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Fractionation of Heavier Stable Isotopes in Planetary Processes

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Investigation of the light stable isotope abundances, particularly those of H, C, N and O, have provided over many years insights into fundamental solar nebular and planetary processes. Natural fractionations of heavier stable isotopes, such as those of the transition metals, are now also being recorded, due in large part to the introduction of multiple-collector plasma source mass spectrometry (MC-ICPMS). In this laboratory, various MC-ICPMS techniques are established for isotope ratio measurements of Mg (24, 25, 26), Ca (42, 44), Fe (54, 56, 57), Cu (63, 65) and Zn (64, 66) in both inorganic and biological materials. These techniques are able to resolve isotope variations at the ε (part per 10,000) level at 95% confidence. In this report we focus on the mass fractionation of transition metal isotopes. Transition metals such as Fe, Cu and Zn, are all biologically utilised, and have different volatilities and redox states. The variations of stable isotopes of these elements are expected to provide new insights into processes such as occurred in the solar nebular, during planetary accretion and evolution, as well as those linking inorganic and biological chemistry in low temperature environments. Two parallel approaches are used to study these isotope systems, namely investigation of the isotope variations in natural systems and experimental documentation of the mass fractionation processes. Samples ranging from marine, terrestrial to extraterrestrial materials have been investigated in some detail. Overall variation of more than 20 ε units are observed in ^{57}Fe/^{54}Fe and ^{65}Cu/^{63}Cu, and over 10 ε units in ^{66}Zn/^{64}Zn ratios. These variations are more than 20 times the analytical precision achieved, and demonstrate the potential offered by these isotope systems in the studies of geochemistry, cosmochemistry and oceanography. As the isotopes of transition metals represent almost completely unexplored systems, applications of these isotopes require an understanding of mass fractionation mechanism. A series of experiments have been carried out to investigate the processes which induce isotope fractionation of transition metals. Biologically induced mass fractionation has been investigated by measuring Fe-, Cu- and Zn-proteins separated from cultured yeast and *E. Coli*. Consistent with our knowledge of the behaviours of C, N and other stable isotopes, the lighter isotopes of transition metals are preferentially partitioned into biological materials. Up to 8 ε units per amu fractionation has been observed during one-step fractionation process. In the redox experiments, Fe(II) was separated from Fe(III) by ion exchange chromatography after it complexed with 2,2'bipyridine. The results show systematic heavy isotope enrichment in the Fe(II) portions, and fractionation of up to ~80 ε units in ^{57}Fe/^{54}Fe ratios has been observed between the two species. The observation suggests that natural fractionation may be large, particularly where variability in redox states of Fe and Cu are present.