SULFUR ISOTOPE COMPOSITION OF INDIVIDUAL COMPOUNDS IN IMMATURE SOURCE ROCKS AND THEIR POSSIBLE GEOCHEMICAL IMPLICATIONS

L. Shawar¹, W. Said-Ahmad¹, G. Ellis² and A. Amrani¹

¹Hebrew University of Jerusalem, Israel, ²US Geological Survey, United States

The sulfurization process of organic compounds during early diagenesis has a significant role in organic matter (OM) preservation in sediments (Sinninghe Damsté and De Leeuw, 1990). Previous studies used bulk S isotope analysis (i.e. organic S and pyrite) as a tracer of sulfurization mechanisms and to understand depositional conditions of organic rich sediments (Shawar et al., 2018). However, since the bulk δ³⁴S analysis of organic S averages all the S-isotopic values of the organic S compounds (OSC), important trends may be overlooked. The novel method of a gas chromatograph coupled to an inductively coupled plasma mass spectrometer, allowed for sulfur isotope study at the molecular level (Amrani et al., 2009). Recent studies have applied this new technique to different fields in earth sciences (i.e. Greenwood et al., 2015). This technique was applied to recent sediment from the Cariaco Basin and showed interesting insights for the timing and mechanisms of OM sulfurization (Raven et al., 2015). Here, we applied this technique, for the first time, to study immature rocks. The immature rocks studied have experienced minimal post diagenetic thermal maturation and no loss of the volatile fraction and thus have good preservation of their organic compounds and associated paleo-environmental signals. Therefore, the study of δ³⁴S values in individual OSC may allow for improved understanding of organic rich sediment formation processes and their depositional environment.

In the present study we measured the compound specific S isotope (CSSI) values of OM extracted from ancient and immature organic-rich sediments from the Ghareb (Shefela Basin) and Monterey (Naples Beach) formations (Figure 1a and 2a). Large variations in the δ³⁴S values of different OSC, that reach up to 28‰ and 36‰ were observed in the Ghareb and Monterey samples respectively (Figure 1b and 2b). Moreover, some common OSC (i.e. C₃₅ hopane thiophene and i-C₂₀ thiophene), in both sections, show a similar trend of ³⁴S values (enriched or depleted) to each other: for example, C₃₅ hopane thiophene is heavier than i-C₂₀ thiophene (Figure 1b and 2b). The constant enrichment in ³⁴S of C₃₅ hopane thiophene relative to i-C₂₀ thiophene in the studied sections probably resulted by different OM sulfurization timing on the Rayleigh distillation sequence of the microbial sulfate reduction (source of reactive inorganic sulfides). Thus, the reactive organic precursors react faster and quench the most ³⁴S depleted reduced S, while the less reactive ones left with heavier portion of reduced S. Therefore, regardless the difference in the depositional environments, the age and the initial δ³⁴S value of the sulfides (represented by the δ³⁴S of pyrite) between the Ghareb and the Monterey, the sulfurization order of common organic compound seems to be similar (Figure 1b and 2b). However, unlike the Ghareb, in the Monterey we observed ³⁴S depleted values of some OSC (i.e. C₂₅-HBI thiophene) relative to the co-existing pyrite (Figure 1b and 2b). Similar phenomenon, of ³⁴S depletion in C₂₅-HBI thiolane relative to the co-existing pyrite was observed in the Cariaco Basin (Raven et al., 2015). They explained this observation by sulfurization of organic compounds within the euxinic water column. Based on their interpretation and on the fact that the existence of HBI alkenes may point to oxygen minimum zone expansion (Erlich et al., 1996), we suggest that the existence of ³⁴S depleted sulfurized HBI may point to euxinic paleo-water column that may developed during the deposition of the Naples Beach sediments (Monterey). We will present other CSSI results trends and interpretations between our two case studies. Further investigation of CSSI values in immature
rocks from other basins may thus help constrain the OM sulfurization process, time scale and depositional conditions.

References


**Figure 1:** a) The stratigraphic column of the Late cretaceous Ghareb Formation, Shefela Basin, Israel, b) δ34S of kerogen, pyrite and individual organic S compounds extracted from the Ghareb Formation

**Figure 2:** a) The stratigraphic column of the Miocene Monterey Formation, Naples Beach, California, b) δ34S of kerogen, pyrite and individual organic S compounds extracted from the Monterey Formation