Comparative study of synthetic and natural iron sulfates and oxides by Raman spectroscopy

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The study of iron minerals, in particular, sulfates and oxides of evaporitic characteristics, has carried a great interest in the last years, not only for their direct application in the analysis of mine drainage, also in their application to the study of the mineralogy of Mars surface. The jarosite discovery[1], as well as of other hydrated sulfates[2] in the surface of the red planet carried out by MERs represent an important focus of interest for the study of the evolution and the geodynamics of the planet and their possible astrobiological implications.

The use of quick and precise techniques, susceptible of being boarded in missions to other planets, is revealed as an important aspect when carrying out so much analysis of synthetic materials as collected materials from different geologic analogs. In particular, Raman spectroscopy as part of the payload of the mission Exomars[3] and that it will be launched in the 2018 to Mars, shows up like a very powerful technique when analyzing in-situ and in a non destructive way the molecular composition of the analyzed materials, besides giving us a quite precise idea of structural aspects that could be extrapolated in reference to their possible genesis.

In this work we present the results of the application of this technique to materials synthesized in laboratory also to materials extracted in diverse campaigns to different Martian analogs as are Rio Tinto River and El Jaroso Ravine, both in Spain[4]. On one hand, the use of materials of synthetic origin provides us so much patterns for reference use and also an approach to the necessary conditions for the formation of one or another compound, in a controlled way. On the other hand, the materials picked up in the natural localizations give us a real panoramic of how they are distributed and this materials become in the geochemical conditions that surround them. This allows us to compare them among and with the synthetic ones being been able to extract conclusions about the conditions of their origin, their structural characteristics and being able to formulate hypothesis on their formation process and could be extrapolated by methods of the analysis in situ in Mars, of the materials that there are.

[1] Klingelhöfer et al. (2004), Science, 306, 1740-1745 [2] Johnson et al. (2007) JGR, V34, L13202 [3] Rull et al (2006) Spect.Now. v18, 18-21 [4] Rull et al. (2008) LPSC XXXIX, #1616.

Multiple sulphur isotope evidence for an oceanic sulphate concentration decrease in the Marinoan glaciation aftermath

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In order to better contrain the sulphur cycle in the aftermath of the Marinoan Glaciation, we performed sulphur isotope composition analysis ($\delta^{33}S$ - $\delta^{34}S$ - $\delta^{36}S$) of Ediacarian carbonates, on both Carbonate Associated Sulphate (CAS) and pyrite. Samples come from Carmelo quarry (Mato Grosso, Brazil) where 20m of white dolomicrite (Mirassol d'Oeste Formation) directly cover the glacial sediments related to the Marinoan glaciation (~635Ma). This dolomicrite is overlying by 150m of Guia Formation limestone's which begin with 40 meters of carbonate-rich siliciclastic material evolving to pure carbonate intercalated with thin layers of marls.

Results show an increase in both $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ upward along the section. $\delta^{34}S_{pyr}$ and $\delta^{34}S_{CAS}$ vary from -10‰ to +26‰ and from +16 to +51‰ respectively. Our $\delta^{34}S_{CAS}$ data are relatively high compared to present day oceanic sulphate value (+21‰), but they are in agreement with previous data reported for the same time period. $\Delta^{33}S$ data show values close to 0‰ (0.03 ± 0.02‰) at the base of the section and significatively higher values in the upper part, up to +0.16 ± 0.02‰.

For steady-state ocean sulphur concentration, an increase in the isotopic values can be partially explained by an increase in pyrite burial rate together with a higher $\delta^{34}S_{sulphate}$ input. However this model cannot account neither for the extremely high values of $\delta^{34}S_{CAS}$ nor for the $\Delta^{33}S$ signal. We thus developped a non steady state model in which we take into account the effect of Rayleigh distillation on $\delta^{34}S_{CAS}$, $\delta^{34}S_{pyr}$ and $\Delta^{33}S$ values. Results show that the increase in both $\delta^{34}S$ (CAS and pyrite) and $\Delta^{33}S$ are well explained by a decrease of ~50% in the oceanic sulphate concentration. We thus propose that the post-Marinoan ocean experienced a decrease in sulphate concentration which could result from an increase in sulphate consumption by BSR relative to the net riverine sulphate delivery input.