

## **A mineralogical archive of the biogeochemical sulfur cycle preserved in the subsurface of the Río Tinto system**

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### **ABSTRACT**

The search for extinct and extant life on Mars is based on the study of biosignatures that could be preserved under Mars-like, extreme conditions that are replicated in different terrestrial analog environments. The mineral record in the subsurface of the Río Tinto system is one example of a Mars analog site that has been exposed to weathering conditions, including the biogeochemical activity of Fe and S chemolithotrophic bacteria, for millions of years. The SEM-EDAX analysis of different samples recovered in the Peña de Hierro area from four boreholes, ranging from 166 to 610 m in depth, has provided the identification of microbial structures that have affected a suite of hydrothermal minerals (~345 Ma) as well as minerals likely produced by biological activity in more recent times (<7 Ma). The hydrothermal minerals correspond to reduced sulfur or sulfate-bearing compounds (e.g., pyrite and barite) that are covered by bacilli- or filamentous-like microbial structures and/or secondary ferrous carbonates (e.g., siderite) with laminar to spherical structures. The secondary iron carbonates can be in direct contact or above an empty interphase with the primary hydrothermal minerals following a wavy to bent contact. Such an empty interphase is usually filled with nanoscale, straight filamentous structures that have a carbonaceous composition. The occurrence of a sulfur and iron chemolithotrophic community in the Río Tinto basement strongly suggests that the association between sulfur-bearing minerals, dissolution scars and secondary minerals of biological origin is a complex process involving the microbial attack on mineral surfaces by sulfur reducing bacteria followed by the precipitation of iron-rich carbonates. In this scenario, iron sulfide compounds such as pyrite would act as electron donors under microbial oxidation, while sulfate minerals such as barite would act as electron acceptors through sulfate reduction. Furthermore, the formation of siderite would have resulted from carbonate biomineralization of iron chemoheterotrophic organisms or other microorganisms that concentrate carbonate through metabolic pathways. Although the distribution of the mineral biosignatures at depth clearly follows a redox gradient, they show some irregular allocation underground, suggesting that the geochemical conditions governing the microbial activity are affected by local changes associated with the fracturing pattern of the Río Tinto basement. The abundance of sulfur- and iron-bearing minerals in the Mars crust suggests that the Río Tinto mineral biosignatures can be useful in the search for extant and extinct subsurface life on the red planet.

**Keywords:** Río Tinto, biomineralization, subsurface, Mars