A New Surface Reaction Model for Anomalous Fractionation of Sulfur Isotopes

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Large deviation from the mass-dependent relationships in multiple S isotope (^{32}S, ^{33}S, ^{34}S, and ^{36}S) systems is termed mass-independent fractionation of sulfur isotope (MIF-S). The MIF-S signatures found in many sedimentary rocks older than 2.45 Ga have been cited by many geoscientists and astrobiologists as unequivocal evidence for a dramatic change from an anoxic to oxic atmosphere around 2.4Ga. More recently, very small deviation from the mass-dependent relationships has been proposed as a possible biosignature, because kinetic and equilibrium isotope fractionations may have slightly different mass-dependent relationships. These interpretations of multiple S isotope data in natural samples are based on the following two premises. The first premise is that equilibrium fractionations of sulfur isotopes in nature always conform to the mass-dependent relationships derived by Bigeleisen and Mayer. The second is that UV photolysis of SO_2 in an O_2-poor atmosphere is the only cause for MIF-S in nature. We evaluated the two premises theoretically by performing *ab initio* calculations.

We calculated the vibrational frequencies, reduced partition function ratios, and fractionation factors (alpha values) for all four stable isotopes of S in simple gaseous and aqueous compounds (HS^-, H_2S, S_2, S_8, CS_2, SO_2, SO_3, and SO_4^{2-}) at T = 0 - 650 degree C. Mass-dependent relationships, (alpha33 - 1)/(alpha34 - 1) and (alpha36 - 1)/(alpha34 - 1) values, converge to 0.515 and 1.89, respectively, at temperatures higher than 500 degree C, but deviate from these values with decreasing temperature and variation in the sulfur species pairs. For example, at T = 0 degree C, (alpha33 - 1)/(alpha34 - 1) values range from 0.505 to 0.517 and (alpha36 - 1)/(alpha34 - 1) values range from 1.88 to 1.96. Therefore, the use of small deviations from mass-dependent relationships to distinguish kinetic processes from equilibrium processes may not be valid unless kinetic processes show larger deviations than those for equilibrium reactions.

While the deviations calculated in equilibrium isotope exchange reactions do not fall in the range of anomalous isotope fractionation, we recognized that the combination of small chemisorption energies (e.g., 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 performed *ab initio* calculations for SO_2 adsorption on a kerogen surface. The results indicate the possibility of creating large anomalous sulfur isotope fractionations by heterogeneous reactions between organic matter and sulfur-bearing solutions under hydrothermal conditions. The results further suggest that UV photolysis may not be the only process that that caused MIF-S in nature.