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Use of the $^{34}\text{S}/^{32}\text{S}$ isotopic ratio for the study of the bioorigin of the sulfur phases located in the corrosion product layer of iron or low alloy-steel samples corroded in anoxic conditions

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The presence of Sulfate-Reducing Bacteria (SRB) may influence the corrosion rate of ferrous objects by inducing iron sulfides precipitation [1]. The same phases are formed by biotic or abiotic ways. An analytic method for detecting bacterial interventions in corrosion processes is required. Yet, biotic iron sulfides are supposed to be depleted in heavy isotopes of sulfur relative to the starting sulfate [2].

The aim of this study is to set-up a methodology based on $^{34}\text{S}/^{32}\text{S}$ isotopic ratio determination to evidence the origin of sulfides in the corrosion product layers of “long term systems”: ferrous archaeological samples studied as analogues of long-term corrosion of nuclear waste package and steel samples issued from anoxic corrosion experiments in contact with claystone. In parallel “model systems”, iron coupons corroded in anaerobiosis with or without SRB, are studied to compare the sulfur isotopic fractionation resulting from a bacterial or an inorganic sulfide source.

Complementary techniques were used to characterize the sulfur-bearing compounds in the samples: FESEM-EDS for their distribution, μ -Raman and nano-Auger spectroscopy for the nature of phases. Then, the $^{34}\text{S}/^{32}\text{S}$ isotopic ratio was determined by NanoSIMS and compared to the one of the sulfates from the surrounding solution. As a result, $d^{34}\text{S}_{\text{sulfate-sulfide}}$ reaches values of ~ 10 ‰ to ~ 60 ‰.

[1] H.A. Videla *and al.*, Int. Biodeterior. Biodegrad. 63 (2009) 896–900.

[2] M.S. Sim *and al.*, Science. 333 (2011) 74–77.