Ab Initio and Experimental Studies of Equilibrium Isotopic Fractionation in Aqueous Ferric Chloride Complexes

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Both iron and chlorine are ubiquitous in natural systems, but not much is known about isotopic fractionation among ferric chloride complexes. To determine the extent of this fractionation, we did integrated theoretical and experimental studies of fractionation among the aqueous ferric chloride complexes: $Fe(H_2O)_6^{3+}$, $FeCl(H_2O)_5^{2+}$, $FeCl_2(H_2O)_4^{+}$, $FeCl_3(H_2O)_3$, $FeCl_3(H_2O)_2$, $FeCl_4^{-}$, $FeCl_5H_2O^{2-}$, $FeCl_5^{2-}$, $FeCl_6^{3-}$.

We developed four sets of *ab initio* models (UHF and modified DFT with different basis sets) for each complex. All sets of models showed a linear decrease in the isotopic fractionation factor as the number of Cl^{-} ions per Fe^{+3} ion increased, with slopes -0.8‰ to -1.0‰ per Cl^{-}, depending on model. At 20°C, 1000 ln $\beta_{56\text{-}54}$ (relative to a dissociated Fe atom) values ranged from 8.93 to 9.73‰ for $Fe(H_2O)_6^{3+}$, 8.04 to 9.12‰ for $FeCl(H_2O)_5^{2+}$, 7.61 to 8.73‰ for $FeCl_2(H_2O)_4^{+}$, 7.14 to 8.25‰ for $FeCl_4^{-}$, and 3.09 to 4.41‰ for $FeCl_6^{3-}$.

To test these models, we mixed two series of low pH solutions of ferric chloride (total Fe = 0.08M and 0.17M) with total chlorine = 0 to 5M. Each solution equilibrated in the presence of immiscible diethyl ether. Only $FeCl_4^{-}$ dissolves in the ether phase. $\Delta Fe_{56\text{-}54} = \delta^{56}Fe$ (total Fe remaining in aqueous phase) - $\delta^{56}Fe$ ($FeCl_4^{-}$ in ether phase) was determined for each solution via MC-ICPMS analysis.

Relative amounts of each complex for each experiment were calculated from a speciation model and then used with the *ab initio* values to calculate the theoretical $\Delta Fe_{56\text{-}54}$ for each experiment. ($\delta^{56}Fe_{aqueous}$ equals the sum of $\delta^{56}Fe$ of each complex times its fractional portion of the whole.) According to the speciation model, Fe^{+3} dominates for $[Cl^{-}]<0.75M$; $FeCl^{+2}$ for $[Cl^{-}]<1.9M$; and $FeCl_2^{+}$ for $1.9M<[Cl^{-}]<5M$.

Theoretical values of $\Delta Fe_{56\text{-}54}$ for each *ab initio* model sets were compared to the experimenal $\Delta Fe_{56\text{-}54}$ values. Both the experimental data and the theoretical models show the same downward trend: $\Delta Fe_{56\text{-}54}$ is highest for low chlorinity where $Fe(H_2O)_6^{+3}$ is the dominant species and lowest at high chlorinity where $FeCl_2(H_2O)_4^{+1}$ is dominant. The theoretical models predict ~0.5‰ to 0.7‰ decrease in $\Delta Fe_{56\text{-}54}$ (depending on the model) for the range of chlorinity studied (0.5M to 5M). The experimental $\Delta Fe_{56\text{-}54}$ ranged from ~1‰ at $[Cl^{-}]=0.5M$ to 0.3‰ at $[Cl^{-}] = 5M$.

The experimental results are in good agreement with the theoretical predictions, suggesting the existence of equilibrium isotopic fractionation among aqueous ferric chloride complexes and a decrease in $^{56}Fe/^{54}Fe$ as the number of Cl^{-} ions per Fe^{3+} ion increases.