Quantum mechanical insights on controls of Fe isotope fractionation

S.D. DOMAGAL-GOLDMAN[1]* AND J.D. KUBICKI[1,2]

[1]Deptartment of Geosiences,
The Penn. State Univ., University Park, PA 16802
(*correspondence: sgoldman@geosc.psu.edu)
[2]Earth and Environmental Sciences Inst.,
The Penn. State Univ., University Park, PA 16802
(kubicki@geosc.psu.edu)

We will present Molecular Orbital/Density Functional Theory (MO/DFT) calculations for a number of aqueous Fe-containing complexes, and use the results of these calculations to gain insights about controls on Fe isotope fractionations in common natrual and laborartory settings. Specifically, we will compare predictions of fractionation factors to predictions of structural and electronic features for these molecules. These comparisons will be used to determine the degree to which covalent bonding, coordination number, molecular mass, Fe association constant, oxidation state, and ligand charge affect the equilibrium Fe isotope fractionation factor of a complex.

The results we will present indicate that the effects of different molecular properties on the fractionation factor can be viewed through the lens of molecular geometry. The average lengths of the bonds made with the Fe atom and the coordination around the Fe atom act as controls on the fractionation factor, through which other properties have their effect. Consider, for example, the redox state of the Fe atom, which exhibits the largest influence on the fractionation factor of a complex. The reason for this dominant influence is the sizeable changes to bond length (and, therefore, bond strength) that result from changes to the oxidation state of the Fe atom. A secondary impact that metallic charge has on the fractionation factor is through changes in the coordination about the Fe atom: Fe(III)-bearing complexes are more likely to exhibit 6-fold coordination about the Fe atom, wheras Fe(II)-bearing complexes are more likely to exhibit 4- or 5-fold coordination about the central Fe atom. Thus, both the primary and secondary ways in which oxidation state affect fractionation factor can be explained and analyzed through consideration of impacts on the geometry of the Fe-ligand complex. Other properties that have a significant influence on fractionation factors can be treated in a similar manner.

This work will expand the set of molecules for which fractionation factors have been predicted, and will place previous experimental work in better theoretical context. We hope to use the conclusions form this work to motivate future studies of isotopic fractionations of other transition metals.

Study on water supply of palaeo lakes during pan-lake period of late Pleistocene in Alxa area, China

Z.H. DONG[1,2]* AND J.S. CHEN[2]

[1]State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Hohai University，Nanjing, China (*correspondence: donghzh@hhu.edu.cn)
[2]Research Academy of Hohai University, Nanjing210098, China

During late Pleistocene there was also palaeolakes in Alxa area. Present Tengger desert, Badain Jaran desert and Gurinai grassland used to be vast lakes. Based on the palaeo-lake deposits and landforms, and the primary analytic results on the typical sections, it was presumed that a vast continual fresh water lake existed in the Northwest area of Tengger desert in the period between 39~23 ka BP [1]. The paleaolake formed the that period is called Megalake Tengger.

Some researchers figured out that the form of paleaolakes in Alxa area attribute to large precipitation caused by local warm and wet climate. However, there are some doubtful points in above deduction. According to the isotopic study and hydro chemistry tests such as ^{14}C, $^{87}Sr/^{86}Sr$, δD, $\delta^{18}O$, T and CFC in Badain Jaran desert and adjacent area, it is proved that groundwater in Alxa area is recharged by water from Tibetan Plateau through deep fault [2].

Since there are groundwater discharge from deep faults to Alxa area, it is possible that the palaeo-lake water was not only from local precipitation but also from deep faults water transportation. Large volume of precipitation in Tibetan Plateau discharges to Alxa area and vast palaeo lakes came into being during late Pleistocene through a huge fault. This huge fault exist at least 42 ka and still water conductive till now.

There is actual geological evidence for the assumption of huge fault. Geological survey shows a series of fault systems such as Altun fault, Xigaze -Langshan fault and Zaduo-Yabulai fault existing in the north and east of Tibetan Plateau. It is a scientific question deserving further study to investigate whether surface and groud water in Tibetan Plateau supply the palaeo lake in Alxa area.

[1] H.C. Zhang *et al.* (1997) *Journal of Lanzhou University (Natural Sciences)* **33(2),** 87-91. [2] J.S.Chen *et al.* (2004) *Nature* **432**, 459-460.