First-principles Models of Equilibrium Tellurium Isotope Fractionation

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In this study, mass-dependent isotope fractionation is estimated among representative Te-bearing species using first-principles thermodynamic calculations. Tellurium is a relatively rare element in group 16, with eight stable isotopes ranging in mass from 120 to 130 and six commonly-occurring oxidation states: -II, -I, 0, +II, +IV, and +VI. Te(-II) forms metal-bearing tellurides in magmatic and hydrothermal ore deposits, including gold and silver tellurides. Te(0) is also found in precious metal hydrothermal ore deposits. However, the higher oxidation states of Te are thought to be the most thermodynamically stable oxidation states at the Earth's surface. The range of valence states in natural systems and large relative mass difference between the heaviest and lightest isotope of tellurium provides an opportunity for finding geochemically useful isotope abundance variations.

Tellurium isotope fractionations were determined for representative molecules and crystals of varying complexity and chemistry. Gas-phase calculations are combined with supermolecular cluster models of aqueous and solid species, these in turn are compared with plane-wave density functional theory calculations with periodic boundary conditions. In general, heavy tellurium isotopes will be enriched in more oxidized species, and depleted in reduced species, in both the gas-phase species and crystals. Isotope fractionations calculated with hybrid density function theory (B3LYP) models using medium-sized and larger basis sets for supermolecular clusters of PbTe (altaite), Ag_2Te (hessite), CdTe, $AuTe_2$ (calaverite), and native Te agree with each other and appear not to depend greatly on the details of basis set choice. PbTe is predicted to have lower $^{heavy}Te/^{light}Te$ than the coexisting CdTe, Ag_2Te, and $AuTe_2$ at all relevant temperatures. $^{130}Te/^{125}Te$ for PbTe, will be about 0.3 – 0.5‰ lower than gold/silver tellurides and CdTe at 100°C. MC-ICP-MS measurements show a range of -2.1 to 0.8‰ for $\delta^{130}/^{125}Te$ in tellurides and native tellurium and -2.1 to 0.6‰ in tellurites and tellurates. Calculated isotope fractionations for supermolecular clusters representating CdTe and native tellurium are in reasonable agreement with plane-wave density functional theory models with periodic boundary conditions but for other crystals the agreement is not as good.