

Theoretical Estimates of Equilibrium Chlorine Isotope Fractionations

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Abstract

An improved understanding of equilibrium fractionations of chlorine isotopes will help to interpret observed variations in natural systems, and will allow us to determine what natural processes can be effectively studied. To this end, we have estimated equilibrium $^{37}\text{Cl}/^{35}\text{Cl}$ fractionations among geochemically interesting crystalline and molecular substances using both published vibrational spectra and force-field modeling. We use the theoretical approach summarized by Urey [1], in which equilibrium fractionations are calculated from the changes in vibrational frequencies caused by isotope substitution. Lattice-dynamics modeling predicts vibrational spectra for isotopically substituted halite (NaCl) and sylvite (KCl), as well as crystalline RbCl, FeCl₂, and MnCl₂. FeCl₂ and MnCl₂ were chosen as analogues for chloride in silicate minerals, because their nearest-neighbor structures around chlorine are similar to those of the OH/Cl⁻ sites in amphibole and mica. Vibrational frequencies of ^{37}Cl -substituted molecules and complexes are derived from published spectra, empirical force-fields, and *ab initio* models. *Ab initio* models reliably predict the effects of isotope substitution on molecular vibrational frequencies. Calculated fractionations agree in both direction and rough magnitude with fractionations inferred from experiments and natural samples. Halite will concentrate ^{37}Cl relative to sylvite (by δ 0.7 per mil at 298 K). Experiments by Eggenkamp et al. [2] suggest that saturated brines will be intermediate between halite and sylvite. Based on this observation, and the predicted behavior of FeCl₂ and MnCl₂, silicates in equilibrium with either alkali halides or brine should have higher $^{37}\text{Cl}/^{35}\text{Cl}$. Chlorinated organic compounds like CH₃Cl, CCl₄, C₂Cl₄, and CFCI₃ all have similar chlorine-isotope partitioning behavior at equilibrium, and will have higher $^{37}\text{Cl}/^{35}\text{Cl}$ than coexisting inorganic chlorides. In general, chlorides with chlorine bonded to cations in higher oxidation states (i.e. Fe²⁺ vs. Na⁺) will tend to concentrate ^{37}Cl . Compounds with oxidized chlorine (ClO, ClONO₂, Cl₂O, OClO, [ClO₄]⁻) have a progressively greater tendency to concentrate ^{37}Cl as the oxidation state of chlorine increases. References: [1] Urey (1947) J. Chem. Soc. (London), 562-581. [2] Eggenkamp et al. (1995) GCA 59, 5169-5175.

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