Sourcing metals in bivalves using combined Pb, Zn and Cd isotopic compositions

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Lead, Zn and Cd isotopic compositions (MC-ICP-MS), elemental concentrations (HR-ICP-MS) and their relationships are used jointly in bivalves to identify their natural and anthropogenic sources. Bivalves (oysters and mussels) from coastal B.C. Canada, France and the USA are included in this study.

B.C. oysters with relatively low Pb concentrations (0.046-0.224 ppm dry tissue) have Pb isotopic compositions consistent with mixing of Canadian anthropogenic emissions and background Pb (Chinese loess) [1]. Although Cd concentrations are relatively high in B.C. oysters (4.6-12 ppm dry tissue), Cd and Zn isotopic signatures are consistent with those of North Pacific seawater. This suggests that the high [Cd] results from a natural oceanographic phenomenon and is not related to anthropogenic contamination.

Bivalves from France have Pb isotopic signatures consistent with industrial pollution as opposed to automotive. Oysters from the Gironde estuary show a marked decrease with time in Pb, Cd and Zn concentrations between 1987 and 2005. This is complemented by resolvable changes in their Pb isotopic compositions (a decrease in ^{208}Pb/^{206}Pb and increase in ^{206}Pb/^{207}Pb): Cd concentration decreases from 129 to 28.7 ppm, Pb from 34 to 3.1 ppm and Zn from 8351 to 3568 ppm. The observed change in Pb ratios indicates a shift toward natural Pb sources (pre-industrial sediments) [2]. Pb isotopes identify the dominant Pb source as polluted water from the Lot River, the local site of mining and smelting activities. The δCd and δZn values of oysters, from both 1987 and 2005, indicate smelting as the dominant Cd and Zn source. More insight into the source of high Cd and Zn is gained through the combined use of Pb isotopes. Bivalves, as bioaccumulators of metals, are used as indicators of bioavailable contamination in the marine environment and the isotopic compositions of these metals offer a tool to resolve unexplained variability in concentrations.

[1] Jones *et al.* (2000) *GCA* **64**, 1405-1416. [2] Sun (1980) *Philos T R Soc A* **297**, 409-445.

Geochemical behavior of Rare Earth Elements during chemical and physical weathering of granitic rocks, southwestern Japan

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The rare earth elements (REEs) contents of granitic rocks in Sannin district of southwestern Japan were determined to study the behavior of REEs during chemical and physical weathering. The weathering of the granite results in the mineral dissolution and precipitation. In this process, the REEs deplete with the dissolution of silicate minerals and then adsorb to the secondary minerals and some are carried out.

This study shows that the REE patterns of weathered granite in Sannin tend to show two patterns: LREE-enriched and HREE-enriched patterns. LREE-enriched samples containing high amounts of REEs occur in upper horizon of weatherd part, while HREE-enriched samples containing low amounts of REEs in lower horizon. The REE patterns and sequential extraction experiments indicate that the LREE dissolved and was retained by clay-rich soils wheareas HREE were dissolved not significantly and adsorbed by secondary minerals. LREE--enriched clay-rich fine grains of secondary minerals were accumulated physically on the surface. Eu- and Ce-anomaly is also obtained by the REE patterns of weathered granite soils due to the enrichement of K-feldspar which does not weather easily. Cerium is rapidly precipitated during weathering and retained with secondary minerals as insoluble CeO_2.