Iron isotopic fractionations between species in solution – from ab initio quantum chemistry calculations

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Theoretical approaches have been used on determining the Fe isotopic fractionations recently. Such as Schauble et al. (2001) used semi-empirical method "MUBFF" to predict the Fe isotopic fractionations between the ferric and ferrous Fe in solution and in minerals, although the results were not convincing enough. Anbar and Spiro groups (2004, 2005) later used a DFT method with PCM continuum model to calculate the fractionation between $Fe^{3+}(H_2O)_6$ and $Fe^{2+}(H_2O)_6$ and got a much better result. Because the geologically important Fe species in the solution include those with Cl^- and OH^- ligands, we therefore use B3LYP/6-311G* level calculations coupled with water-droplet method to investigate the Fe isotope fractionations between hydrous $Fe^{III}Cl^{2+}$, $Fe^{III}Cl_2^+$, $Fe^{III}Cl_3$, $Fe^{II}Cl^+$, $Fe^{III}(OH)^{2+}$, $Fe^{II}(OH)^+$, etc.. Several mineral fragments (e.g., the fragment of Ferrihydrite）also have been studied by the same way. The results can help people to understand the possible Fe fractionations during the Fe migration processes.

Several interesting points have been found :

(1) The RPFR value of hydrous $Fe^{III}(OH)^{2+}$ is just slightly smaller than that of $Fe^{3+}(H_2O)_6$; the RPFR value of hydrous $Fe^{II}(OH)^+$ is also just slightly smaller than that of $Fe^{2+}(H_2O)_6$. This means the Fe fractionations between the ferric and ferrous Fe will be almost the same for a quite large range of pH conditions.

(2) The RPFR values of Fe-Cl species are obviously smaller than those of pure Fe-aqua complexes (i.e. $Fe^{3+}(H_2O)_6$ or $Fe^{2+}(H_2O)_6$). This means if the Fe (ferric or ferrous) migrates away as Fe-Cl complex, it will become lighter.

References
[1] Jarzecki, A. A., et al.(2004) JPCA **108,** 2726-2732.
[2] Anbar, et al.(2005) GCA **69**, 825-837.