A ‘mass-anomalous’ vapor-pressure isotope effect for SF_6

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Large mass-anomalous isotope fractionations of O and S are commonly attributed to photochemical reactions. It is unclear whether more subtle mass-anomalous fractionations of O and S can arise from exchange equilibria or other non-photochemical reactions. Statistical thermodynamic models of a simple harmonic oscillator may [1] or may not [2] predict mass-anomalous equilibrium fractionations of light elements. Experimental devolatilization of carbonate [3] and sulfate [4] reveal mass-anomalous net fractionations of O and S, respectively, but have unconstrained reaction mechanisms and may reflect mixing and/or distillation rather than novel chemical isotope effects.

We present experimental observations of the vapor pressure isotope effect (VPIE) for solid, liquid, and adsorbed SF_6 between temperatures of 300 and 141 K. SF_6 exhibits a reversed (for ice and sorbate) or negligible (for liquid) VPIE under all studied conditions. In this respect, it resembles the VPIEs for $^{13}CO_2/^{12}CO_2$ and other cases in which mass substitution involves a central atom in a non-polar molecule. The size of the VPIE for solid SF_6 is approximately -2.5 ‰ for $^{34}S/^{32}S$ (solid/vapor) at 150 K. The mass exponent, $\beta^{3/4} = \ln\alpha^{33}/\ln\alpha^{34}$, averages 0.56 ± 0.01 and is nearly constant across all explored temperatures. Time series experiments suggest these results reflect equilibrium VPIEs; bracketing the ice/vapor equilibrium through reversal experiments is challenging, presumably due to slow solid-state diffusion in SF_6 at these temperatures, but has been achieved for long-duration, ice-dominated experiments.

The mass exponent we observe is significantly higher than those for canonical equilibrium or kinetic fractionations ($\beta^{3/4}$ = 0.515 or 0.508, respectively). Its value, occurrence at low temperatures, and lack of variation with T differ from predictions of the harmonic-oscillator model that yields non-canonical mass laws for sorption[1]. $\beta^{6/4} = \ln\alpha^{36}/\ln\alpha^{34}$ varies more complexly than $\beta^{3/4}$ but is also generally ~10 % higher than canonical mass-dependent values. We suggest our results are explained by the interplay between isotope effects on intermolecular and intramolecular vibrational and rotational energies. Support for this conjecture can be found in prior observations of the mass laws of vapor pressure isotope effects for H-D-T and ^{12}C-^{13}C-^{14}C. Potential relevance for S-bearing molecules of natural significance will be discussed.

[1] Lasaga *et al.* (2008) *EPSL*. [2] Balan *et al.* (2009) *EPSL*. [3] Miller *et al.* (2002) *PNAS*. [4] Watanabe *et al.* (2009) *Science*.

Structural evolution and fluid flow in the Wealden and Hampshire basins, southern England, U.K

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From Permian to late Cenozoic southern England went through a complex structural evolution. A tensional stress regime during the Permian and Mesozoic produced a pattern of subsidence dominated by E-W striking normal faults. This tectonic regime was followed by a reversal of the subsidence pattern and inversion of the Wealden sedimentary basin in response to compressive tectonic stresses that converted the Mesozoic depocentres into structural highs during late Cretaceous and early Cenozoic times. Also during the Cenozoic the Hampshire basin formed as a direct result of crustal flexure. These events have produced a wide range of large- and small-scale structures that provide valuable record of structural evolution

The migration of petroleum and solute bearing fluids may have been controlled by the tectonic features such as faults. The timing and migration paths of these fluid movement events remain poorly constrained. Understanding the present day distribution of hydrocarbons and cements relies on understanding both the structure and fluid movement in these basins. The complex structural history of the Wealden and Hampshire basins provides an excellent opportunity to investigate links between structural evolution, petroleum migration and water movement.

Structures in outcrop and displayed on published geological maps have been examined in order to determine the geometries, relative ages and stratigraphic ages of faults, veins systems and folds throughout Wealden and Hampshire basins. Samples of cemented faults and veins have been collected from a wide range of stratigraphic units (Early Cretaceous to late Tertiary) in different structural positions. The faults and veins are concentrated in four locations, two on the Isle of Wight around the zones of flexure, Eastbourne and Dover. Petrographical analysis indicates that these samples are dominantly calcite with minor amounts of pyrite and barite and the veins in different orientations share the same mineralogy. The validity of this apparently simple pattern is examined using fluid inclusion studies. By integrating these results with the chemistry of the source rocks and hydrocarbons found within the basins a model of fluid flow and the evolution will be established.