Iron isotope fractionation between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$

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We are investigating equilibrium fractionation between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ using density functional theory (DFT) as an *ab initio* method to predict vibrational frequencies of isotopically-substituted complexes and, hence, equilibrium fractionation factors. Johnson *et al.* (2002) reported an experimentally-determined $^{56}Fe/^{54}Fe$ fractionation factor of $1000\ln\alpha = 2.75 \pm 0.15$ ‰. This is ~50% smaller than predicted theoretically by Schauble *et al.* (2001) using a modified Urey-Bradley force field (MUBFF) model. Unlike DFT-based calculations, the MUBFF method requires as input data on vibrational frequencies, correctly assigned to specific fundamental modes, for one isotopomer of each complex. The MUBFF method also makes simplifying assumptions about molecular symmetry and does not account for interactions with solvent molecules.

The DFT calculations reveal that all fundamental IR-active vibrations with frequency < 1000 cm^{-1} are sensitive to iron isotope substitution. This includes 15 and 18 fundamentals for the ferric and ferrious complexes, respectively. Most significantly for isotopic predictions, the DFT calculations predict vibrational frequencies for the ferric complex that differ from assigned spectroscopic bands. These theoretical predictions are considered more robust than inferences based on obervations, prompting a revision of vibrational assignments.

The result is a significant decrease in the magnitude of the reduced partition function ratio of $Fe(H_2O)_6^{3+}$. Hence, we predict $1000\ln\alpha = 2.49 – 2.95$ ‰ at 22°C between $Fe(H_2O)_6^{2+}$ and $Fe(H_2O)_6^{3+}$ for a range of model cases. The good agreement between these predictions and the findings of Johnson *et al.* (2002) increases confidence in the experimental results, which were recently questioned (Bullen *et al.*, 2003). These findings also suggest that DFT calculations can be used to predict the magnitude of isotope effects not yet determined experimentally.

References

Bullen *et al.* (2003) *Earth Planet. Sci. Lett.* **206:** 229-232
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Mantle heterogeneity, stratified convection and the origin of plumes.

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The only chondritic material isotopically consistent with the Earth mantle and Redox-consistent with the Earth as a whole is also the most remote in composition from that used by the average Earth modelist. Its composition implies that the lower mantle is chemically significantly different from that of the upper mantle, with a higher Si/Mg ratio. Schematically it is very close to pure Fe-Mg perovskite. It is also distinctly poorer in radioactive elements than the primitive upper mantle.

Hence the density contrast between both mantles has a strong chemical component which has stabilized the two-level convection mantle inherited from the earth's formation time, the great impact and core formation.

From outgassing features it appears that the lower and upper mantles initially had essentially equal masses, whose frontier is witnessed by the geophysical indicators observed around 1000 kilometers depth.

The 650 kilometers discontinuity is only a phase transition limit, whose presence strongly impedes the convection in the upper mantle and helps develop transition zone characteristics in the region between 650 and 1000-1100 km depth.

The last important feature is the necessary presence of oxygen in the core to explain the density contrast between liquid and solid core. This iron oxide transport has generated iron concentration heterogeneities throughout the mantle and particularly between the lower mantle and the D" zone.

Hence there are two long-lasting mantle zones from where hot spot volcanism can originate:

-The D" zone, which can dynamically generate big bodies and is probably the source of flood basalts, poorer in Mg and richer in silica and iron.

-The 650-1000 kilometers transition zone, which can be the source of OIB volcanism.