

## Microbial induced mineralization in Co-rich ferromanganese crusts from the Scotia Sea

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Co-rich ferromanganese crusts were collected at 2000-2500 m water depth in oceanic ridges and seamounts from the Scotia Sea during the SCAN-2004 and SCAN-2008 oceanographic cruises. Fe-Mn crusts form botryoidally pavements up to 50 mm thick on tholeiitic oceanic basalts.

According to data of X-ray diffraction and petrographic observations the crusts are essentially composed by poorly crystalline feruginous-vernadite ( $\delta$ -MnO<sub>2</sub>), and goethite and detrital quartz and phyllosilicates as accessory minerals. The Mn/Fe ratio in bulk samples is 1.1, indicating precipitation from cold ambient of seawater onto hard rock substrates. All the studied Fe-Mn crusts concentrate strategic elements (Co, Ni, Tl, REE or PGE) several orders of magnitude above the mean concentration in the Earth's crust.

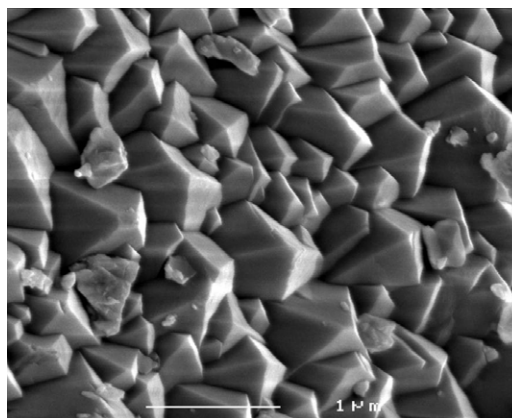
Fe-Mn crusts occur as fine laminated manganese oxides structures. SEM imagings reveal abundant like-microbe tubular sheaths (less than 1 $\mu$ m in diameter and 10-200 $\mu$ m long). These textural features can be due to the Mn-biomineralization action of chemolithoautotrophic microorganisms (*Leptothrix* spp.?, *Metallogenium*?). We interpret these filaments as fossilised bacteria (mineralised biofilms) according to their morphology, size ranges and textural features of colonial associations, similar to modern bacteria. They could be easily formed by action of Mn-oxidizing bacteria forming sheaths stained by vernadite, precipitated within extracellular structures. EDX-SEM and Electron Microprobe analyses show the chemical composition of fossilised bacterial biofilms with enrichments in strategic elements with respect to the bulk sample: 22.6% Mn, 22.4% Fe, 1.6% Ti or 1.5% Co and also 7.6% C and 6.8% F. Biomarkers like n-alkanes (n-C<sub>18</sub>) and nitrogen compounds, detected by GC-MS analysis, could be related to the bacterial mineralization. These findings suggest a link between the microbial and the mineralization. The microbes could have played a critical role in the accumulation of metals through sorptive, catalytic and oxidative processes forming Fe-Mn crust deposits with economic potential. It also remarks the high scavenging efficiency of vernadite for remediation or recovery of trace metal contamination.

## Arsenic biomineral formation leads to partial encrustation of thermoacidophilic archaea

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Acidophilic iron oxidizing *Sulfolobales* spp. mediate the formation of jarosite nanoprecipitates and bioscorodite precursors [1]. In batch experiments, scorodite biomineral formation by *Sulfolobales* spp. was induced at a pH of 1 and 75°C [2]. At these conditions, we observed formation of precursors (nuclei) of scorodite on the cell surface. This suggests that the mechanism of scorodite formation begins with the sorption of ferric iron and arsenate onto the cell surface, followed by the formation of ferric arsenate nuclei from the adsorbed metal species. By growth of the nuclei and ageing of the precipitates, scorodite crystals were formed on the cell surface, which led to a partial encrustation of the cells. In the absence of arsenic, jarosite precipitates were found on the cell surface, but this did not result in encrustation.



**Figure 1.** SEM photograph of the biomineralized scorodite by *Sulfolobales*. Photograph with 30000 magnification and SE detection at 3.5 KV.

[1] Gonzalez *et al.* (2010) *Environ. Science & Tech.* [2] Gonzalez *et al.* (submitted). *Geochimica Cosmo. Acta.*