Estimating Equilibrium Isotopic Fractionation in the Environment Using Density Functional Calculations

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Isotopic fractionation is a widely used to explore environmental processes. For instance, the relative $^{13}C/^{12}C$ and $^{2}D/^{1}H$ ratios can be used to identify the source of methane, an abundant atmospheric gas with several sources, each with a unique isotopic fingerprint (Figure 1). One source is hydrogenotrophic methanogenesis, an archaeal process whereby hydrogen and carbon dioxide are converted to methane in a process involving seven reaction intermediates and nine different enzymes. My experimental collaborators (Dr.. Itay Halevy, Department of Earth and Planetary Sciences, Weizmann Institute of Science) are working on a model to understand how each step affects the overall isotopic fractionation. The model is built by solving Michaelis–Menten-type equations for each step and all relevant side

Figure 1. Methane source as a function of $^{13}C/^{12}C$ and $^{2}D/^{1}H$ ratios. (Adapted from reference 2.)

reactions. For this purpose, they need equilibrium isotopic fractionations calculated as part of this project, used in conjunction with some assumptions for the kinetic isotopic fractionations.

Another example is sulphate incorporated into calcium carbonate minerals, or carbonate-associated sulphate (CAS) – a promising proxy for the sulphur isotope composition of seawater sulfate over Earth's history. In a set of carbonate precipitation experiments at variable sulphate concentration, an intriguing dependence was found of the sulphur isotope fractionation on the sulphate–carbonate ratios in solution (and the concentration of CAS). As sulphate is incorporated into the carbonate lattice at concentrations of hundreds to thousands of ppm, it is conceivable that it affects the energetics of the crystal lattice sufficiently to influence the equilibrium sulphur isotope fractionation.

Isotopic fractionation (α) can be calculated using the vibrational frequencies (ω_i) of each species:

$$\alpha = \beta_{CH_4}/\beta_{CO_2}$$

$$\beta = \frac{Q_H}{Q_L} = \frac{\sigma_H}{\sigma_L} \cdot \prod_{i=1}^{3N-6} \frac{u_{H_i}}{u_{L_i}} \cdot \frac{\exp\left(-\frac{u_{H_i}}{2}\right)}{\exp\left(-\frac{u_{L_i}}{2}\right)} \cdot \frac{1 - \exp(-u_{L_i})}{1 - \exp(-u_{H_i})}$$

where N is the number of atoms, Q is the partition function, σ is the rotational symmetry number, H and L denote the heavy and light isotopes, respectively, and $u_i = \frac{h \cdot c \cdot \omega_i}{k_B \cdot T}$.[1] In this study, density functional theory is used to estimate the isotopic fractionations. While the reactant and product molecules are small, the reaction proceeds through several intermediates that are much larger in size, making DFT a reasonable compromised between cost and accuracy. In addition to estimating the fractionations, key factors influencing the accuracy of the calculations are considered.

[1] H. C. Urey, *J. Chem. Soc.* 562-581 (1947).
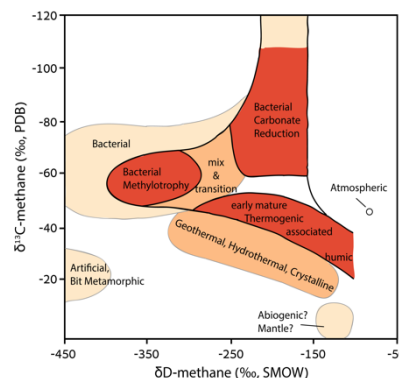[2] M. J. Whiticar, *Chem. Geol.* **161**, 291-314 (1999).