Biogeochemical sulfur cycling in the reactive iron-rich marine sediments

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Hydrogen sulfide, which is produced in sediments by microbial reduction of sulfate, is prone to chemical and microbial oxidation. If microbial sulfate reduction takes place in sediments, which are rich in electron acceptors such as reactive iron(III) (hydr)oxides and manganese(IV) oxides, hydrogen sulfide may undergo nearly quantitative reoxidation to sulfate. Such "cryptic" sulfur cycling results in fast sulfur turnover combined with degradation of organic carbon by suite of metabolic and chemical processes, which leave no or very limited geochemical evidence, and thus may be easily overlooked or misinterpreted. Recent research indicated that cryptic sulfur cycle is a common feature for the reactive iron-rich surface marine sediments. Such sediments are present in the areas affected by aeolian dry deposition [1], glacial [2] and riverine [3] sediment inputs.

Fast transport of the particles bearing high content of highlyreactive to sediments may result in only minor alteration of their composition in the water column. This process results in flux of iron with high ratios of highly reactive to total iron directly to the surface sediments followed by further preservation during the early diagenesis. Such sequence of processes results in iron speciation, which may be interpreted as false positive palaeoproxy for anoxic and ferruginous water column, while in fact it is rich in oxygen [4].

Quantitative assessment of processes involved in the cryptic sulfur cycle in the reactive iron-rich sediments requires integrated application of various analytical techniques including measurement of sulfate reduction rates, sulfur and oxygen isotope composition of sulfur species, and of sub-micromolar concentrations of hydrogen sulfide in the porewaters. These analytical techniques should be combined with incubations of amended sediments under controlled conditions.

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[2] Wehrmann, L.M., et al. (2017) Chem. Geol. 466:678-695.

[3] Zhu, M.-X., et al. (2016) J. Geophys. Res. Biogeosci. 121, 2811-2828.

[4] Boyko, V., Blonder, B., Kamyshny Jr., A. (2019) Mar. Chem. 216:103691.