ELUCIDATING SULFURIZATION PROCESSES IN SULFUR-RICH MUDSTONES: AN X-RAY ABSORPTION SPECTROMETRIC STUDY

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Introduction

Preservation through sulfurization of organic matter (OM) is an important process in the formation of hydrocarbon reserves, but this process remains poorly understood (Amrani 2014), despite the attention given to understanding how sulfurization of OM and pyrite (FeS 2 ) precipitation occur (Werne et al. 2008). It is conventionally thought that FeS 2 precipitation outcompete sulfurization. However, recent analyses suggest that sulfurization of OM might start in the water column (i.e. on timescale of days; Raven et al. 2016). This implies that sulfurization of OM precedes FeS 2 formation, contrary to the convention that iron sulfide formation is favoured over OM sulfurization in iron-rich oceans and porewater (Raiswell et al. 1994; Canfield et al. 1996). To the best of our knowledge, Raven et al. (2016) is the only study documenting sulfurization of OM outcompeting FeS 2 formation. Moreover, there is a lack of data on the micron/nano/molecular-scale necessary to fully comprehend these complex processes. The aims of this study are to use synchrotron-based techniques to non-destructively spatially resolve (map), and provide detailed information about, oxidants and reductants critical in sulfurization and FeS 2 precipitation processes, using sulfur-rich mudstones as a model system.

Experimental approach, results and discussion

Thin sections were made of three organic/sulfur-rich mudstones from different depositional environments, - the Blackstone Band of the Jurassic Kimmeridge Clay Formation, UK; the Miocene Monterey Formation, California; and the Grey Shale Member of the Jurassic Whitby Mudstone, UK. These thin sections were mapped and analysed using the new large-range rapid-scan X-ray fluorescence imaging station at beamline 6-2 at the Stanford Synchrotron Radiation Lightsource at SLAC National Accelerator Laboratory. Sulfur and phosphorous maps and associated sulfur X-ray absorption near edge spectroscopy (S-XANES) spectra revealed the distribution of sulfur (organic and inorganic) at high resolution and at various beam energies (eV) (Fig.1). S-XANES analyses of the Blackstone Band map indicate an organic sulfur presence throughout the entire map (1A), in line with previous observation that OM in the Blackstone Band is mainly preserved through sulfurization (van Dongen et al. 2006). The Miocene Monterey Formation map indicates a series of intercalations of siliceous (map not shown) and phosphatic layers with organic sulfur (confirmed by S-XANES) only present in the siliceous strata (Fig. 1B). This suggest that sulfurization of OM aided the preservation of OM in the Miocene Monterey Formation but only during well-defined periods in time, i.e. not a continuous process. S-XANES showed that the sulfur observed in the Grey Shale Member of the Whitby Mudstone map was, in contrast to the previous maps, not organically bound but a reduced sulfur form, likely iron sulfides, as shown by the beam energy (Fig 1C). This is confirmed by elemental X-ray fluorescence, electronmicroprobe and environmental scanning electron microscopy-energy dispersive spectroscopy analyses, indicating that this is largely pyrite. This further indicates
that preservation though sulfurization plays little or no role during the formation of the Grey Shale Member of the Whitby Mudstone.

Conclusion

This study presents for the first time the use of a unique rapid-scan X-ray fluorescence imaging station at Stanford Synchrotron Radiation Lightsource to image S (organic and inorganic) and P (as well as other elements; not shown) in the Blackstone Band of the Kimmeridge Clay Formation, the Miocene Monterey Formation and the Grey Shale Member of the Whitby Mudstone. The results coupled with electronmicroprobe analysis provide further information about sulfurization processes in mudstones. This study not only provides direct, and spatially-resolved measurements to validate current source rock preservation models, but also allows for a more robust modelling of redox-driven sulfur transformations which is likely to impact OM quality, maturity and preservation potential, rock composition and porosity development in petroleum systems (shale-gas and shale-oil reservoirs).

Figure 1: Tender X-ray imaging of thin sections of the (a) Blackstone Band of the Kimmeridge Clay Formation showing organic S (yellow colour; 2471.77 eV), (b) Miocene Monterey Formation showing organic S (yellow colour; 2471.77 eV) and phosphate (blue colour) and (c) the Grey Shale Member of the Whitby Mudstone showing inorganic S (yellow colour; 2481.19 eV).

References

Raiswell et al. (1994) A comparison of iron extraction methods for the determination of degree of pyritisation and the recognition of iron-limited pyrite formation, Chemical Geology, 111, 101–110.