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Stable isotope study using Fe: implication to understand the Fe-biocycles in marine environment

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Iron is one of the most important inorganic nutrients for almost all plants and animals. For marine organisms, because of very low concentration range of Fe ($<10^{-7}$ wt%) in the seawater, intake efficiency of Fe could become very high to avoid possible loss of many biochemical functions associated with Fe. This is well demonstrated by the small changes in the Fe isotope ratios ($^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$) among the marine organisms of various trophic levels (TL) (e.g., plankton, shrimp, tuna : Jong et al., 2007; Bergquist and Boyle, 2006). This lack in the changes in the Fe isotope ratios can be explained by the high-intake efficiency of Fe from the dietary foods. This is contrasting with those for the land organisms. For land organisms, the $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios vary significantly with the increase of the trophic level (Walczyk and Blankenburg, 2002, 2005). This could be explained as reflecting the large isotope effects on Fe isotopes, mainly due to the low intake-efficiency of Fe. In fact, availability of Fe for land organisms would be much higher than that for marine organisms, because Fe concentrations in the most rocks, minerals or soils would be much greater than that in the seawater. However, the intake efficiency would not be a major source of the changes in the Fe isotope ratios. Chemical form or oxidation status of Fe would also affect be magnitude of isotope effect on Fe. Moreover, it should be noted that the Fe bio-cycle can not be evaluated only by the traditional trophic level, defined by the $^{13}C/^{12}C$ and $^{15}N/^{14}N$ ratios, which should reflect the food chain of the organic substances, such as amino acids or proteins. This suggests that the conventional trophic level did not reflect the food chain of Fe. To investigate this, we have measured the $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ for series of marine organisms, especially for higher trophic level animals.

In this presentation, *Peponocephala electra* (n=23; TL=4.3), *Thunnus alalunga* (n=7; TL=4.0), *Thunnus obesus* (n=1; TL=4.0), *Kajikia audax* (n=1; TL=4.0), *Berryteuthis magister* (n=5; TL=3.4), and *Octopus longispadiceus* (n=2; TL=3.3) were subsidized to the Fe isotope ratio analysis. After the chemical decomposition and chemical separation procedures, the $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios were measured by the multiple collector-ICP-mass spectrometer (MC-ICP-MS). The measured $^{56}Fe/^{54}Fe$ and $^{57}Fe/^{54}Fe$ ratios varied significantly from those for lower trophic level organisms. Several important features of the Fe isotopes for marine organisms could be derived from the present results. The changes in the $^{56}Fe/^{54}Fe$ isotopes could be explained either by the poor intake efficiency of Fe from the dietary foods, or by the changing chemical form of Fe in the dietary foods for the marine organisms of higher trophic levels. If in the case that the Fe was adsorbed as a heme-Fe (Fe(II)) from the dietary foods, the magnitude of the isotope fractionation would be smaller than that found in adsorption of non-heme Fe (e.g., Fe (III)). This suggests that the major source of Fe for higher trophic animals would be non-heme Fe. Another possible cause of changes in the $^{56}Fe/^{54}Fe$ ratio would be originating from the definition of the trophic level of the marine organisms. This suggests that the food-chain for the inorganic nutrients should be defined by the separate definitions. The details of the mechanism in the variation of the $^{56}Fe/^{54}Fe$ ratios for the marine organisms will be discussed in this presentation.

Keywords: stable isotope of iron, iron biocycle, marine organisms, multiple collector-ICP-mass spectrometry, trophic level