IRON MOBILITY DURING DIAGENESIS DEDUCED FROM CHEMCAM OBSERVATIONS AT GALE CRATER, MARS.

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Geological context: The Curiosity rover reached a local topographic high named Vera Rubin Ridge (VRR) on sol 1800 after more than 17 km of traverse since landing at Gale crater, Mars. The lack of clear discontinuity between the VRR and the underlying fluvial and lacustrine fine-grained sandstones and mudstones of the Murray formation suggests a continuity in deposition consistent with the lack of obvious facies change. The VRR ridge is characterized by a hematite signature in orbital spectra [1]. The presence of hematite at VRR was confirmed during the approach by both Mastcam multispectral and ChemCam passive spectra observations [2-3]. However, hematite was observed along the Murray lacustrine mudstones located stratigraphically below VRR. In addition, iron abundances since sol 1800 did not show any strong increasing FeO_T trend in the host rock [4], thus questioning the origin of the enrichment in hematite. In contrast, anomalously high Fe detections were observed on local dark-toned features [5-6]. These observations are often associated with light-toned Ca-sulfate (bassanite) veins, which were observed consistently across the rover traverse [6-7]. In this study, we focus on these dark-toned diagenetic features using the ChemCam instrument throughout the traverse of the rover in the VRR unit from sol 1800 to 2260, and especially in the so-called Jura member. Chemcam is a Laser Induced Breakdown Spectroscopy (LIBS) instrument, with an associated Remote Micro-Imager (RMI) [8]. Chemical quantifications for major elements are obtained using an updated multivariate analysis technique [9] or ratios of individual emission peaks.

Observations: The Jura member is composed of a fractured host rock composed of laminated mudstones to fine-grained sandstones predominantly of red color but including 10-20m large grey patches of host rock. Dark-toned concretions are preferentially encountered along Ca-sulfate light-toned veins, as inclusions and fracture fills (Fig. 1) in the grey Jura member. Dark-toned features are also observed in the host rock as scattered polygonal crystal-shapes, suggesting pseudomorphosis of previous minerals. In a few occurrences, the dark-toned concretions are surrounded by light-toned bleached halos in the host rock (Fig. 1).

The chemical compositions of all these dark-toned diagenetic features are summarized in ternary diagrams in Fig. 2 (in molar percentages, based on quantified oxide weight percent reported by ChemCam). Dark-toned features, including dark-toned material within crystal-shaped features, show a composition dominated by an enrichment in Fe to the detriment of other major elements (notably Si, Al, Mg, K and Na) compared to the host rock compositions. High-Fe observations are not associated with detection of volatile content (S, Cl, P or C). The H emission line is also very low, thus pointing toward poorly hydrated Fe-oxide mineralogy. Passive reflectance spectra do not show ferric absorptions (or only weakly) associated with the dark-toned features (535 nm band, downturn after 750 nm), contrasting with typical spectra associated with VRR host rocks. These spectral signatures could represent coarse-grained (gray) hematite or another iron oxide phase, such as magnetite [4-5]. In contrast, the bleached halo has a very low FeO abundance (6-10 wt.%) compared to other VRR host rock observations (18-22 wt.%). Interestingly, lower Fe abundances are not correlated with depletion in any other major elements, which preserve the same relative abundances, except for MnO which is also depleted.

Fig. 1: Fe relative content (red lines) for each ChemCam sample location at the target Rhynie illustrating associations of high Fe with dark-toned features and of low Fe with bleached light-toned halos.

In terms of temporal sequence, dark-toned fracture fills and nodular concretions form interconnected complexes with light-toned Ca-sulfate veins. Fracture-fills appear to transition laterally from light-toned to dark-toned material within the same fracture, and some dark minerals are locally present inside Ca-sulfate veins (target Grange). Light-toned veins do not crosscut the dark-toned features even though both features appear to be spatially associated, which suggests that dark-toned features and light-toned veins formed simultaneously (or near so), as a late-diagenetic mineral paragenesis in the grey facies of the Jura member.

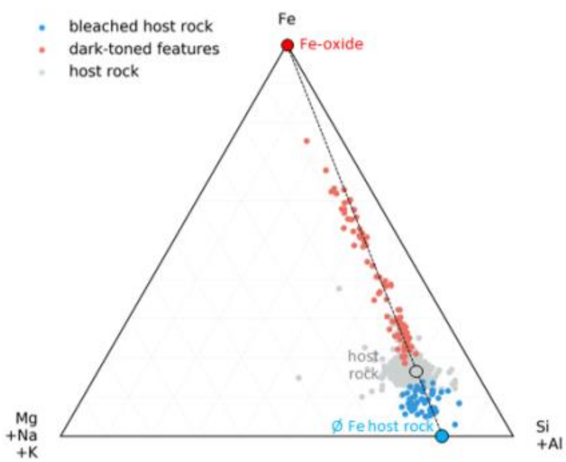

Fig. 2: Ternary diagrams showing ChemCam quantified abundances (molar percentages) for major elements: dark-toned features (in red) are associated with very high Fe content, trending toward a pure Fe composition, contrasting with low-Fe observations on bleached light-toned halos such as that observed around Rhynie (Fig. 1).

Interpretations: Fe enrichments at VRR appear to be mainly associated with dark-toned features often encountered along Ca-sulfate filled fractures, pointing toward a potentially coeval diagenetic origin for the formation of Fe-rich and Ca-rich phases. In contrast, the bleached halos with depleted FeO abundance suggest preferential leaching of Fe in compared to the local host rock suggesting reducing fluids. Moreover, Fe-rich and Fe-poor observations in dark-toned features and bleached halos, respectively, neatly plot along a mixing line between a Fe-oxide end-member and Fe-free host rock composition, which indicates that Fe was mobilized from the host rock in the same diagenetic episode.

The formation of Fe-oxide mineral phases is especially subject to pH and Eh variations, as shown in the Pourbaix diagram on Fig. 3. In presence of SO_4^{2-}, aqueous Fe is only observed in solution for pH<6 and moderate (as Fe^{2+}) to oxidizing (as Fe^{3+}) redox conditions. Hematite formation occurs in a large range of pH and Eh but magnetite appears to be thermodynamically unstable in the presence of SO_4^{2}. In this context, magnetite may form under extremely reducing (Eh < −0.5V) and alkaline conditions (pH > 11 − 13 depending on temperature and pore-pressure), as well as pyrrhotite (FeS) in slightly less alkaline conditions. Increase in SO_4^{2-} activity would expand the stability field of pyrite at the expense of magnetite (and pyrrhotite), and lead Fe^{3+} to complex in solution forming $FeSO_4^{+}$ ions. An associated increase in Fe^{2+} activity would also trigger the formation of melanterite (Fe^{2+} sulfate), but no Fe-sulfate or Fe-sulfur has been observed.

Discussion: Associations of high FeOT abundances and Ca-sulfates were previously observed by ChemCam at several locations along the rover traverse [10]. Here, the Fe enrichments in the VRR are also encountered alongside light-toned Ca-sulfate veins, but they are connected to locations depleted in FeOT and MnO abundances without depletions of orther major elements, suggesting reducing fluids. These new observations highlight the significant role played by ground water circulation and diagenesis in the mobility and distribution of Fe in the Vera Rubin Ridge, highlighted here by reducing fluids observed late in the sequence of diagenesis. In this context, the presence of hematite in the “red outcrops” presumably preceded this reducing phase, but its formation by depositional or early diagenetic processes remains unknown.

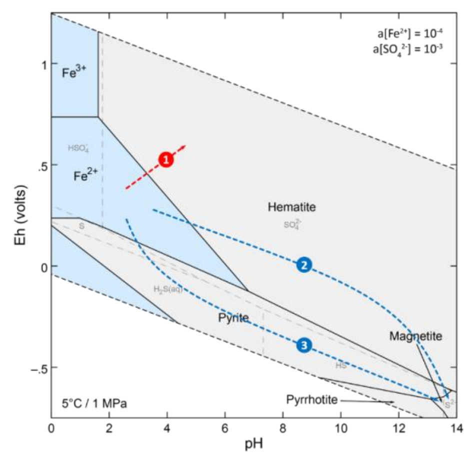

Fig. 3: Pourbaix diagram of Fe species for low T, low P, diagenetic conditions with iron and sulfur-bearing fluids.

References: [1] Fraeman, A. et al. (2013), Geology, 41(10), 1103–1106 [2] Johnson, A. et al., this meeting. [3] Frydenvang, Y. et al., this meeting. [4] L’Haridon et al., 2018, AGU abstract P41A-07. [5] David, G. et al., this meeting. [6] Nachon, M. et al. (2016), *Icarus*, *281*, 121. [7] Rapin, W. et al. (2016), EPSL, 452, 197–205. [8] Wiens, R.C., et al. & Maurice, S. et al. (2012), *Space Sci. Rev.*, 170. [9] Clegg, S. et al. (2017) *SCAB.* [10] L’Haridon, J. et al. (2018), *Icarus*.