

ALTERATION OF SULFATE MINERALS FROM RIO TINTO, SPAIN.

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Introduction: The sulfate mineral jarosite was detected at Meridiani Planum, Mars, based on spectra obtained with the miniaturized Mössbauer spectrometer (MIMOS II) on the Mars Exploration Rover Opportunity [1, 2]. Analog studies were performed with a laboratory MIMOS II version on sulfate-bearing evaporite samples from the Rio Tinto region in southwestern Spain. A first series of measurements was completed in summer 2008, immediately following the field trip. Instrument settings, in particular the resolution related to the drive velocity, were chosen as similar as possible to the settings used for Opportunity's instrument [3].

All samples were then stored at ambient temperature in closed vessels, i.e. in an atmosphere defined by the vapour pressure of the compounds. A second series of measurements was conducted in January 2011, with instrument settings providing a higher resolution (i.e. reduced drive velocity). This more recent data set allows for a more detailed distinction between different ferric sulfates [cf. 4] and provides an opportunity to monitor transformations of Rio Tinto sulfate minerals, with respect to the given conditions and time frame.

Rio Tinto: The water of Rio Tinto exhibits a deep red color and a nearly constant acidic pH value of ~2.3 along its approximately 100 km long course. Sulfate minerals mainly form from aqueous alteration of the iron-rich sulfide minerals of the Iberian Pyrite Belt and precipitate from the river during dry, hot seasons [5].

Sulfate minerals generally precipitate close to the stream margin. Precipitates with popcorn-like texture a few centimeters in diameter are very common, usually colored white or yellow, sometimes mixed with small amounts of red or grey (Figure 1a). Crusts ~5 mm thick and several centimeters in diameter occur with a variety of colors including white and different shades of yellow, green and blue (Figure 1b).

Identification of sulfate minerals: The combination of Mössbauer spectroscopy and XRD was used to identify sulfate minerals.

Popcorn-texture evaporites were found to contain ferric sulfates, including

- ferricopiapite ($\text{Fe}^{3+}_5\text{O}(\text{SO}_4)_6\text{OH}\cdot 20\text{H}_2\text{O}$),
- coquimbite ($\text{Fe}_2(\text{SO}_4)_3\cdot 9\text{H}_2\text{O}$), and
- rhomboclase ($(\text{H}_5\text{O}_2)^+\text{Fe}^{3+}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$).

Crusts were found to contain ferrous sulfates, mainly

- melanterite ($\text{Fe}^{2+}\text{SO}_4\cdot 7\text{H}_2\text{O}$),
- rozenite ($\text{Fe}^{2+}\text{SO}_4\cdot 4\text{H}_2\text{O}$), and minor
- szomolnokite ($\text{Fe}^{2+}\text{SO}_4\cdot \text{H}_2\text{O}$).



Figure 1: typical occurrences of (a) popcorn-texture evaporite and (b) crust at rio Tinto, close to the stream margin.

Alteration of Rio Tinto sulfate minerals: The comparison of Mössbauer spectra recorded in 2008 and 2011 on the same samples provides information on the alteration of sulfate minerals with respect to the given laboratory conditions. Three different alteration categories can be distinguished; example spectra are shown in Figure 2.

- 1) Ferric sulfates, either jarosite or ferricopiapite, have formed in samples that were originally found to be practically pure ferrous sulfates (melanterite or rozenite, Figure 2a).
- 2) Some spectra suggest that coquimbite has formed from rhomboclase (Figure 2b). This process would require both hydration and neutralization.
- 3) In many cases, spectra obtained on samples originally identified as ferricopiapite or coquimbite or mixtures thereof remain practically identical over the given time frame (Figure 2c) and therefore point to the relative stability of these minerals.

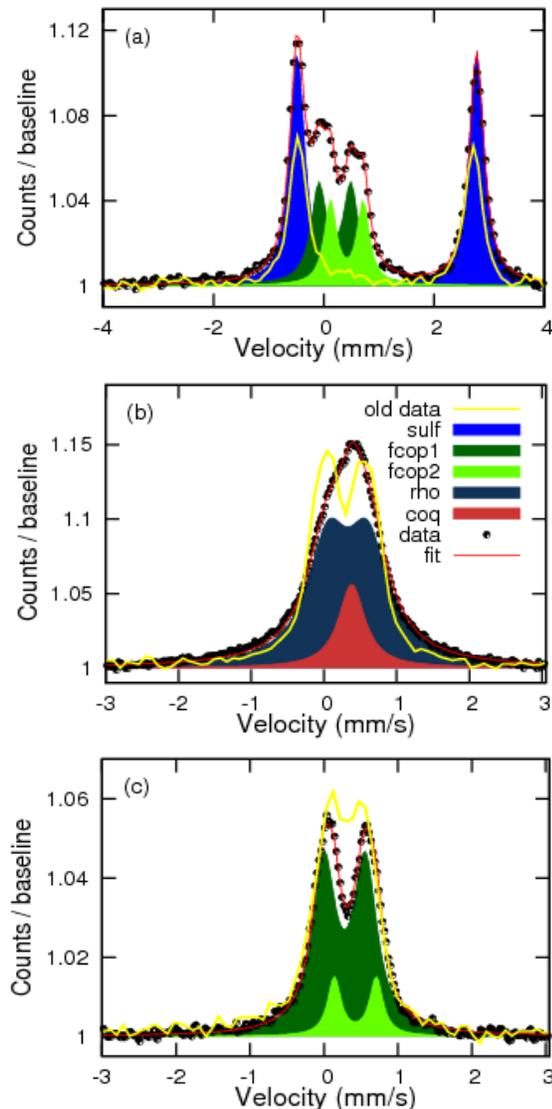


Figure 2: Example spectra of Rio Tinto sulfates. Data obtained in 2008 (yellow lines) is shown in direct comparison with data and fits from 2011. The alteration pathways shown here include: a) the formation of ferricopiapite (fcop) from ferrous sulfate (sulf), b) the formation of coquimbite (coq) from rhomboclase (rho), c) the relatively high stability of ferricopiapite.

Interpretation: Alteration processes suggested for sulfate minerals include oxidation, neutralization and hydration, alteration pathways depend on environmental conditions [6-8].

We have observed transformations of sulfate minerals from Rio Tinto, Spain, over a period of 31 months. Under the given laboratory conditions, these transformations are different from alteration pathways described for either natural environments or the martian surface [6-8]. For the samples considered here, the small-scale environment defined by humidity levels in the containers appears to be the most important factor and it would be interesting to complement our observations by a third series of measurements in ~2 years.

For further comparison, we also investigated sulfate minerals that had been stored in a collection for significantly longer times (i.e., ~50 – 100 years). We found significant discrepancies between the original sample descriptions (sample labels) and their actual mineralogical composition [4]. These differences can be explained by alterations similar to those observed for the Rio Tinto sulfates.

References: [1] G. Klingelhöfer et al. (2003), *J. Geophys. Res.* 108, E12, 8067. [2] G. Klingelhöfer et al. (2004), *Science*, 306, 1740-1745. [3] I. Fleischer et al. (2010), *J. Phys.: Conf. Ser.* 217 012062. [4] M. Schäfer (2010), diploma thesis, Univ. Mainz. [5] Fernandez-Remolar, C., et al.: *Earth Planet Sci. Lett.* **240**, 149–167 (2005) [6] J. K. Jerz and J. D. Rimstidt (2003), *Am. Mineralogist* 88, 1919-1932. [7] P. L. King and H. Y. McSween Jr. (2005), *J. Geophys. Res.* 110, E12S10. [8] M. D. Lane et al. (2008), *Am. Mineralogist* 93, 728-739.