

Rapid sulfur quantitative and isotopic analysis of sedimentary rocks by Rock Eval 7 coupled with MC-ICPMS and development of new geochemical proxies

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The sulfur cycle is directly linked to the global carbon and iron cycles, and it plays an important role in the preservation of organic matter (OM) over geological time scales. Both pyrite and organic sulfur are formed during early diagenesis and carry the sulfur isotopic signature of various paleo-environmental depositional conditions. Sulfurization processes affect also the type and distribution of S-bonds in sedimentary OM and profoundly affect fossil fuels generation, production and burning processes. However, the quantification and S isotopic analysis of kerogen and pyrite require several tedious and time-consuming analytical steps. Here, we present a new tool and proxies for the rapid (~1 hour) quantification and sulfur isotopes distribution of pyrite and kerogen in sedimentary rocks. The method is based on the new Rock-Eval 7S analyzer (RE-7S, Vinci Technologies) connected to a MC-ICPMS. A progressive temperature increases of the RE-7S pyrolysis enables separation between signals of the organic- and inorganic-S fractions in the rock. Sulfur is then quantified by a UV detector of the RE-7S and the ³⁴S/³²S ratio measured by the MC-ICPMS. Precision and accuracy are better than 10% (quantification) and 1‰ (δ³⁴S) for most rock samples.

Analysis of a suit of immature source rocks of natural heterogeneity (e.g. mineralogy and types of kerogen) by the RE-MC-ICPMS reveals several interesting empirical correlations. The elution temperature of kerogen sulfur during pyrolysis (T_{max-S}) varies between different immature rock samples and is linear to the percentage of pyrolysis organic-S out of the total organic-S in the rock (PyOS%). We hypothesize that T_{max-S} depends on the distribution of different S-bonds in the organic molecule because they have different thermal stabilities. For example, sulfide and sulfoxide, are less thermally stable than thiophenes. Indeed T_{max-S} strongly correlates with the distribution of sulfidic and thiophene compounds of the rock. Therefore, T_{max-S} value may also serve as a proxy for organic-S structure. Moreover, the sulfur isotopic difference between kerogen and pyrite (δ³⁴S) of different rocks correlates with their T_{max-S}. This correlation may point on the link between specific sulfurization pathways and paleoenvironmental conditions and the organic-S structures represented by T_{max-S} and PyOS%.