Enhance your IQ (isotope quotient) through crystal chemistry

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Advances in theoretical and experimental determinations of equilibrium isotope fractionation factors are providing the foundation for using new isotope systems as tracers in the geological sciences. Even where equilibrium partitioning of isotopes between phases is unlikely, equilibrium fractionation factors are nonetheless vital for interpretations. Crystal chemistry provides a sound basis for gaining insights into the sources of fractionation between crystalline phases, especially where measurements or detailed calculations are lacking.

Ab initio calculations provide the means to derive fractionation factors, but do not always convey an understanding of the controls on fractionation. Pauling's rules have proven effective in this regard. Although they are based on the precepts of ionic structures, they remain a "useful fiction" that is effective in rationalizing, and in some cases even predicting, structures and site occupancies. A simple expression for bond force constants rooted in Paulings rules:

$$k_f = \frac{z_i z_j e^2 (1-n)}{4\pi \varepsilon^o r_o^3}$$

where z_i (z_j) refers to the valence of cations (anions), r_o is the interionic distance, and n is a Born-Mayer repulsion constant, is an effective means for understanding and predicting fractionation factors between mineral phases. Because logarithms of Pauling's bond strengths, $s_i = z_i/\upsilon_i$ where υ_i is the coordination number, correlate with bond lengths, effective ionic radii can be used to estimate force constants, and therefore vibrational frequencies and fractionation.

Fractionation fractors for various rock-forming isotope systems are amenable to interpretation using the principles outlined above. While consideration of the coordination of the element of interest (Mg, Si, Fe, etc.) is becoming more common, differences in nearest neighbor coordination numbers are often overlooked when considering the sources of inter-mineral fractionation. For example, these concepts "predict" that the Fe isotope fractionation between clinopyroxene and olivine should be small and positive based on the presence of ^{III}O in pyroxene and its absence in olivine. Definitive experiments are lacking, but the prediction is consistent with natural data collected to date. These and other examples will be examined in this presentation as a means of enhancing one's stable isotope fractionation acumen.