

**MARS SULFATE FORMATION SOURCED IN SULFIDE -ENRICHED SUBSURFACE FLUIDS: THE RÍO TINTO MODEL.** D. C. Fernández-Remolar<sup>1</sup>, O. Prieto-Ballesteros<sup>1</sup>, M. R. Osburn<sup>2</sup>, D Gómez-Ortíz<sup>3</sup>, R. E. Arvidson<sup>2</sup>, R. V. Morris<sup>4</sup>, D. Ming<sup>4</sup>, R. Amils<sup>1</sup>, L. R. Friedlander<sup>2</sup>, <sup>1</sup>Centro de Astrobiología, Torrejón de Ardoz, Spain (fernandezrd@inta.es), <sup>2</sup>Dept. of Earth and Planetary Sciences, Washington University, St. Louis, MO, 63130, <sup>3</sup>Área de Geología, Universidad Rey Juan Carlos, 28933 Móstoles, Madrid, Spain, <sup>4</sup>NASA Johnson Space Center, Houston, TX, 77058.

**Introduction:** The extensive evidence for sulfate deposits on Mars provided by analyses of MER and Mars Express data [1-6] shows that the sulfur played an essential role in the geochemical cycles of the planet, including reservoirs in the atmosphere, hydrosphere and geosphere. Overall the data are consistent with a fluvial/lacustrine-evaporative origin of at least some of the sulfate deposits, with mineral precipitation through oversaturation of salty acidic fluids enriched in sulfates. This scenario requires reservoirs of sulfur and associated cations, as well as an acidic and oxidizing hydrochemistry which could be provided by surface and subsurface catching of meteoric waters resulting in the presence of sulfur-bearing gases and steam photochemistry [7].

In this work we suggest a new scenario for the extensive generation of sulfates in Mars based on the observation of seasonal changes in the redox and pH of subsurface waters enriched in sulfur that supply the acidic Mars process analog of Rio Tinto [10]. This model considers the long-term subsurface storage of sulfur during most of Noachian [11] and its release from the late Noachian to Hesperian time through weathering by meteoric fluids that would acidify and oxidize the sulfur bearing compounds stored in the subsurface.

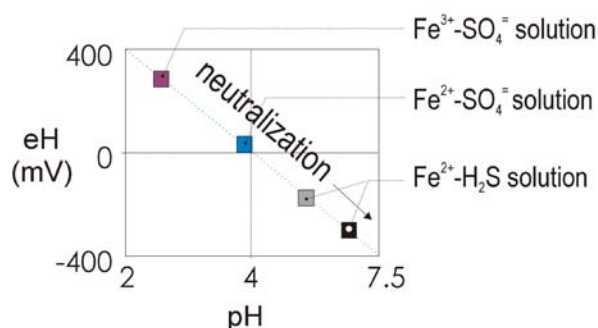
#### Sulfur cycling in the Rio Tinto Mars analog:

Sulfur cycling in Río Tinto is coupled to the microbial weathering of the sulfides enclosed in the volcanosedimentary complex of the Iberian Pyritic Belt [see 12]. The Rio Tinto waters are supplied by several acidic springs associated with major and minor fractures which transport sulfur and iron to the surface environment in form of sulfate and ferric and ferrous ionic complexes [13]. Underground fluids are seasonally replenished by rainfall that provides oxygenic and neutral waters to the sulfide aquifers through fractures [10]. Under aerobic conditions provided by the meteoric waters, the sulfide orebodies are weathered through biotic and abiotic processes releasing different sulfate and ferric/ferrous complexes to the subsurface waters, which reduce to ferrous sulfides in deeper areas of the aquifer where the exhaustion of the oxidizing compounds is produced [10].

In the last year, two water sampling campaigns in late summer and fall were focused on recovering un-

derground fluids to understand the dynamics of the sulfur cycling in the system. Water samples were obtained from three wells: 4 and 8 going through the Peña de Hierro sulfide aquifer, and borehole 1 affecting the younger gray shales [12] that store subsurface waters sourced in the Peña de Hierro aquifer. Wells were generated during the drilling operations of the MARTE Project devoted in searching subsurface life in the Rio Tinto Mars analog [10].

The late summer campaign recovered water with low redox, neutral pH and enriched in sulfides and ferrous complexes (Fig. 1). Samples obtained during fall provided fluids with lower pH, higher eH and enriched in sulfates with varying concentrations in ferric and ferrous ions (Fig. 1). As an interpretation, the subsurface waters in the Rio Tinto system show seasonal variations in chemistry and composition from neutral anoxygenic and sulfidic solutions to acidic solutions enriched in sulfate due to the supply of seasonal meteoric waters that oxidize sulfides to sulfates. The pH decrease in fall is produced by the oxidation of sulfides by the oxygen and ferric, and mediated by microbes, which releases protons to the subsurface fluids [10].



**Figure 1.** Scatterplot showing pH and eH changes from summer underground fluids (black to blue squares) to fall underground fluids (blue to red).

**Sulfate generation in Late Noachian:** Rio Tinto sulfur cycling may provide some answers to the massive generation of sulfates during the late Noachian to Hesperian proposed by Bibring et al. [11] as a consequence of a dramatic Mars climatic change. Based on

the extensive deposits (showed by orbiters) and active subsurface fluid reservoirs (estimated by MER) we offer a new perspective on the sulfur cycling on Mars without the need for a high sulfur flux to atmosphere from volcanic sources. In this proposal the Mars sedimentary deposits would result from the oxidation and/or sulfate remobilization of a long-term subsurface storage of sulfur-bearing compounds (as sulfide minerals or dissolved molecules) dating from the early Noachian times. As mineral and geomorphic evidences suggest warm and wet conditions during the early Noachian [11, 14], an active hydrosphere might have transported to subsurface regions great quantities of sulfur. Moreover, volcanic and hydrothermal activity may have introduced sulfides into the crust that might eventually release sulfur dissolved compounds under alteration.

Oxidizing and acidifying compounds would date from the Late Noachian climatic event, powered by a new episode of global volcanic activity that introduced volatiles to power greenhouse warming that caused groundwater recharge and flow [15, 16]. Therefore, through the photochemistry of different volatiles including steam, carbon dioxide, sulfur-bearing gases and methane, would provide oxidants and acidifying molecular species to weather the buried materials produced during the warm and wet early Noachian episode. As a result, the massive production of sulfates might have been the global oxidation of sulfides precipitated underground in continuous (regolith) or discontinuous (basement fractures) porous media when these older materials were exposed to a late Noachian–early Hesperian event [11] of oxidant production in the Mars atmosphere.

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