Anomalous S isotope fractionations during reactions with an organic surface: I. Theoretical investigations

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A*b initio* calculations were performed to investigate: (1) the validity of mass-dependent approximations [1] during equilibrium isotope fractionations and (2) a new surface reaction model to produce anomalous isotope fractionations. We use the term "anomalous sulfur isotope fractionation" when the $\Delta^{33}S$ and $^{33}\theta$' ($\approx\delta^{33}S/\delta^{34}S$) values of a sample fall outside of 0±0.2‰ and 0.51±0.01‰, respectively, and/or when the $\Delta^{36}S$ and $^{36}\theta$' ($\approx\delta^{36}S/\delta^{34}S$) values of a sample fall outside of 0±0.4‰ and 1.9±0.1‰, respectively.

We have calculated the vibrational frequencies, reduced partition function ratios, and fractionation factors for all four stable isotopes of S in simple gaseous and aqueous compounds at T = 0 – 650°C. Mass-dependent coefficients, $(^{33}\alpha - 1)/(^{34}\alpha - 1)$ and $(^{36}\alpha - 1)/(^{34}\alpha - 1)$ values, converge to 0.515 and 1.89, respectively, at T > 500°C, but deviate from these values with decreasing temperature and depending on the sulfur species pairs. For example, at T = 0°C, $(^{33}\alpha - 1)/(^{34}\alpha - 1)$ values range from 0.505 to 0.517 and $(^{36}\alpha - 1)/(^{34}\alpha - 1)$ values range from 1.88 to 1.96. However, these deviations do not fall in the range of "anomalous isotope fractionation".

On the other hand, we have recognized that the combination of small chemisorption energies (<30 kJ/mole) with possible discontinuities in the number of bound energy levels for different sulfur isotopes may lead to anomalous isotope effects in heterogeneous reactions between a surface and sulfur-bearing species. The magnitude of anomalous fractionation effects during a heterogeneous reaction increases with increasing temperature. We have performed *ab initio* calculations for SO_2 adsorption on a kerogen surface. The results indicate the possibility of creating large anomalous sulfur isotope fractionations (e.g., $\delta^{33}S/\delta^{34}S \approx 1.08$, $\delta^{36}S/\delta^{34}S \approx 0.84$, $\Delta^{33}S$ = 7.0 – 13.6‰, $\Delta^{36}S$ = -13.0 – -25.2‰) by heterogeneous reactions between organic matter and sulfur-bearing solutions under hydrothermal conditions.

[1] Bigeleisen and Mayer (1947) *J. Chem. Phys.* **15**, 261-267.

A multi-proxy approach to look at the paleoclimatic variability in the upwelling zone off NW Africa

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This study applies a multi-proxy approach, using alkenone- and Mg/Ca-based (from *G. bulloides*) sea surface temperature (SST), alkane and TOC estimates to reconstruct the paleoceanographic conditions of the upwelling area off NW-Africa for the past ~55 kyrs. Investigations were carried out on two sediment cores (GeoB8507-3 and GeoB9601-3) south of ~20°N in the NE Atlantic. In this region, upwelling is seasonal, occurring during winter and early spring [1].

The alkenone-derived SST record of GeoB9601-3 clearly shows a cooling in surface water during the time intervals of Heinrich Events 1-5. This correlates with the GeoB8507-3 SST record which indicates an increase in temperature during the last glacial compared to modern conditions. However, the SST record based on Mg/Ca ratios shows a cooling. These observed opposing trends in the SST records could be related to the overall varying ecological preferences of the different plankton groups. However, our findings could also reflect seasonal differences in productivity in response to changes in the location and intensity of the upwelling during the last glacial.

[1] Wooster, Bakun & McLain (1976) *Journal of Marine Research* **34**, 131-141.