

Combining spectroscopic, isotope and modeling techniques to reveal the fate of sulphur in petroleum system studies

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Introduction

The subsurface geochemical distribution of non-hydrocarbon “sour” gases (H₂S, CO₂) in oil/gas reservoirs is controlled mainly by thermochemical sulphate reduction (TSR) and organic matter cracking of organic sulfur compounds (OSC) in high temperature reservoirs versus bacterial sulfate reduction (BSR) in low-temperature reservoirs [1]. Their subsequent interactions with the hydrocarbon phase yield organic sulfur compounds in reservoirs and can result in sulfur rich bitumen formation via natural vulcanization processes [2]-[4].

To elucidate such mechanisms as sulfur incorporation and bitumen formation, we developed an integrated experimental approach of organic/inorganic geochemical and spectroscopy methods combined with in-house modeling capabilities. With presenting the main elements of the analytical workflow involving bulk geochemical data, X-ray absorption and photoelectron spectroscopy techniques, isotope geochemistry, fluid inclusion studies and modeling approaches, we aim for a profound understanding of gas/fluid-rock interactions involving sulfur geochemistry in the subsurface realm.

The workflow was developed on stacked Upper Devonian to Mississippian sour gas reservoirs situated in the Rocky Mountains Foothills of Alberta, Western Canadian Sedimentary Basin (WCSB), Canada. Production from these reservoir units is mainly dry gas and condensates with different forms of sulfur. H₂S contents range from 5% to almost 90%.

Results and Conclusions

Preliminary data on studied bitumens from WCSB assets revealed a sequence of solid bitumens with increasing amounts of sulfur incorporated. The distribution of sulfur compounds in the bitumen matrix comprises various oxidation states from -2 to +6. Major sulfur compound classes quantified are sulfide bridged compound classes, thiols, thiophenes and sulfates.

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[3] Kelemen et al. (2008) *GCA* **72**, 1137-1143.

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Uniform distribution of p-process ¹⁷⁴Hf in extraterrestrial materials

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Nucleosynthetic heterogeneity in extraterrestrial materials is found for several (but not all) p-process isotopes, and reflects the injection of material synthesized by at least one supernova event shortly before the first solar system objects formed. Further information on the distribution of p-process isotopes is relevant to characterise the source of this “late injection” and to unravel the different nucleosynthetic processes producing p-process isotopes. Here we present high precision MC-ICPMS measurements of p-process isotope ¹⁷⁴Hf in silicate materials that have originated at different ages and from different regions within the inner solar system. ¹⁷⁴Hf is of particular interest because of its similar mass range to p-process ¹⁸⁰W, which displays large excesses in iron meteorites [1].

For Hf purification, we optimised the existing protocol by [2]. This was necessary to (1) successfully correct for the interference by isobaric ¹⁷⁴Yb; and (2) avoid matrix effects. Furthermore, we extensively tested sample cones with a large aperture (“Jet cones”) in combination with an OnTool™ Booster interface pump. This setup enhances instrument sensitivity by a factor of more than 5 (ca. 3000 V/ppm Hf), but we also observed anomalous mass bias behavior in the presence of only minute amounts of matrix. All samples were therefore measured in setup with standard sample and X-skimmer cone, typically consuming ~60 ng Hf at precisions of ±70 ppm (2σ).

¹⁷⁴Hf/¹⁷⁷Hf ratios in analysed EL, H, L and CV chondrites, eucrites, and one lodranite sample are indistinguishable from the terrestrial value. In contrast, a silicate inclusion of the El Taco IAB iron meteorite and one EL6 chondrite (Pillistfer) exhibit higher ¹⁷⁴Hf/¹⁷⁷Hf ratios than the terrestrial standard, namely 190 ±72 ppm and 210 ±75 ppm respectively. These are correlated with higher ¹⁷⁸Hf/¹⁷⁷Hf ratios (18±5 and 21±5 ppm, respectively). The latter most likely result from secondary neutron capture reactions at epithermal energies due to the high Fe content of the samples [3]. The high ¹⁷⁴Hf/¹⁷⁷Hf ratios therefore most likely reflect a deficit in ¹⁷⁷Hf. ¹⁷⁴Hf itself has a low neutron capture cross-section (RI ~345 barn [4]) and is expected to be unaffected by cosmic ray interactions.

The absence of nucleosynthetic heterogeneity in ¹⁷⁴Hf indicates that either the protosolar nebula was homogenous in ¹⁷⁴Hf, or, alternatively, that existing ¹⁷⁴Hf heterogeneities had been efficiently homogenized by the time of parent body formation. The second scenario would be consistent with a single source for p-process ¹⁸⁰W and ¹⁷⁴Hf, and is therefore more plausible.

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