

## Mass-independent isotope effects in chemical exchange reactions

# Toshiyuki Fujii[1]

[1] KURRI, Kyoto Univ.

<http://hlweb.rii.kyoto-u.ac.jp/npc-lab/>

The classic theory of stable isotope fractionation in chemical exchange reactions has been established by Bigeleisen, Mayer, and Urey in 1947. The theory was based on the difference of molecular vibrational energies of isotopomers that are proportional to the respective masses, and hence, results in mass-dependent isotope effect only. In 1996, this conventional mass-dependent theory has been expanded by Bigeleisen to include a mass-independent term named the nuclear field shift effect. The nuclear field shift is an isotope shift in orbital electrons, which results from the isotopic difference in nuclear size and shape. The new equation defined by Bigeleisen (at a constant temperature) can be simply expressed as,  $\ln \alpha = \Delta(r^2)A + (\Delta m/m)B$ , where  $\alpha$  is the isotope separation factor,  $\Delta(r^2)$  isotopic difference in mean-square nuclear charge radius,  $\Delta m$  difference between isotopic masses  $m$  and  $m'$ .  $A$  and  $B$  are scaling factors of the nuclear field shift effect and the conventional mass effect, respectively. Since this new theory was presented, the mass-independent isotope fractionation of various elements, e.g. Ti, Cr, Ni, Zn, Sr, Zr, Mo, Ru, Cd, Te, Ba, Nd, Sm, Gd, Yb, and U, found in chemical exchange systems has been successfully explained as the nuclear field shift effect.

We demonstrated on several elements (Cr, Mo, Ru, Cd, and Te) the existence of the mass-independent isotope fractionation in laboratory experiments with a ligand exchange system or a redox system. The isotope ratios were analyzed by multiple-collector inductively coupled plasma mass spectrometry with a typical precision of less than 100 ppm. For each element, obtained isotope fractionation factors showed mass-independent property, which was explicable with the nuclear field shift theory. These results suggest that the isotope fractionation chemically created in the nature would have mass-independent property due to their nuclear radii. We subsequently set out to compare the prediction of Bigeleisen's (1996) theory with the isotopic anomalies found in meteorites ('FUN inclusions' of Allende, carbonaceous chondrites, or ordinary chondrites). Some of these anomalies are clearly inconsistent with nucleosynthetic effects (either *s*- or *r*-processes), and for these, the nuclear field shift theory fitted extremely well. In meteorites, the nuclear field shift effect may originate both during condensation/evaporation processes in the nebular gas and during the metamorphism of the meteorite parent bodies. The isotope exchange reactions between chemical species which have been generated in the condensation/evaporation processes and metamorphism may have been affected by the nuclear field shift.