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Sulfur Isotope Systematics of Individual Organic Compounds During Thermochemical Sulfate Reduction

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Thermochemical sulfate reduction (TSR) coupled with oxidation of hydrocarbons occurs in hot carbonate petroleum reservoirs (>110°C) and in hydrothermal environments. It is one of the most important organic-inorganic interactions and is well documented by many geologic observations from around the world.

Sulfur isotopes are useful for detecting the occurrence of TSR, because the $\delta^{34}\text{S}$ value of H_2S approaches that of the CaSO_4 being reduced. Organosulfur compounds and pyrobitumen resulting from back-reactions with TSR-derived H_2S have been proposed to have $\delta^{34}\text{S}$ values close to parent sulfates, though this has not been directly tested.

We have measured a suit of Upper Jurassic oil and condensate samples generated from the Smackover Fm. source rock in the Gulf of Mexico. We employed a new technique capable of measuring precise $\delta^{34}\text{S}$ values in individual compounds by GC-MC-ICPMS (Amrani et al., 2009).

S-isotopic differences of up to ~50‰ were observed between individual organosulfur compounds in Upper Jurassic oil and condensate samples generated from the Smackover Fm. source rock in the Gulf of Mexico (Fig. 1). There is a clear distinction between oils that experienced thermal sulfate reduction (TSR) versus oils that did not. Oils that did not experience TSR are relatively depleted in ^{34}S and have small $\delta^{34}\text{S}$ variations between individual compounds. Oils that did experience TSR have significant isotopic differences between benzothiophenes (BTs) and dibenzothiophenes (DBTs). BTs are ^{34}S enriched, close to the $\delta^{34}\text{S}$ values of sulfate evaporites in the Smackover Fm. The $\delta^{34}\text{S}$ values of DBTs are spread over a wider range and are always more negative. These differences reflect different degrees of TSR alteration and S addition in the oils.

We also conducted a series of gold-tube hydrous pyrolysis experiments using three representative oils and isotopically distinct CaSO_4 to determine the factors controlling $\delta^{34}\text{S}$ values of individual organic S compounds at different stages of TSR. Our laboratory experiments show that isotopic alteration readily occurs under TSR conditions and can significantly affect the $\delta^{34}\text{S}$ values of individual compounds. Our results show that BTs are sensitive tracers for TSR as

they form readily under TSR conditions, with $\delta^{34}\text{S}$ values that are similar to that of the CaSO_4 derived H_2S .

In contrast, DBTs exhibit relatively small $\delta^{34}\text{S}$ changes, preserving their original $\delta^{34}\text{S}$ values longer than do BTs because of their greater thermal stability and slow rate of formation. Our observations support the notion that DBTs can preserve the original (non TSR-altered) $\delta^{34}\text{S}$ composition of the oils through low to moderate TSR alteration.

The use of these two groups of tracers in combination allow us to detect TSR alteration of oils from the very early stages up to highly altered oils, all without measuring H_2S or sulfate isotopes and other geochemical parameters. The approach should find numerous uses in exploration, as well as for understanding the basic reaction mechanisms and kinetics of thermal sulfate reduction and the secondary sulfur incorporation into oils.

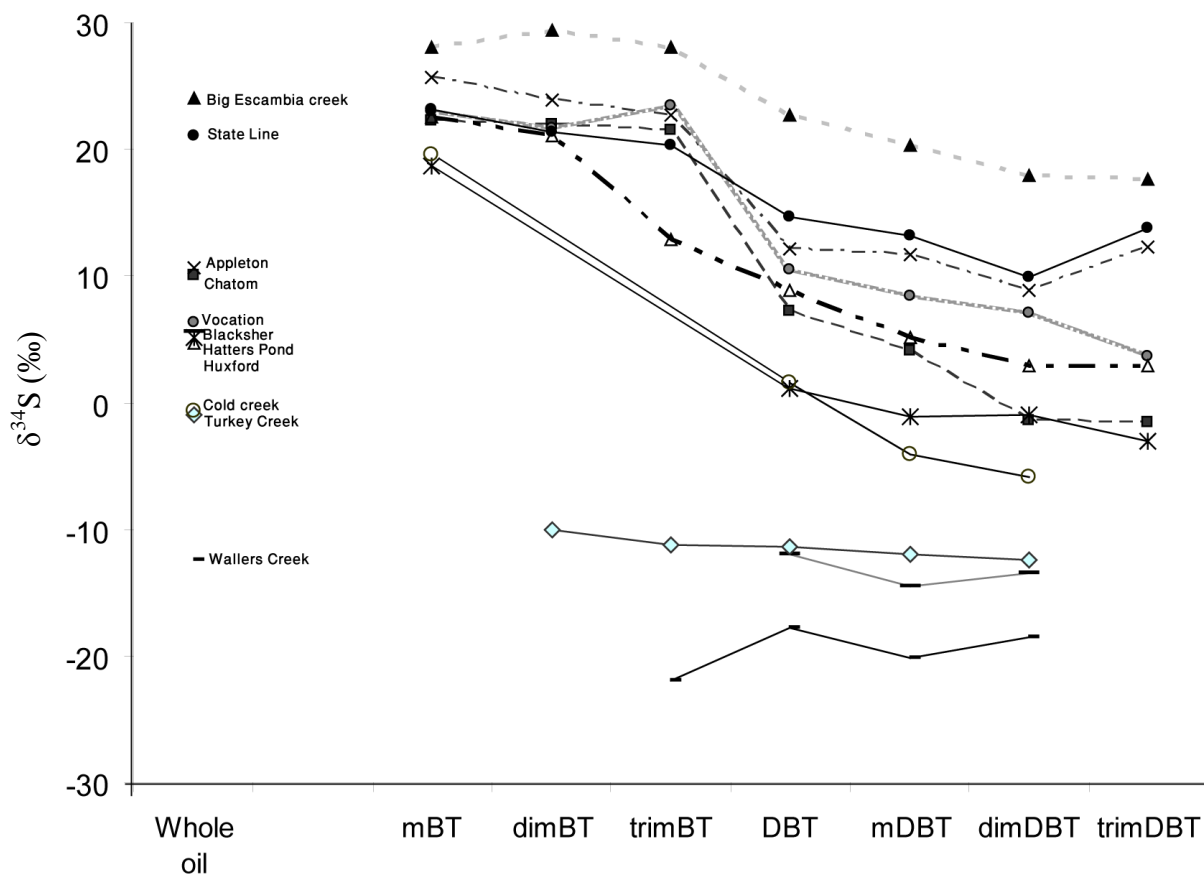


Fig 1. The $\delta^{34}\text{S}$ values of individual organosulfur compounds of Upper Jurassic oil and condensate samples generated from the Smackover Formation source rock in the Gulf of Mexico.