

EVAPORATION PATHWAYS AND SOLUBILITY OF FE-CA-MG-RICH SALTS IN ACID SULFATE WATERS. A MODEL FOR MARTIAN ANCIENT SURFACE WATERS

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Introduction: It has been suggested that Martian sulfate deposits enriched in iron and mixed iron oxyhydroxide were precipitated from meltwaters [1], thought to have been acidic. Alternatively, iron(III)-rich hydrated sulfates from oxidized sulfides observed in the outcrops may occur as a result of long-term reactions. More recent characterizations of Martian materials support the idea that they are the product of hydrothermal activity, which is highly consistent with the observation of enriched in iron, magnesium, silicon and calcium materials [2]. Independently of the nature of the sulfate formation mechanisms on Mars, characterizing the interaction of saline mineral assemblages and the aqueous solutions necessary for their formation is of key importance in assessing Mars' hydrological and mineralogical evolution history.

In this work we have characterized a layered deposit (Fig. 1) formed from the evaporation of stream water from Pena del Hierro, in Rio Tinto, Spain, a relevant Mars analog site. The minerals detected in-situ, confirmed later via high resolution laser Raman spectroscopy in the laboratory, are, from bottom to top: (A) mixture of goethite and an unidentified iron-oxyhydroxysulfate, probably schwermannite ($\text{Fe}^{3+}_{16}\text{O}_{16}(\text{OH})_{12}(\text{SO}_4)_2$); (B) goethite ($\text{Fe}^{3+}\text{O}(\text{OH})$); (C) mixture of gypsum ($\text{Ca}(\text{SO}_4) \cdot 2(\text{H}_2\text{O})$) and highly hydrated ferric sulfates; (D) hexahydrate ($\text{Mg}(\text{SO}_4) \cdot 6(\text{H}_2\text{O})$); and (E) mixture of hexahydrate and epsomite ($\text{Mg}(\text{SO}_4) \cdot 7(\text{H}_2\text{O})$).

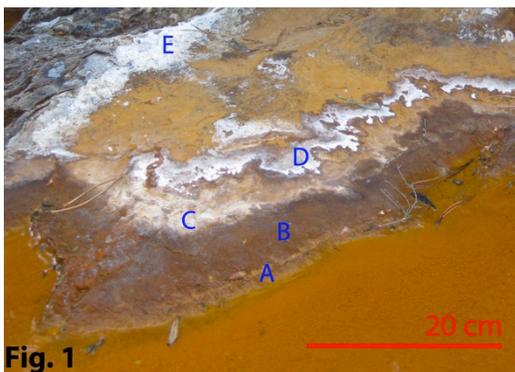
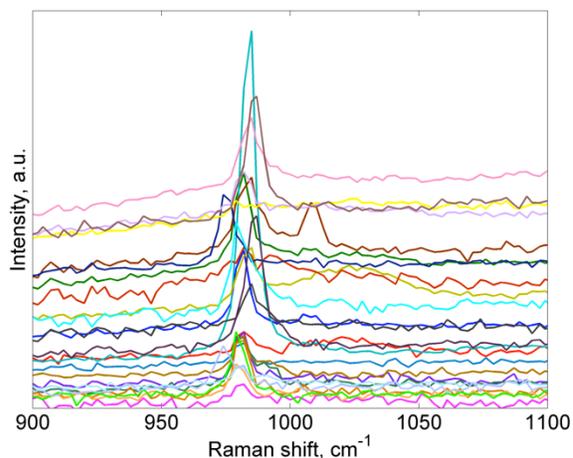


Fig. 1

What we observed in this deposit is the precipitation of relatively insoluble hydroxysulfates (schwermannite admixed with goethite), followed by the precipitation of other relatively insoluble ferric and

Ca-sulfates (gypsum), and finally the occurrence of the very soluble Mg-sulfates hexahydrate and epsomite. Raman spectra in recorded in the mesh shown in Fig. 2. The peak at $\sim 980 \text{ cm}^{-1}$ belongs to the asymmetrical stretching vibration of SO_4^{2-}



We are currently investigating the correlation of the mineralogy of this evaporite deposit with the hydrochemistry of the stream water from which it evaporated through dedicated laboratory analysis of natural mineral and aqueous natural and synthetic samples. A solubility model including the minerals identified in this work will be reported at the conference.

The study of this particular acid sulfate system (which includes analog mineralogy to that observed in Meridiani [3]) provides constraints on the evaporation pathways that may lead to a better understanding of the composition of ancient surface waters on Mars from which certain complex mineral assemblages are thought to have been formed.

References:

- [1]Knoll A. H., et al. (2004). *EPSL*, 240, 179–189.
- [2]McCubbin F. M., et al. (2009). *Geochim. et Cosmochim. Acta*, 73, 4907–4917.
- [3]Squyres S., et al. (2004). *Science*, 306, 1709–1714.