HEMATITE MINERAL GRAINS OBSERVED BY CHEMCAM ACROSS THE VERA RUBIN RIDGE SEDIMENTARY ROCKS AT GALE CRATER, MARS. G. David¹, A. Cousin², O. Forni¹, P-Y. Meslin¹, N. Mangold², J. L’Haridon², E. Dehouck³, N. L. Lanza³, A. A. Fraeman⁴, A. M. Ollila⁵, A. R. Newell⁶, O. Gasnault⁷, R. C. Wiens⁸, W. Rapin⁹, S. Maurice⁸, M. Salvatore⁸; ¹IRAP, Toulouse, France, ²LPG, Nantes, France, ³LGL, Lyon, France, ⁴LANL, Los Alamos, USA, ⁵JPL, Pasadena, California, USA, ⁶Caltech, Pasadena, USA, ⁷NAU, Arizona, USA.; [gael.david@irap.omp.eu]

Introduction: After more than ~1800 sols (Martian days), the Curiosity rover reached Vera Rubin ridge (VRR), located ~300 m up Mount Sharp. Spectral reflectance observations of VRR by both orbital remote sensing with CRISM data [1,2,3], and in situ by Curiosity [4,5] show that the ridge’s spectral signature is strongly dominated by red crystalline hematite (Fe₂O₃). Constraining the nature and chemistry of iron oxides is important as they are geochemical markers of past environments during their formation, such as redox conditions. However, none of the chemistry instruments onboard Curiosity (APXS or CheCam [6,7]) recorded any significant iron enrichment in the bulk of the ridge compared to previous terrains [8,9]. Within VRR, only sporadic Fe-rich diagenetic features have been observed in the gray rocks of the Jura member (upper terrain of the ridge). Specifically, mm-scale, dark-toned nodular concretions within or in close association with light-toned Ca-sulfate veins (fig. 1) revealed >40 wt% FeO from CheCam data [10]. This is beyond the range of our current FeO calibration.

Fig.1: Illustration of the dark-toned features (Rhynie ChemCam target - Sol 1934) from the grey Jura member.

Therefore, we have built a specific iron calibration curve, based on experiments using LIBS (Laser-Induced Breakdown Spectroscopy) and dedicated to iron oxide mixtures with basaltic conditions. The objective of such experimental calibration curve is to assess the composition of these dark-toned features as well as to track the hematite through the VRR. However, it is important to keep in mind that this quantification method, based on the experimental calibration curve, is only suitable for iron oxides/basaltic mixtures, whereas the current Major Oxide Compositions (MOC) method [11] used to quantify iron with ChemCam quantification is supposedly more robust for all other kinds of mineralogical assemblages.

Methods: We prepared different mechanical mixtures with powders of hematite, goethite and magnetite. These iron oxides were then mixed at different concentrations with basaltic materials, simulating VRR bedrocks, at various abundances from 0 up to 100 wt%. Four different matrices were used: 1) pristine JSC martian simulant [12]; 2) a mixture of JSC martian simulant with ilmenite (FeTiO₃) in order to match the iron content of martian basalts (~20 wt% FeO); 3) Magnesium sulfate (kieserite) and 4) calcium sulfate (mixture of bassanite, anhydrite and gypsum). Mixtures were then pressed and analyzed with the ChemCam setup in Toulouse, in a chamber that mimics martian conditions for atmospheric pressure (~ 7 mbar) and compositions (mainly CO₂). Each pellet was probed at 5 observation points (of 30 laser shots each). Data were processed the same way as flight data [6]. Then, in order to improve the instrumental response correction, the Pearson correlation factor (PCF) was calculated between each laboratory sample spectrum and the spectrum of the Mont Dieu iron meteorite [13], acquired with our terrestrial setup. In the same way, the PCF was computed between flight data and the Aeolis Mons 001 iron meteorite, obtained with ChemCam on Mars (from Sol 1505 [14]). This allowed PCF for laboratory and ChemCam Mars data to be directly compared, and enabled us to estimate the iron abundance of VRR martian bedrocks.

Results: Our experimental calibration curve applied to dark-toned features observed at VRR (dark concretions and vein fillings) predicts iron contents that are consistent with iron oxide compositions. The compositions reach 80.40±5.42 FeO₇ wt.% (fig. 2) for the purest Fe oxide targets (with no contamination from surrounding bedrock or calcium sulfate veins). The morphological analysis of these dark-toned crystals is consistent with grey hematite [10], and these features have been interpreted to have formed from a diagenetic process. As iron, manganese is also sensitive to redox-driven chemical processes. MnO quantification, based on the Mn peak areas at 403.19, 403.42 and 403.5 nm (see method in [15]), reveals relatively low abundances in these dark-toned features. The purest targets display an average value of 0.13 ±0.03 MnO wt.%, relatively similar to the mean abundance of the host rocks in the Grey Jura (0.16 ±0.16 MnO wt.%).
All bleached halos or concretions have been removed for the calculation.

In addition to dark-toned features, bedrock observed in the Pettogrove Point member (PPM - lower portion of the ridge) also show some local enrichment in iron abundance (up to 24.5 wt% FeO\textsubscript{T} for individual observation points), compared to the average martian bedrock content observed in the Gale crater (~19.5 wt% FeO\textsubscript{T}). Higher iron abundances are observed in several observation points of same ChemCam rasters and are not randomly distributed along the ridge. ChemCam shot-to-shot analyses on these specific points reveal that the iron is antecorrelated with other major elements, and no correlation is observed with any minor or trace elements like S, P, Cl or F. This suggests that the iron is mostly present as iron oxide grains. Indeed, hematite is the major Fe-bearing phase in PPM from the CheMin perspective, with ~16 wt. % of the bulk mineralogy [16]. Other iron phases like magnetite, akaganite and jarosite represent only ~2 wt. % [16]. Consequently, we are probably mostly probing basaltic mixtures with more important hematite contribution. This group of bedrock also displays a higher Mn abundance in contrast to the dark-toned features of the grey Jura. Shot-to-shot correlation between Fe and Mn elements is not obvious (fig.2) in these grey Jura bedrocks, but their higher abundance in iron as well as a subtle increase in the average Mn content compared to the PPM host rocks (respectively 0.42±0.17 and 0.33±0.23 MnO wt.%) could suggest collocalation of both Mn and Fe-oxides. Collocation of such an assemblage could hint at the involvement of red-ox driven processes. Co-precipitation of both hematite and Mn-oxide minerals would involve relatively oxidized and/or alkaline fluids during their formation. A diagenetic origin, including groundwater fluid circulation, will be favored rather than direct precipitation from the lake water as bedrock localization with higher iron abundances appears to not be stratigraphically controlled (verified as the rover made multiple ascents and descents of the ridge).

In the grey Jura, hematite is also the most abundant Fe-bearing phase found at the Highfield drill location [16]. Indeed, CheMin recorded grey hematite in this area [16], which was also suspected from ChemCam passive reflectance observations [4]. Regarding bedrock from the grey Jura member with >21.5 wt% FeO\textsubscript{T}, a similar population to PPM bedrock is observed (fig. 2) with a relatively high Mn content compared to dark-toned features. Indeed a different trend can be observed for this population compared to that of the dark-toned features (grey circles and black squares in fig. 2). This observation could suggest that a least part of the hematite content located in the grey Jura bedrock shares a similar origin or formation process to the hematite of PPM, and consequently a distinct origin relative to the dark-toned grey hematite features.

**Conclusion:** This study confirms that dark-toned features observed in the grey part of the Jura have a composition consistent with iron oxide. These dark-toned features generally have relatively low Mn abundances. Local increases in iron abundances are also observed in some VRR bedrock (>21.5 wt% FeO\textsubscript{T}), which are probably associated with hematite content. In addition to slightly higher Fe abundances, this specific PPM bedrock shows average Mn abundances that are slightly higher than that of the other PPM regular rocks (with iron abundance < 21.5 wt% FeO\textsubscript{T}). Bedrock presumably enriched in hematite in the Jura seem to have the same Mn signature as PPM bedrocks (>21.5 wt% FeO\textsubscript{T}). These observations could suggest that the grey hematite of grey Jura is probably more related to the red hematite of the PPM than the grey hematite of dark-toned features. This suggests that the different units of VRR underwent different episodes of fluid circulation with variable red-ox conditions, the relative timing of which is not well constrained.

**References:**