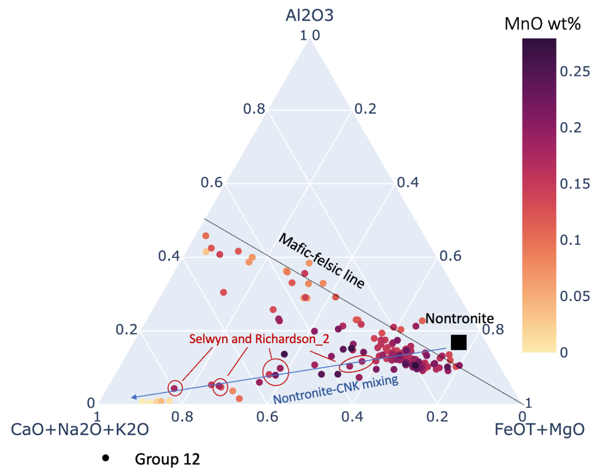

Fig. 2: Ternary diagram with Al_2O_3 (A), FeO_T+MgO (FM), and CaO+Na_2O+K_2O (CNK) apices. Observation points from targets in Group 12, the miscellaneous category, are shown as circles with an MnO wt.% color scale. Darker colors represent higher concentrations of MnO wt.%. The points circled in red are the high-Mn points in the targets Selwyn and Richardson_2. The blue arrow represents the possible mixing line between CNK and nontronite. The black square represents the approximate location of pure nontronite.

Results: In the ChemCam targets Selwyn and Richardson_2, we observed both elevated-Mn points and Ca sulfate veins (Fig. 2). Both of these targets were sorted into the miscellaneous category (group 12) [4] and consist primarily of calcium sulfate deposits surrounded by dark-toned regions of elevated Mn. The elevated-Mn points in these targets plot along a possible mixing line between nontronite, a sodium iron aluminum silicate clay, and the soluble elements Ca, Na and K in an A-CNK-FM ternary diagram (Fig. 2).

Facies 13 contains targets with “light-toned crystals surrounded by a dark-toned matrix” [3]. We interpret these targets as altered basaltic material. The points that have elevated Mn generally lie on the dark-toned regions of targets in this facies (e.g., Fig. 3).

The elevated-Mn points in Facies 13 also plot along the possible nontronite-CNK mixing line (Fig. 4). The light-toned points in Fig. 4 have high amounts of Al_2O_3 and plot on the felsic end of the mafic-felsic line, but trend towards the Al_2O_3 apex. These points have a high chemical index of alteration (which suggests that they might be clay-rich, but of a different phase compared to nontronite). However, they are not elevated in Mn or Ca.

As described in [5], correlation heatmaps (e.g., Fig. 1) between Al_2O_3 and the other major oxides help illuminate any strong correlations with aluminum. Fe and Al are positively correlated in Facies 9, 10 and, 11, the three diagenetically altered facies. These facies contain light-toned rocks with concretions, dark-toned rocks with concretions, and altered mudstones with veins, respectively [3, 4]. There are elevated-Mn points within these facies, as well, that plot along the possible nontronite-CNK mixing line.

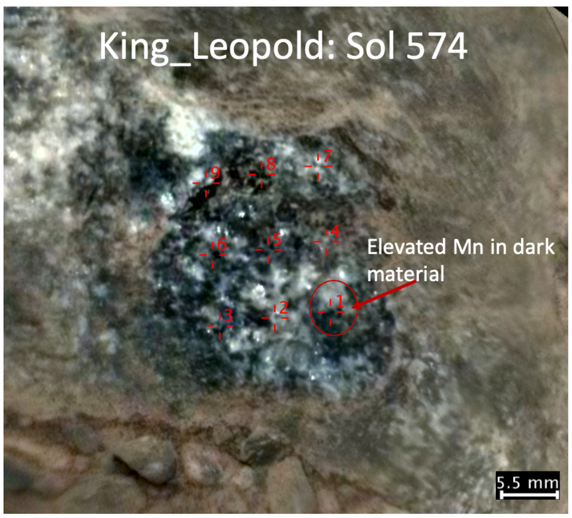

Fig. 3: Cropped RMI of the ChemCam target King_Leopold from sol 574 in Facies 13. The red arrow points to an area between the light-toned crystals that shows elevated MnO and plots on the possible nontronite-CNK mixing line (see Fig. 4).

Discussion: Nontronite, which typically forms in altering basaltic material, has been detected using orbital spectral measurements in many places on Mars, including in Gale crater [6]. Fe and Al do not occur in a single mineral phase in igneous rocks, so any positive correlation would imply the presence of clays, possibly nontronite. Interestingly, Al is positively correlated with Fe, Ca, and Na in Facies 9, 10, and 11 (Fig. 1), which all have diagenetic material (e.g., veins and concretions). As Mn is a fluid-mobile element in the right conditions [1], the elevated-Mn points in these facies imply that the fluid that may have caused alteration of the phases to nontronite was also Mn-rich.

In addition, in this work, as in [3], we observed a relationship between calcium-sulfate veins and elevated Mn. Many other recent studies have seen ubiquitous Mn-rich fracture fills [e.g., 1, 7] and potential concretions [e.g., 7, 8, 9] throughout Gale crater. Our more recent analysis shows a trend between elevated-Mn and other alteration materials, such as concretions and clays, e.g., nontronite. Together, these observations are further evidence of multiple diagenetic events having occurred after the original dissolution of basaltic materials. This provides a stronger foundation for our hypothesis that Mn deposition was at least partially decoupled from rock weathering, and thus multiple early- and late-stage fluid events involving Mn took place in Gale crater [7].

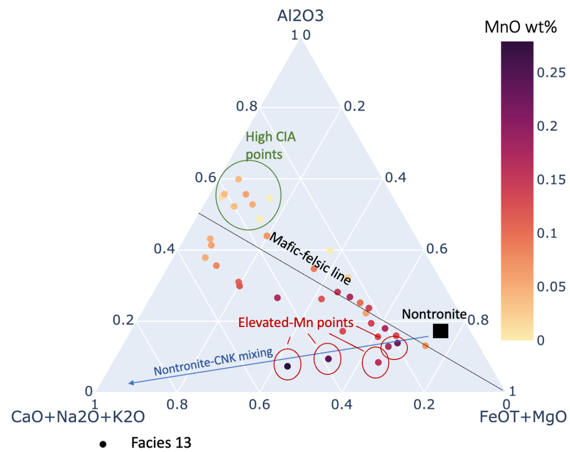

Fig. 4: Ternary diagram with Al_2O_3 (A), FeO_T+MgO (FM), and CaO+Na_2O+K_2O (CNK) apices. Observation points from Facies 13, targets with "light-toned crystals in dark matrix," are shown as circles with a MnO wt.% color scale. Darker colors represent higher concentrations of MnO wt.%. The points circled in red are the elevated-Mn points along the possible nontronite-CNK mixing line. The points circled in green are the points with high Chemical Index of Alteration values. The black square represents the approximate location of pure nontronite.

Conclusion: We observed a correlation between possible clay material (e.g., nontronite) and diagenetically altered targets with elevated-Mn points. This relationship supports the hypothesis that the same fluid that altered the basaltic material to form the clay also carried and deposited Mn. The existence of other diagenetic material (e.g., veins and concretions), together with the possible elevated-Mn and nontronite correlation, could be evidence of multiple fluid events in the history of Gale crater.

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References: [1] Lanza et al. (2016) *Geophysical research letters*, 43(14), 7398-7407, [2] Maynard et al. (2010) *Economic Geology*, 105(3), 535-552, [3] Comellas et al. (2021) *LPSC 52#2176*, [4] Essunfeld et al. (2021) *LPSC 52#2180*, [5] Morris et al. (2022) *this meeting*, [6] Gainey et al. (2014) *Elsevier* 194-211, [7] Gasda et al. (2021) *JGR, in review*, [8] Lanza et al. (2021) *LPSC 52#2231*, [9] Gasda et al. (2021) *LPSC 52#1272.*