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Application of ToF-SIMS for sulfur isotopic fractionation in sulfide phases of iron corrosion layers: determination of bacterial impact on the formation of these phases

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To a better understanding of the iron corrosion mechanisms, it is crucial to elucidate the role of bacteria. Thus, in order to have a diagnosis of the action of bacteria in the iron corrosion, the objective of this study is to determine by ToF-SIMS the isotopic sulfur fractionation $\delta^{34}S$ in iron sulfides of (sub)micrometric size located in the corrosion product layers of the ferrous objects corroded in anoxic soils and marine environment. These iron sulfides may have two origins: an abiotic origin resulting in the dissolution/reprecipitation of sulfides from the surrounding medium (for example from pyrite in a soil) or a biotic origin by the action of the sulfate-reducing bacteria that reduce sulfate ions into sulfides leading to the formation of iron sulfides with ferrous ions issued from the aqueous dissolution of metal iron.
A difference in the isotopic sulfur fractionation $\delta^{34}S$ in the sulfur phases according to the abiotic or biotic origin of these phases is reported in the literature. Thus in this study, the isotopic sulfur fractionation $\delta^{34}S$ in the iron sulfides formed in the corrosion product layers of iron was determined to identify the formation origin of these phases and the role of bacteria in the iron corrosion.

After characterization of the distribution of the different iron sulfides within the layers (optical microscopy, SEM-EDS, μRaman spectroscopy), the local isotopic fractionation of sulfur is measured by the imaging and spectroscopy ToF-SIMS technique. Some important results have been obtained. First of all, the reproducibility and the accuracy of the method were established by the choice and the validation of a hydrothermal pyrite sample calibrated relatively to the international sulfur isotopic standard Canon Diablo Troilite. Secondly, it was observed that there was no or little variation in the isotopic sulfur fractionation $\delta^{34}S$ with the degree of oxidation of sulfur. Finally, a noticeable difference in the isotopic sulfur fractionation $\delta^{34}S$ between iron sulfides formed in laboratory under abiotic or biotic conditions was evidenced: $\delta^{34}S$ is close to 0 in abiotic conditions whereas in biotic conditions it is shifted from 0 with values up to up to some tens per mil.

These first results being promising, the study is actually in progress to determine the formation origin (abiotic/biotic) of the Fe-S present in the corrosion product layers of natural systems of iron corrosion, from soils, subaquatic and marine environments.