Temperature Dependence of Equilibrium Fractionation Factors: Insights from *ab initio* and NRIXS

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Equilibrium fractionation factors provide the framework through which natural stable isotope variations are interpreted [1]. Several approaches can be used to estimate equilibrium fractionation factors (or β-factors) [2]. One is to run laboratory experiments in which coexisting phases reach or approach equilibrium, and to then measure the isotopic compositions of these phases. Another is to use *ab initio* approaches to estimate those β-factors. Finally, for some elements, one can use the method of Nuclear Resonant Inelastic X-ray Scattering (NRIXS). The equilibration experiments are often limited to a few experimental data points and rely to temperature extrapolations beyond the experimental range to apply the measured β-factors to conditions relevant to natural systems. At high temperature, the extrapolation is relatively straightforward as the β-factors simply scale as $1/T^2$. At lower temperatures, the situation is often more complicated and a commonly used approach is to write the β-factors as the sum of even powers of the inverse of the temperature; $1000 \ln \beta = A/T^2 + B/T^4 + C/T^6$. This formula can be obtained by expanding the reduced partition function ratio in a Bernoulli series [3] or by using the kinetic energy [4]. Experimental determinations have insufficient precision and accuracy to derive meaningful coefficients in such a polynomial fit.

I will show how the temperature-dependence of the β-factors can be well approximated by a function with a single parameter (corresponding to the mean force constant of the chemical bonds) [5]. The exact functional form of this one-parameter formulation can be improved by supplementing lab experiments with NRIXS and *ab initio* data on a range of phases. I will apply this approach to iron isotope systematics, which has been the focus of many studies by NRIXS and *ab initio* techniques. A single temperature anchor is sufficient to extrapolate β-factors to a wide range of temperatures.

References: [1] Teng F.Z. et al. (2017) RiMG 82, 1-26. [2] Shahar et al. (2017) RiMG 82, 65-83. [3] Dauphas et al. (2012) GCA 94, 254-275. [4] Polyakov et al. (2005) GCA 69, 1287-1300. [5] Dauphas et al. (2017) RiMG 82, 415-510.