

## ADVANCED SULPHUR SPECIATION AND QUANTIFICATION IN MARINE SHALES: EMERGING PERSPECTIVES FROM JURASSIC NORTH YORKSHIRE BLACK SHALE

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### Introduction

Sulphur speciation and quantification in shales has wide applications, to support paleo-environmental reconstructions and to address fundamental issues relevant to petroleum exploration and production. To contribute to these challenges, we present latest developments of an advanced sulphur speciation and quantification method, using a Rock-Eval 6 adapted for sulphur analysis in comparison to complementary XRD and SEM-EDX analyses. The modified Rock-Eval 6 permits, as a novel concept, the study of relationships between carbon (Lafargue *et al.*, 1998) and sulphur in organic and inorganic phases in tandem. Once fully calibrated, this new technology provides reliable assignment of the sulphur signals to different types of sulphur compounds, including elemental sulphur, organic sulphur, pyritic sulphur and sulphates. With this perspective, the technology enables fast, cost-effective and detailed characterization of organic carbon and sulphur in natural samples (shale, soils, etc.) and anthropogenic products (e.g. waste), urgently needed in the strategic investigation of fossil fuel resources (e.g. unconventional), soil carbon stocks, and environmental pollution sites.

Speciation of these sulphur components is not yet fully possible, due to pyritic sulphur and organic sulphur convolution and chemical reactions involving and modifying the original sulphur compounds. We developed a strategy by combining different technologies to tackle these issues:

- ❖ Deciphering the pyrite thermal transformation during the Rock-Eval analysis.
- ❖ Deducing an advanced method to quantify organic sulphur and pyritic sulphur using Rock-Eval.
- ❖ Testing this new method on marine shale samples, and comparing organic sulphur and pyritic sulphur contents with data from an independent method.
- ❖ Using SEM-EDX analysis to provide independent information on the abundance and nature of pyrite of the selected samples.

### Initial results

Results from Rock-Eval analyses of a pure pyrite show that it releases a fraction of about 43% of its total sulphur content during the pyrolysis phase, with the remaining 57% being mobilized during the oxidation phase. This transformation rate is in accordance with results from complementary in-situ XRD analysis, represented by the following reactions:

- ❖ Pyrolysis phase: thermal transformation of pyrite ( $\text{FeS}_2$ ) into pyrrhotite ( $\text{Fe}_7\text{S}_8$ ); confirming other pyrolysis experiments (Coats *et al.*, 1966; Lambert *et al.*, 1980).
- ❖ Oxidation phase: oxidation of the neofomed pyrrhotite ( $\text{Fe}_7\text{S}_8$ ) into hematite ( $\text{Fe}_2\text{O}_3$ ), consistent with paper from Hu *et al.*, 2006.

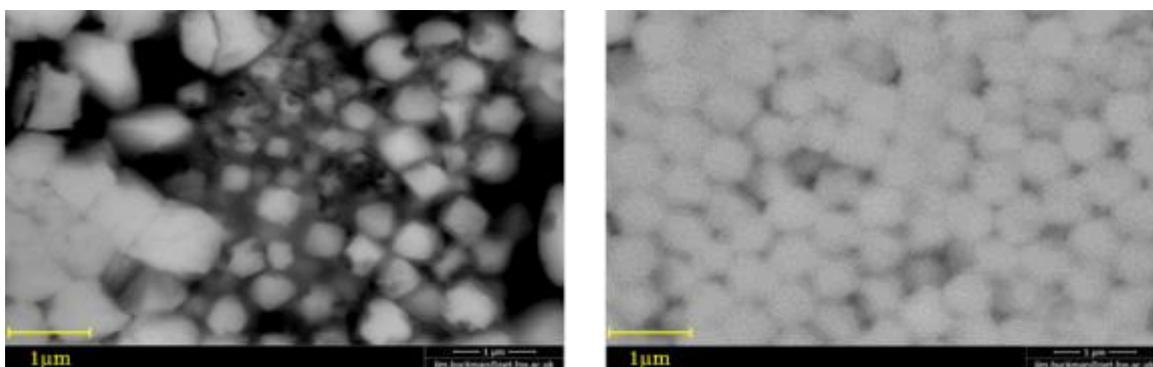
It has been assumed that this transformation of pure pyrite during pyrolysis would happen proportional to the pyrite transformation in a shale. Therefore, the modified Rock-Eval enables to quantify the pyritic sulphur released during the pyrolysis phase of the analytical cycle and subsequently the fraction of organic-bound sulphur, following:

$$\text{Pyritic sulphur (wt\%)} = \text{pyrolysis pyritic sulphur} * 100/43$$

$$\text{Organic sulphur (wt\%)} = \text{total sulphur} - \text{pyritic sulphur}$$

This approach was tested against an independent sulphur speciation and quantification method based on iron elemental analysis. In our experimental study we used a set of 13 shale samples from the Grey Shale Member, which constitutes the base of the Whitby Mudstone Formation in Cleveland Basin (Toarcian, North Yorkshire, UK) (Chowns, 1966). A good correlation line is obtained by comparing the two methods. However, Rock-Eval data seem to underestimate the pyritic sulphur content and so to overestimate the organic sulphur content (by approximately 30%).

We also analysed the 13 shale samples using Scanning Electron Microscopy coupled with Energy-Dispersive X-ray spectroscopy (SEM-EDX). The outcomes showed the presence of two pyrite particle groups: normal pyrite and sulphur-depleted pyrite (figure 1). As the Rock-Eval method is based on the assumption that shales contain exclusively normal pyrite, the observation of depleted pyrite in the studied samples is one possible explanation of the Rock-Eval underestimation of pyritic sulphur. Further quantitative work is needed, also using other types of shale and other rocks, to validate and develop these interesting first results.



**Figure 1:** SEM images of depleted pyrite (left) and normal pyrite (right) of shale samples

## References

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