FIRST SUPERGENE ENRICHMENT ZONE DISCOVERED IN SHALBATANA VALLEY: CONSTRAINS ON MARTIAN EARLY ATMOSPHERE.

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Introduction: Few processes/events that preserve the record of the interaction between the first meters of the crust with the hydrosphere and atmosphere. Even fewer events preserve this record for more than 3.5 Ba. The supergene enrichment is the only process known to record these events. The process acts on elements with multiple oxidation states in a controlled complex manner related to eV, pH, and ionic matrix. In this particular case, the variable oxidation state element is copper. In this work, we present the implication of the discovery of a supergene alteration on Mars, covering the time range cited above. A chrysocolla/malachite bearing unit in Shalbatana Valley constitutes the proof for this process. The water permanence at the formation time is the main implication of this finding. Furthermore, the potential of biogenic involvement at the mineralization stage adds scientific importance to the discovery.

Data: We mapped the chrysocolla outcrop using MRO-CRISM standard reduction pipeline CAT Tools v. 7.2 (Figure 1).

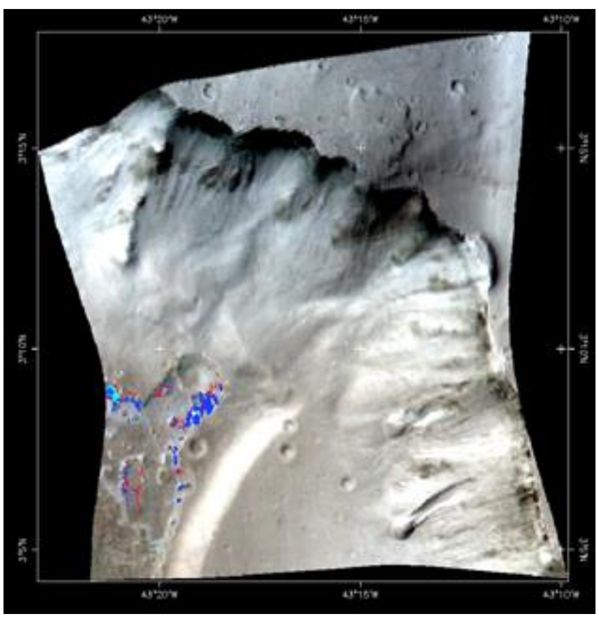

Figure 1. Distribution of hydrated minerals in the Shalbatana Valley. The copper minerals outcrop in the cyan area.

The presence of the 1.4, 1.9, and 2.265 µm bands characterize the supergene alteration (see Figure 2). These spectral bands do not present single phases but a paragenesis closely matched using laboratory measurements.

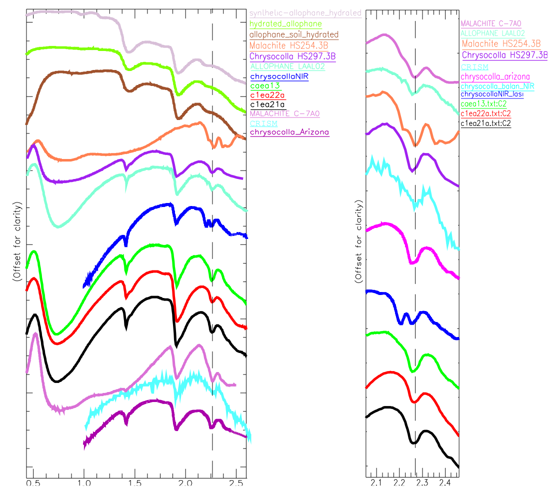

Figure 2 Spectral characteristics of the cyan area compared to spectral library.

Laboratory analysis: Figure 2 shows that the position of the band at 2.265 µm does not match the pure chrysocolla sample we analyzed, while it partly characterized the malachite spectra. This fact suggests that the spectral signature relates to the presence of malachite in paragenesis with chrysocolla.

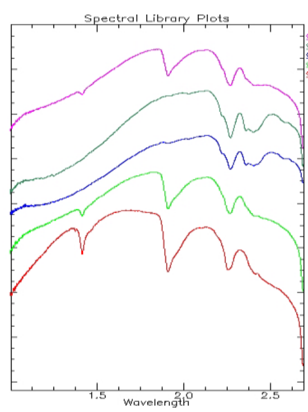

Figure 3. Quantitative analysis of the chrysocolla-malachite mixture. The green spectrum is the best match to CRISM extracted spectrum.

A mixture of 4:1 between chrysocolla and malachite gives the best match for the extracted CRISM spectral response (Figure 3).

Discussion: The finding has large implications on the permanence and behavior of water at the surface as the main carrier of oxygen for the oxidation of copper from the presumably primary sulphides (e.g. chalcopyrite). Unless oxygen was brought into the system from underneath (less likely), t the path for altering the primary sulphide minerals must be similar to the terrestrial one. In order to have oxygenated water there is a need of cyclic water replenishing, obtained on Earth via rain (A, B, C fields in Figure 4).

Extrapolating the time needed to form an entire supergene alteration profile [1], while adjusting for the Martian alteration rate [2] and oxygen composition variation on early Mars [3] may point to an event lasting an overall 140 Ka of water/sediments interaction. This event precedes the formation start of the observed supergene species in the area.

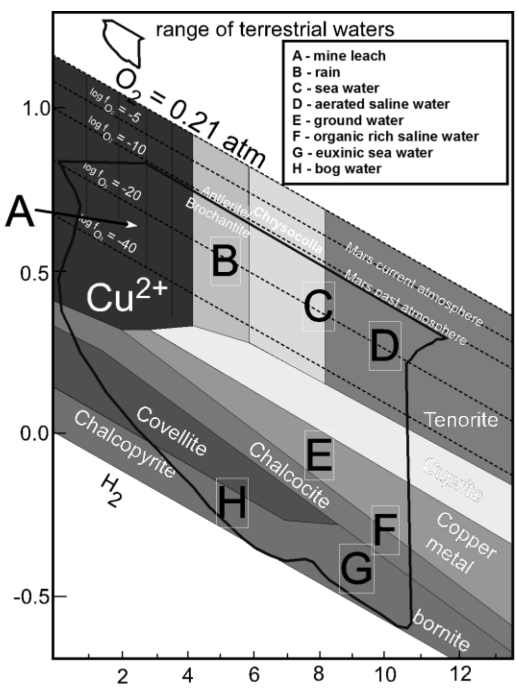

Figure 4. The Pourbaix diagram representing a similar terrestrial system.

Furthermore, the settings where the initial sulfide minerals occurred (within the Shalbatana lake sediments) may point to a similarity to well defined deposit types on Earth. Amongst the candidate processes the stratiform (Fe-Cu-Zn?) sulphide deposits (e.g. Kupferschiefer) [4] or the conglomerate-hosted copper deposits (e.g. Caleta Coloso, Chile) [5] are the best candidates. Further constrains need to be added to correctly classify this type of deposit. The overall settings may make the latter type to be the one closer characterizing the Shalbatana deposit where chrysocolla outcrops. On the other hand the scarceness of constraints on the composition of sediments in the center of the lake cannot rule out completely the stratiform type of the deposit. The possibility of the presence of the Zn silicate (hemimorphite) in the eroded buttes toward the center of the lake may point to a stratiform type of deposit. The analogy cited in support for this type is the Cu-Pb-Zn zoning in the sedimentary deposits [5]. The life involvement in the process of copper sulfide (as a proxy for sulfur reduction) mineralization could be of paramount importance for the Martian scientific program and landing site choice for future missions [6].

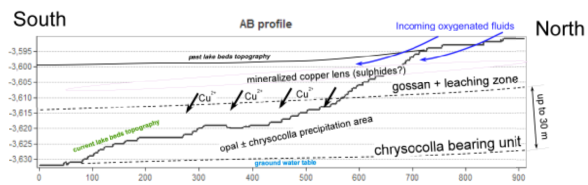

Figure 5. Simplified schematic of the vertical profile crossing the supergene alteration outcrop.

Conslusion: The current work presents the evidences for the first ever supergene deposit on Mars. The deposit oucrops on a slope on the northern shore of the dessicated Shalbatana lake [7], being exposed via erossion. By similarity to Earth supergene process, we calculated the time for the water permanence required to suply oxygen to the system to be in the range of 10^5 years, post-dating the lake residence event. There is a good chance that the mineralization (prior to the alteration process) may have involved biogenic activity, as in many terrestrial analogues. This indirect evidence may be as close as one might get to a possible life related process using remote sensed data.

The downward migration of the copper rich solution eventually led to the precipitation of Cu from the solution as secondary sulfides (e. g. chalcocite, covellite, bornite etc.) just under the water table in the enrichement reduction zone (Figure 5). The enrichment area is exposed at the foothill of the chrysocolla bearing slope, being accesible to a robotic mission for biogenic signature analysis (e.g. S isotope measurements).

References: [1] Ague, J. J. (1989) *Ec. Geol.*, *84*, 506-528. [2] Tosca, N. J. et al. (2008) *JGR*, *113*, A74. [3] Catling, D. C. (1999) JGR, v. 104, 16453–16469. [4] Evans A. M., Ore geol. Ind. Min. (1993), p. 34. [5] Barnes H. L. (1975) Tans. Royal Soc. of Edinb., v. 69, 295-311. [6] Grant, J. A. (2010), Pl. & Sp. Science, v. 59, 1114-1127. [7] DiAchille, G. et al. (2009), GRL, v. 36, L14201.