Determination of sulphur speciation in recent sediments via Rock-Eval® 7S thermal analysis

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Résumé

Sediments often contain sulphur in the form of a variety of iron sulphides. This results from the activity of sulphate-reducing bacteria, which form H2S from SO42- anions. At the Earth's surface, this process is responsible for the production of the vast majority of sulphides (> 95%). With the notable exception of stable and poorly soluble pyrite (FeS2), most produced phases are soluble and metastable in sedimentary environments (*e.g.*, marcassite FeS2, mackinawite FeS, greigite Fe3S4). However, some can be preserved during early diagenesis, and records of the nature of these pyrite precursors can provide evidence of microbiological activity and palaeoenvironmental conditions conducive to the formation of sedimentary archives. To retrieve such information, it is necessary to determine sulphur speciation, *i.e.*, the relative proportions of the diverse sulphate and sulphide phases in presence. With this objective, chemical extraction methods are commonly used to distinguish pyrite from metastable phases by identifying sulphides readily dissolved by HCl to form H2S gas, called acid volatile sulphide (AVS). Such distinction is most often a mistake, as a significant proportion of the content of metastable sulphide can remain insensitive to such acid attacks. Sulphur speciation can be accurately determined through X-ray absorption spectroscopy (XAS), but this technique is time-consuming and cost-intensive. To overcome these limitations, we used recent developments in Rock-Eval® thermal analysis (RE7S) to study the signatures of various reference sulphur species and assess the potential of this method to determine sulphur speciation in sediments. By comparison with reference samples, we show that the detection of SO2 emission from sediment samples during the pyrolysis and oxidation phases of the RE7S procedure provides the possibility of distinguishing specific signatures associated with the different sulphide phases and the so-called AVS. Cracking reactions indeed occur at different temperatures due to distinct thermal stabilities. The quantification of such signatures identified in RE7S thermograms of recent sulphur-rich sediments (< 1000 years old) from Lake Tignes was correlated with the sulphur speciation determined by XAS. These results provide promising perspectives for the use of RE7S as a new tool for the rapid and accurate determination of sulphur speciation in sediments.

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Mots-Clés: diagenesis, sulphur, speciation, sulphides, acid volatile sulphides, Rock Eval 7 Soufre