Development of new proxies for sulfurization and paleo-environmental conditions using a Rock-Eval coupled to MC-ICPMS

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The sulfur (S) cycle is directly linked to the global carbon and iron cycles. Sulfur plays an important role in the preservation of organic matter (OM) over geological time scales. Assimilatory and dissimilatory sulfate reductions (ASR and DSR, respectively) are the main processes shaping the sulfur cycle and carry different sulfur isotopic fractionation (-1 to -3 ‰, and -20 to -75 ‰, respectively). The reduced S species produced by DSR react during early diagenesis with OM (sulfurization) to form organic-S, and/or with iron (Fe) to form pyrite. Although in most cases organic- and pyritic-S have a common origin (i.e., DSR), organic-S in marine sediments is typically ³⁴S enriched relative to its co-existing pyrite by up to 40 ‰ (global average is ~10‰). This isotopic difference is assumed to depend on specific paleo-environmental conditions and different sulfurization pathways (open-closed system for sulfate, Fe availability, redox state, OM type, etc.). Different sulfurization pathways may affect the type and distribution of S-bonds in sedimentary OM and thus can strongly affect the structure and character of sedimentary OM.

Recently, new instrumentation and methods were developed for the rapid determination of organic- and pyritic-S concentrations and δ³⁴S values using a Rock-Eval analyzer (RE) coupled to a MC-ICPMS. A new parameter, Tmax-S (the temperature at maximum peak of organic-S generation), was suggested to represent the organic-S thermal stability in pyrolysis conditions. Applying this parameter to thirteen organically rich and thermally immature samples of various geological settings and paleo-environmental origins revealed several interesting empirical correlations. The Tmax-S value was found to differ among the rocks and to linearly correlate (R²=0.98) with the percentage of pyrolyzed organic-S out of the total organic-S in the rock. Moreover, Tmax-S was strongly correlated with the distribution of sulfidic and thiophene compounds in the rock (R²=0.87). This suggests that Tmax-S may be used as a tool to evaluate the distribution of different S-bonds in the organic molecule, and, as a proxy, their sulfurization and paleoenvironmental conditions.

The rock samples’ Tmax-S values also correlate with their isotopic difference between organic- and pyritic-S (Δ³⁴Sorganic-pyrite; R²=0.76). The Δ³⁴Sorganic-pyrite values of the rocks extended between 1 to 40‰ where marine samples characterized by low Tmax-S values (~400-450 °C) and large Δ³⁴Sorganic-pyrite values (~20-40‰) and lacustrine samples by high Tmax-S values (~450-480 °C) and
small $\Delta^{34}S_{\text{organic-pyrite}}$ values (~1-5‰). This correlation further supports the link between paleo-environmental conditions, specific sulfurization pathways, and the organic-S structures (represented by $\text{Tmax-S}$). It may shed light on some fundamental questions regarding the role of S isotopic distribution between pyrite and OM during deposition and diagenesis.