

## Iron isotopic fractionations between species in solution—From ab initio quantum chemistry calculations

Y. LIU, M. TANG

Key Laboratory of Ore deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, 46 Guanshui Road, Guiyang, Guizhou 550002, PR China (lyun2003@yahoo.com)

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  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  and  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$  and got a much better result. Because the geologically important Fe species in the solution include those with  $\text{Cl}^-$  and  $\text{OH}^-$  ligands, we therefore use B3LYP/6-311G\* level calculations coupled with water-droplet method to investigate the Fe isotope fractionations between hydrous  $\text{Fe}^{\text{III}}\text{Cl}_2^{2+}$ ,  $\text{Fe}^{\text{III}}\text{Cl}_2^+$ ,  $\text{Fe}^{\text{III}}\text{Cl}_3$ ,  $\text{Fe}^{\text{II}}\text{Cl}^+$ ,  $\text{Fe}^{\text{III}}(\text{OH})^{2+}$ ,  $\text{Fe}^{\text{II}}(\text{OH})^+$ , 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 RPFRR value of hydrous  $\text{Fe}^{\text{III}}(\text{OH})^{2+}$  is just slightly smaller than that of  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$ ; the RPFRR value of hydrous  $\text{Fe}^{\text{II}}(\text{OH})^+$  is also just slightly smaller than that of  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ . 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 RPFRR values of Fe–Cl species are obviously smaller than those of pure Fe-aqua complexes (i.e.,  $\text{Fe}^{3+}(\text{H}_2\text{O})_6$  or  $\text{Fe}^{2+}(\text{H}_2\text{O})_6$ ). This means if the Fe (ferric or ferrous) migrates away as Fe–Cl complex, it will become lighter.

### References

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## Coral REE characters as an indicator of sea level rise in the Xigong waters, Hong Kong

YI LIU<sup>1</sup>, ZICHENG PENG<sup>1</sup>, GANGJIAN WEI<sup>2</sup>, P.O. ANG<sup>3</sup>,  
JIANFENG HE<sup>1</sup>, GUIJIAN LIU<sup>1</sup>

<sup>1</sup>School of Earth and Space Science, University of Science and Technology of China, Hefei 230026, China

<sup>2</sup>Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China

<sup>3</sup>Department of Biology, the Chinese University of Hong Kong, Hong Kong, China

High resolution records of the rare earth elements (REE) from 1991 to 2002 in the *Porites* coral, from the Xigong waters (22°20'N, 114°16'E), Hong Kong, located at the west coast of Pearl River Estuary, have been determined using inductively coupled plasma mass spectrometry. The distribution pattern of REE in the coral is similar to that in the seawater with the characters of Ce negative anomaly and heavy REE enrichment on the basis of normalization by use of a shale in Post-Achaean average Australian sedimentary rock (PAAS). The REE contents in the coral from Hong Kong are much higher than that from the other areas, except the corals from Misima Island, Papua New Guinea, where the REE contents are affected by an open-cut gold mining. However, the high REE contents in the Hong Kong coral are a direct response to high REE contents in the Pearl River and nearby surface sedimentary deposit, rather than to anthropogenic impacts.

Moreover, the decreasing trend of annual REE contents in the Hong Kong coral is very apparent, with severer Ce negative anomaly and heavy REE enrichment, from 1991 to 2002. The REE contents in the coral are significantly negatively correlated with sea level values ( $R = -0.7 \sim -0.9$ ), and the heavy REE linear correlation coefficients are much higher than the light REE ones. These results are associated with sea level rising, caused by globe warming, polar ice melting and more important by decadal warming of upper seawater of the South China Sea in 1990s. The rising speed of sea level in Hong Kong is as high as 13.5 mm/a, which is almost six times of the globe average. When the sea level is quickly rising, the terrestrial REE influence to the Hong Kong coral is being reduced.

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