

SECULAR CHANGE IN THE STABLE SULFUR ISOTOPE COMPOSITION OF CRUDE OILS RELATIVE TO MARINE SULFATES AND SULFIDES

Michael H. ENGEL¹ and John E. ZUMBERGE²

1. School of Geology and Geophysics, 100 East Boyd St., University of Oklahoma, Norman, OK 73019, USA

2. GeoMark Research, 9748 Whithorn Drive, Houston, TX 77095, USA

Secular changes in the stable sulfur isotope composition of seawater sulfate have been commonly inferred from that of evaporite minerals and from sulfate in carbonate shell matrices. The stable sulfur isotope compositions of marine sulfides follow a similar secular trend to that of sulfate, although substantially depleted in ³⁴S owing to fractionation via bacterial sulfate reduction. Few if any studies of secular changes in the stable isotope composition of organic matter have been attempted. This is in part because of the complexity of diagenetic pathways for the incorporation of sulfur into organic matter subsequent to biosynthesis (e.g. Werne *et al.*, 2003). However, given the range for the stable sulfur isotope composition of seawater sulfate (and resulting sulfide) during the Phanerozoic (~25 to 30‰), it is hypothesized that the magnitude of this isotopic variability will be generally reflected by marine organic matter, irrespective of diagenesis. Our approach is based on an initial observation by Thode (1981) that oils sourced from Ordovician age rocks were enriched in ³⁴S relative to Mississippian age oils, which in turn were enriched in ³⁴S relative to Pennsylvanian age oils, a trend that is consistent with that reported for seawater sulfate for these time intervals. Simulation studies by Amrani *et al.* (2006) also support previous observations that crude oils generally reflect the stable sulfur isotope composition of their source materials and that the effects of thermal maturation on the stable sulfur isotope composition of oils are much less than for kerogens.

The stable sulfur isotope compositions of fifteen nondegraded crude oils (containing 1-3% sulfur) ranging in source rock age from Neoproterozoic to Neogene were determined. For seven of the oils, the stable sulfur isotope compositions of their respective aromatic, NSO and asphaltene fractions were also determined. Except for the siliceous Monterey, the source rocks for the oils were all marine carbonates/marls of low to moderate maturity.

The secular changes for the stable sulfur isotope compositions of the oils tracked the sulfate curve (Fig. 1) having $\delta^{34}\text{S}$ values intermediate to those of sulfate and sulfide. The secular trend exhibited by the stable carbon isotopes of the oils is also shown. The stable sulfur isotope values for the aromatic, NSO and asphaltene fractions of the oils were within 1-2‰ of the whole oil values. Oils formed from source rock depositional environments exhibiting photic zone euxinia (PZE) based on the presence of abundant aryl isoprenoids,

biomarkers for green sulfur bacteria (Summons and Powell, 1987), were more depleted in ^{34}S than oils of similar ages from phytoplankton/bacterial dominated sources. Based on these initial findings, the stable sulfur isotope composition of crude oils may provide the first independent method to check the secular sulfur isotope curves presently based on marine sulfate and sulfide minerals.

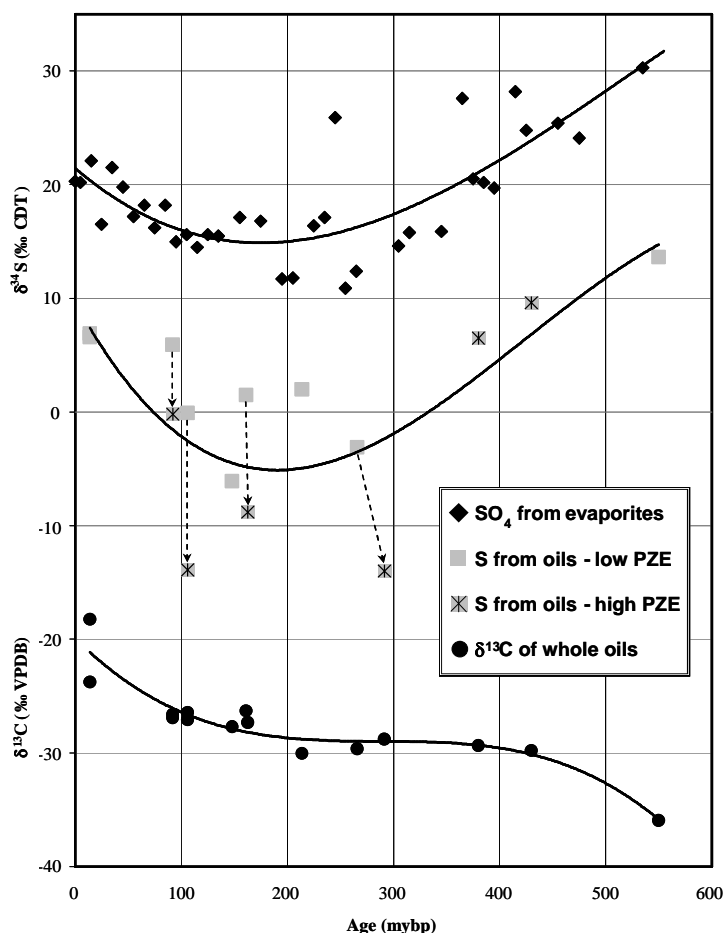


Figure 1. Stable isotope curves for sulfates (S; after Strauss, 1999) and crude oils (C,S).

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