Behaviors of incompatible elements in the western North Pacific Ocean

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Incompatible elements, such as Zr, Hf, Nb, Ta, Mo and W [1], have a great interest in the field of geochemistry. In contrast to their intensive study in the solid-terrestrial environment, their study in the hydrospheric environment were scarce. Here we present determination of these six elements at K1 (51°N, 165°E), K2 (47°N, 160°E) and 35N (35°N, 160°E) stations in the western North Pacific Ocean. We found that each twin-elements pair (Zr/Hf, Nb/Ta and Mo/W) has a unique behavior in seawater. Furthermore, Zr/Hf show a potential to be used as a water masses tracer. Different water masses of Western North Pacific Central Water (WNPCW), North Pacific Intermediate Water (NPIW), Pacific Subarctic Upper Water (PSUW) and Pacific Deep Water (PDW) give a unique set of Zr/Hf and Sigma-θ [2]. The four water masses are clearly identified in Figure 1.

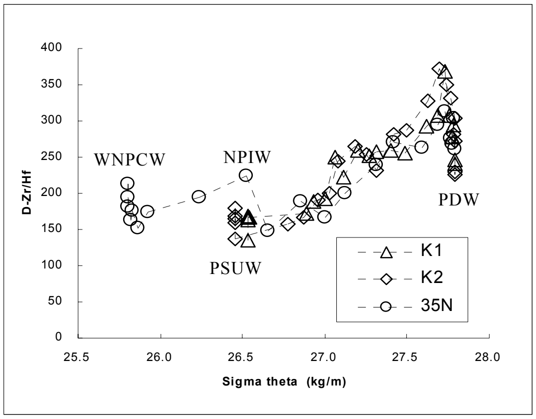

Figure 1: Plot of Dissolved-Zr/Hf mole ratios to Sigma-θ.

We also found that although the Zr/Hf, Nb/Ta and Mo/W ratios lies in a narrow range in most rocks, the ratios start to become fractionated when the metals are introduced into the hydrosphere. The Zr/Hf, Nb/Ta and Mo/W ratios generally increase in the order continental crust < river water < coastal sea < open ocean.

[1] Rudnick & Gao (2005) The crust, in *Treat. Geochem.*, Elsevier. [2] Firdaus *et al.* (2008) *J. Oceanogr.* **64**, 247-257.

Two-dimensional isotope fractionation approach (TDIFA) for elucidating benzene and toluene biodegradation pathways

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Recently, the combined carbon and hydrogen isotope fractionation approach has emerged as a powerful tool for the characterization of reaction mechanisms relevant for the removal of organic pollutants. Here, we applied this two-dimensional isotope fractionation approach (TDIFA) in order to differentiate benzene and toluene biodegradation pathways under oxic and anoxic conditions in laboratory experiments. Carbon as well as hydrogen enrichment factors (εC, εH) varied for the specific pathways and degradation conditions, respectively, so that from the individual enrichment factors only limited information could be obtained for the identification of biodegradation pathways. However, using the slope derived from hydrogen vs. carbon isotope discriminations or the ratio of hydrogen to carbon enrichment factors ($\Lambda = \Delta H/\Delta C \approx \varepsilon H/\varepsilon C$), degradation mechanisms could be distinguished.

Although experimentally determined Λ-values partially overlapped, specific ranges could be determined for different benzene biodegradation pathways. Λ-values were < 2 for dihydroxylation, between 7 and 9 for monohydroxylation and > 17 for anaerobic degradation. Moreover, variations in Λ-values suggest that more than one reaction mechanism exists for benzene monohydroxylation as well as for anaerobic benzene degradation.

For toluene biodegradation, the highest Λ-value was estimated for methyl monohydroxylation ($\Lambda = 53$). The lowest value was observed for ring dihydroxylation ($\Lambda < 2$). Λ-values for organisms attacking toluene under anoxic conditions by benzylsuccinate synthase were significantly different and ranged from $\Lambda = 4$ for a phototrophic strain, $\Lambda = 11 - 15$ for nitrate reducers to $\Lambda = 27 - 28$ for sulfate reducers.

Our results show that TDIFA has great potential to elucidate biodegradation pathways of pollutants in field and microcosm studies.