Zr, Nb, Hf, Ta, and W in the northwest Pacific Ocean

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Our knowledge on chemical oceanography of the 2nd and 3rd transition series metals is still limited. Here we report an improved method for the determination of Zr, Nb, Hf, Ta, and W in seawater and their distributions in the northwest Pacific Ocean.

Zr, Nb, Hf, Ta, and W in seawater were collected with a column of fluoride-containing metal alkoxide glass immobilized 8-hydroxyquinoline (MAF-8HQ, Fujishima et al., 2001) and eluted with 0.5 M HNO_3-10^{-3} M oxalic acid. The concentrations of the metals in the eluate were determined by ICP-MS. We have decreased the procedure blank through selection of materials and improvement of cleaning and concentration procedures. For example, the procedure blank of Nb decreased from 0.95 pM to 0.03 pM.

Dissolved Zr and Hf showed a recycled-type vertical profile in the northwest Pacific. The concentrations in deep water were ~330 pM for Zr and ~1.2 pM for Hf. Dissolved Nb and Ta showed a more uniform profile and their concentrations in deep water were ~3 pM and ~0.02 pM, respectively. The concentrations substantially increased in an upper part of a water column in the transition zone between the subarctic gyre and the West Wind Drift. Dissolved W showed a uniform profile (~50 pM) with a small surface maximum. The observed concentrations for Hf and Ta were significantly lower than those previously reported by us (Sohrin et al. 1998). It seems the previous data were influenced by contamination.

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Steryl chlorin ester formation by freshwater crustaceans

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Steryl chlrin esters (SCEs), transformation products of chlorophyll *a* or *b*, have been observed in a number of marine and lacustrine sediments[1]. SCEs are formed during the grazing of phytoplankton by zooplankton and are egested in fecal pellets[2]. Sterols have been known as indicators for phytoplankton, and the composition of SCEs sterols in sediments have been considered to reflect well the composition of sterols in precursor phytoplankton. Furthermore SCEs have been considered to be good paleolimnological indicators of phytoplankton community as SCEs are remarkably stable in sediments.

In a long sediment core obtained by the "Baikal Drilling Project", we found that photosynthetic pigments preserved in the sediment layers representing down to 6.5Ma were mainly SCEs[3]. Although the observed various patterns in HPLC chromatograms were due to different sterol compositions of SCEs, their relation with the original composition of sterols in phytoplankton has not been sufficiently understood, especially for diatoms.

We examined formation of SCEs by freshwater crustaceans in laboratory feeding experiments. Freshwater crustaceans (*Daphnia magna*, *Asellus hilgendorfi*) were fed on a culture of green algae (*chlorella sp.*, *scendesmus sp.*, *stigeoclonium sp.*). *Asellus* was also fed on phytoplankton concentrated from pond water where diatoms were dominant. Sterols of SCEs in collected fecal pellets were determined by GC/MS after hydrolysis of SCEs separated by HPLC and were compared with those of dietary algae. The sterols of SCEs apparently underwent biotransformation by the crustaceans which are incapable of sterol biosynthesis but convert phytosterols to cholesterol[4]. Cholesterol was most abundant in the SCEs, but was scarce in the dietary algae. The sterols of SCEs other than cholesterol are considered to be resistant to biotransformation to cholesterol. The biotransformation of algal sterols before incorporation into SCEs should be taken into acount when one tries to deduce phytoplankton community structure from SCEs composition.

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