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SIDERITE-RICH LAMINAE AT THE MARKER BAND CONTACT IN GALE CRATER. W. Rapin¹, M. Loche¹, P. Beck², P-Y. Meslin¹, G. Caravaca³, T. Magnin¹, J. Schieber⁴, S. Gupta⁵, G. Dromart⁶, B. Tutolo⁷, E. Kite⁸, P. Gasda⁹, A. Fau¹, O. Gasnault¹, N. Lanza⁹ ¹IRAP, CNRS, Univ. Toulouse, France (william.rapin@cnrs.fr). ²IPAG, Univ. Grenoble Alpes. ³GET, Univ Toulouse. ⁴DGS, Indiana Univ. ⁵Imperial College London. ⁶Univ. Lyon, LGL-TPE. ⁷Univ. of Calgary. ⁸Univ. of Chicago. ¹⁰LANL, Los Alamos.

Introduction: The apparent near absence of carbonate minerals in Noachian and Hesperian strata [1,2], despite predictions on their abundance [3], has cast doubt on the mechanisms proposed for their formation and the nature of early Mars environments [4]. Carbonate formation can sequester CO₂ from volcanic outgassing, a key driver in early climate evolution and habitability [5,6]. Understanding the role and fate of carbonates and its impact on early climate regimes requires both orbital mapping and *in situ* geological investigations. Mg-rich carbonates have been identified in a few locations *in situ* at Gusev and Jezero craters [7,8] as isolated replacements by late-stage diagenetic fluids, but more recently the Curiosity rover showed the extensive presence of siderite (FeCO₃) within strata of the hundreds-meters thick sulfate-bearing unit [9]. Whereas chemical sedimentation is hypothesized as the mode of formation and deposition, a clear sedimentological context is so far lacking for the upper sulfate-bearing unit and the deposition of siderite [10]. In addition, its abundance (5-10 wt.%) makes it a significant though not a dominant component of the sediments. Here we report on a previously unidentified unit of the Amapari Marker Band (AMB) [11,12] that is composed mostly of siderite. This siderite-rich bed occurs at the base of the main wave-rippled AMB interval which itself has a comparatively lower Fe-content [13]. Examining this type of carbonate deposit within a regional sedimentary context (Fig. 1) provides new insights on the mechanisms for carbonate formation on early Mars.

Data and methods: This investigation of AMB geochemistry relies mostly on data from the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument which is uniquely sensitive to volatile elements including carbon, as well as minors and major elements [14]. Yet, the detection of carbon using LIBS is made extremely challenging on Mars due to the contribution from the CO₂-rich atmosphere to the plasma emission. The carbon emission peaks can be extracted from the spectra, but due to this limitation the carbonate limit of detection is about 50 wt.% [15]. Using this method and applying a correction for seasonal changes in instrument focus and atmospheric pressure we determined the LIBS carbon signal from bedrock data at and around the AMB. We use this corrected carbon signal to constrain carbonate abundance based on validation via both laboratory data and a calcite calibration sample acquired in Jezero crater [7]. Major-element Oxide Composition (MOC) data are processed via multivariate regression methods [16], but importantly, the Fe content has been recalibrated with an updated method that is more accurate for high iron abundances [17].

Unique facies and composition: The AMB bedrock visited by the Curiosity rover is a decimeter to meter-thick erosion-resistant outcrop, comprised of a series of planar or rippled bed that are variably nodular, siliciclastic dominated, but enriched in Fe, as well as Mn and Zn. We classified the bedrock into different lithofacies and identified a specific facies assemblage associated with the ChemCam target “Mapiripana”.

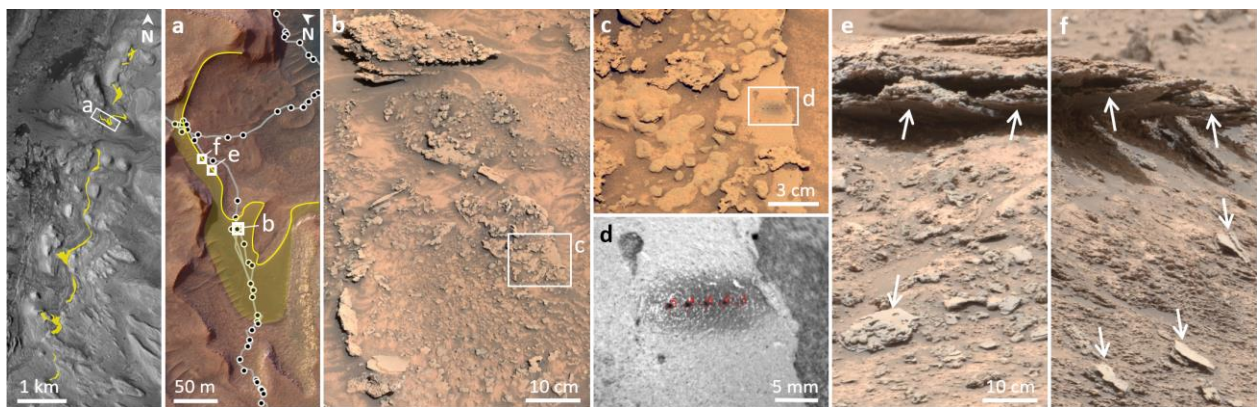


Figure 1: Context of the marker band analyses with (left) regional map and (a) rover traverse onto outcrops. (b) Location of the bedrock and (c) smooth coalescent nodules with underlying laminae and (d) Mapiripana LIBS raster (red reticles). (e-f) Lower contact (upward arrows) and fragments (downward arrows) with similar lithology.

This assemblage is a set of two or three planar millimetric laminae with a very fine-grained to silty texture and superimposed smooth and coalescent centimetric nodules (Fig. 1c-d). We mapped this facies assemblage laterally and found that it is restricted to the base of the AMB, at the contact with the underlying Mg-sulfate-enriched Catrimani member (Fig. 1e-f). Due to the recessive nature of the contact, it is only rarely observed and accessible and the target Mapiripana is the only LIBS analysis available. This target shows a rare chemical composition with the first carbonate signal detected using LIBS at Gale, and an associated FeO_T content in the 50-60 wt.% range (Fig. 2). This unique composition suggests a siderite content ~ 70 wt.%, likely mixed with Fe-oxides. It is clearly distinct from other facies of the AMB, all variably nodular, with iron content ranging from 20-30 wt.% FeO_T (Fig. 2). The carbon signal in these other nodular bedrocks suggests 10-15 wt.% siderite, much lower than Mapiripana, and also likely associated with Fe-oxides. No association of Mn with carbon has been observed, pointing to the presence of Mn-oxides rather than rhodochrosite or Mn-bearing siderite.

Discussion and perspectives: The amount of siderite specifically within the thin laminae, draping the lower contact, with a silty texture and smooth flat nodules, contrasting with surrounding strata, is consistent with lacustrine deposition rather than pedogenesis or a late-stage diagenetic scenario. These facies could have resulted from a lake transgression that occurred in association with the erosive event that shaped the basal AMB contact surface. It may represent a stark change in both depositional environment and hydrochemistry. Unlike other sedimentary context associated with carbonates, this chemical deposit could be modeled without invoking complex reactions pathways and linked directly to the environmental conditions. The co-occurrence of iron oxides and siderite might indicate a redox disequilibrium of the fluid during evaporative concentration [18]. Using large sensitivity tests of kinetic evaporation models, we could estimate the parameter window in which siderite and/or oxides are able to form [4]. We would be able to estimate ranges of lake composition (cations, pH, and initial alkalinity), evaporation rate, temperature and atmosphere composition (pO_2 and pCO_2). Using previous estimations on the sediment flux and evaporation rates of the endorheic Gale lake [19], we could build even more constrained steady-state evaporation scenarios reproducing the observed composition. The amount of siderite, Fe-oxides and sedimentary matrix is of primary importance to model the conditions, further work will refine uncertainties associated with these abundances.

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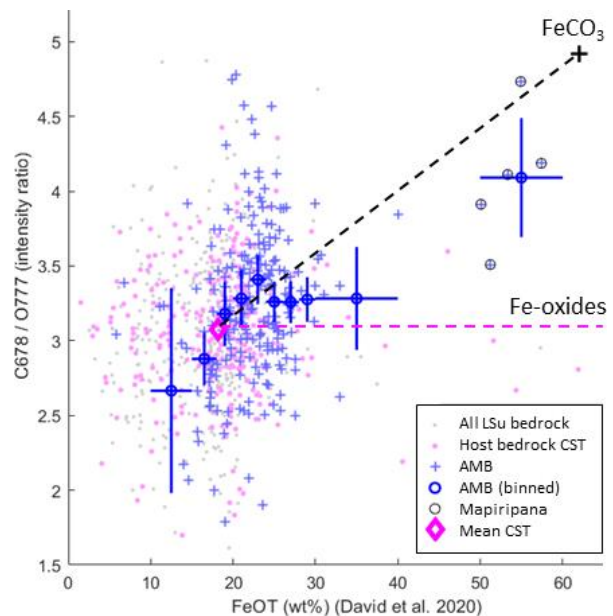


Figure 2: Carbon signal (normalized [15]) as a function of Fe content [17] inferred by ChemCam LIBS analyses at the marker band. Comparison with bedrock in the carbonate-free layered sulfate unit (LSu) and clay-sulfate transition (CST) is used as reference for estimation of siderite abundance in laminae documented by the Mapiripana target (Fig 1d). Data from the AMB bedrock is shown binned with Fe-content with standard deviation on vertical error bars.