NICKEL-COPPER DEPOSITS ON MARS? DISCOVERY OF ORE-GRADE ABUNDANCES, AND IMPLICATIONS ON FORMATION AND ALTERATION.

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Introduction: After its landing in February 2021 in the Jezero crater, the Perseverance rover identified two distinct magmatic formations called Máaz and Séítah on the crater floor [1]. The Máaz formation is thought to consist of different lava flows and/or possibly pyroclastic flows originating from the same parental magma and/or the same magmatic system [2]. They are not petrogenetically linked to the underlying Séítah formation which is the deep ultramafic member of a cumulate series derived from the fractional crystallization and slow cooling of the parent magma at depth [3]. In this paper, we will present observations of high-grade nickel- and copper geological samples obtained by the SuperCam instrument [4, 5, 6] on-board Perseverance that support this hypothesis since high nickel concentration can only derive from processes affecting ultramafic rocks [7]. Therefore, it put constrains on the nature of the original protolith and demonstrate that the presence of ultramafic rocks might be common at the surface of Mars. This is the first time that nickel at the 1+ wt % level is found at the surface of Mars. This is one order of magnitude larger than the Ni content found in martian meteorites with at most 788 ppm in NWA 2737 [8] although Ni-enriched pyrrhotite has been identified in shergottites [9]. Nickel has also been detected by the several Alpha Particule X-ray Spectrometer (APXS) experiments on board the Opportunity and Curiosity rovers. [10] reported values of Ni enrichment of about 4000 ppm in dendritic and subspherical concretions in the Pahrump Hills and Hartmann's Valley members that contain MgO and SO_3 with strong positive correlation. The concretions are interpreted to be Mg-sulphates that precipitated from diagenetic fluids in situ. On the coatings in the Esperance location analysed by Opportunity, [11] reported values of around 900 ppm not associated with sulphur. In Jezero crater, no Ni enrichments have been observed with the PIXL instrument in the olivine-rich abraded patches at the detection limit of about 300 ppm [12]. All the Ni enrichments in Jezero have been observed in Al-rich, light-toned float rocks along the traverse and nowhere else. Those rocks have also undergone an intense episode of leaching followed by heating [13]. We will describe these data up to sol 913 focusing on Ni, its quantification and its relationship with the other major and minor elements to try to constrain the processes that led to its enrichment and to the alteration of these rocks.

Data and methodology: To perform our analyses, we use the data from the SuperCam instrument--mainly the LIBS that gives chemical information and VISIR data that provides mineralogical information. Since the LIBS observations usually consist of 30 shots, shot-to-shot correlation between elements can bring useful insights into the mineral phases. Major-element Oxide Composition (MOC) data are derived from multivariate regression methods [14]. SuperCam passive reflectance spectra cover the 0.39–0.85 μm (VIS) and 1.3–2.6 μm (NIR) ranges, which allow the identification of a wide variety of minerals, especially hydrated species [15]

Results: The LIBS spectra as well as the MOC compositions of the Al-rich rocks exhibit some very peculiar properties. For the major elements the targets are strongly depleted in Fe, Mg, Ca, and Na and strongly enriched in Ti, and Al (on average >25.0 wt. %). No S was detected in the targets. For the minor elements the targets are strongly enriched in Ni and Cr. Ba and Sr are also locally enriched but Mn is depleted in comparison to all the data. The VISIR spectra also exhibit some peculiar features, in particular the detection of spinel in the Dolgoi_Island target (Sol 657) and the detection of kaolinite in target Chignik (Sol 680).

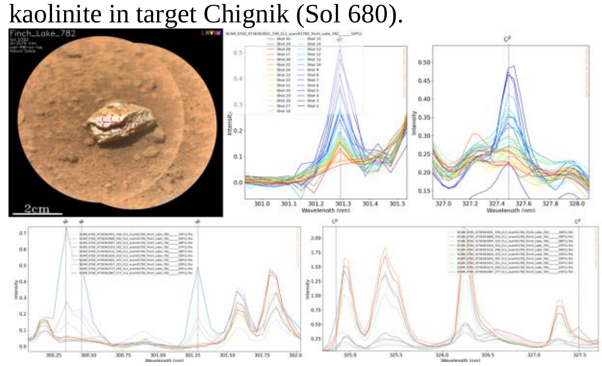

Figure 1: Ni and Cu emission peaks in the Finch_Lake target (image in upper left). These two elements are correlated both within a given observation (a shot-to-shot perspective) and among different observations.

Ni enrichment: Ni is identified through the lines at 302.3 nm and 310.2 nm. Almost all of the Al-rich targets exhibit the signature of Ni which is unusual (Fig. 1). A preliminary quantification of this element was performed thanks to the identification of Fe-Ni meteorites by the ChemCam instrument in Gale crater [16], in which the Ni content varied between 4.0 and 24.0 wt. %. A calibration was possible between the two instruments since the spectrometers in the UV range where the main lines of Ni are present are nearly identical. This preliminary calibration gives Ni content up to 8.0. ± 1.0 wt. % in the Jezero target Finch_Lake (Sol 784), point #1, and half of the points contain more than 0.5 wt.% Ni.

Cu detection: Cu is identified by two lines at 324.8 nm and 327.5 nm. Cu has the strongest detection in Finch_Lake point #10 and is present in other high Ni points. From the shot-to-shot perspective Cu is also strongly correlated with Ni.

Discussion: *A magmatic or impact melt origin:* On Earth, the joint presence of a high proportion of Ni and Cu is diagnostic of the so-called Ni-Cu-PGE (Platinum Group Element) sulphide deposits. They are thought to derive from magma that has experienced high degrees of partial melting. This magma must then be rapidly transported to the crust to reduce the possibility that Ni is removed from the magma by crystallization of olivine also segregation of sulphide from the silicate magma [17, 18]. Ni-Cu sulphide ore deposits are found at the base of mafic and ultramafic bodies. All their host rocks, except the Sudbury Igneous Complex, are thought to be mantle-derived melts. The Sudbury Igneous Complex is the product of complete melting of continental crust in a gigantic impact [19]. In the case of mantle-derived magmas, a high degree of partial melting of the mantle is needed to extract compatible elements (Ni and PGE) from mantle rocks (mainly olivine) into the silicate magma. Ni and Cu are deposited from an immiscible sulphide liquid in rapidly crystallising ultramafic extrusive rocks. Pentlandite ($(Fe,Ni)_9S_8$) is the major Ni sulphide while chalcopyrite ($CuFeS_2$) is the major Cu sulphide. Sulphur saturation can occur as a result of cooling deep-sourced melts enriched in mantle-derived sulphides or by the assimilation of sulphide-rich sedimentary host rocks. Due to the high density of the sulphide phase, deposits are typically located at the base of flows [20]. Those deposits are also generally associated with the Ti- and Cr-spinels [21, 22].

A Nickel alteration formation hypothesis: Although the Al-rich targets contain spinel, they don't show any evidence of sulphides. Given the high chemical index of alteration (CIA), intense alteration and leaching must have taken place to explain the composition and the mineral phases that are identified and the disappearance of the sulphides. However, some hint of the presence of sulphides has been proposed by [23] in Gale Crater and it has been suggested that the large sulphate deposits that are observed in Valles Marineris [e.g., 24] and elsewhere might result from the oxidative weathering of sulphide minerals [25]. Additionally, oxyhalogens may be responsible for the loss of magmatic sulphides in surface materials given the prevalence of oxyhalogen brines and the reactivity of the sulphides [26]. These alteration processes could also be responsible for the formation of phyllosilicates (smectites and kaolinite). In these, the Ni would likely be located in the octahedral layer of the smectites. Ni-bearing smectites are, for example, encountered in clay silicate Ni laterite deposits where the principal ore minerals are Ni-rich saponite and smectite i.e. garnierite [27]. The sulphates produced by the alteration are then removed by the intense leaching, leaving the spinel and Al-rich phyllosilicates, or removed during loss of volatiles with high-T metamorphism.

However, the alteration of pentlandite and chalcopyrite under Martian conditions has not been studied yet and experiments like the ones performed by [26] on pyrite and pyrrhotite could bring some insights into the processes that led to this high concentration of Ni and Cu. Moreover, the analysis of the spinel by (Th-U)/He thermochronometry [28] in returned samples to Earth might directly date the exhumation and cooling history of spinel-bearing mantle peridotite and constrain the sulphide evolution processes during the formation of magmatic Ni-Cu deposits [22].

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