

## Rare earth elements in sulfides of submarine hydrothermal vents of the Atlantic Ocean

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REE distribution in 10 sulfides collected from Rainbow, Broken Spur and TAG hydrothermal fields on Mid Atlantic Ridge have been studied. All sulfides are enriched in LREEs with respect to HREEs. The REE distribution patterns for all samples from the Rainbow field show a positive Eu anomaly, which is similar to that observed in the hydrothermal fluids. Two samples from the TAG field and chalcopyrite from the Broken Spur field demonstrate the negative Eu anomaly. Only sphalerite from the TAG field exhibits small positive Eu anomaly. As compared to hydrothermal fluids from the corresponding fields, sulfides are about 10–100 times depleted in REEs. The REE content in sulfides of the Rainbow field does not depend on the mineral composition of the sample. Sulfides from the Rainbow field inherit the characteristic LREE-rich pattern of hydrothermal fluid. The similarity of REE patterns of fluid and sulfides suggests that all REEs in sulfides were derived from hydrothermal fluid.

By normalizing the REE content in sulfides to that in a fluid, we obtained REE fractionation during the formation of sulfide ores. Sulfides from the TAG and Broken Spur fields show LREE depletion with respect to HREE and exhibit the negative Eu anomaly. The latter is also typical for the Rainbow field. With decrease of radius from La to Lu, the relative REE accumulation in sulfides increases. The size of the ionic radius of REEs decreases from La<sup>3+</sup> to Lu<sup>3+</sup> and approaches the radius of Cu<sup>2+</sup>, Zn<sup>2+</sup> and Fe<sup>2+</sup>. The low distribution coefficient between sulfide and fluid for Eu<sup>2+</sup> may be explained by large differences in effective ionic radii of the crystal lattice (Cu, Fe, and Zn) and Eu. The distribution coefficients between sulfide and fluid for trivalent REEs in the TAG and Broken Spur fields range between 0.01 and 1, while the distribution coefficient for Eu is ten times lower. The distribution coefficients for trivalent REE and Eu in the Rainbow field reveal the same proportions, but are about ten times lower relative to the TAG and Broken Spur fields.

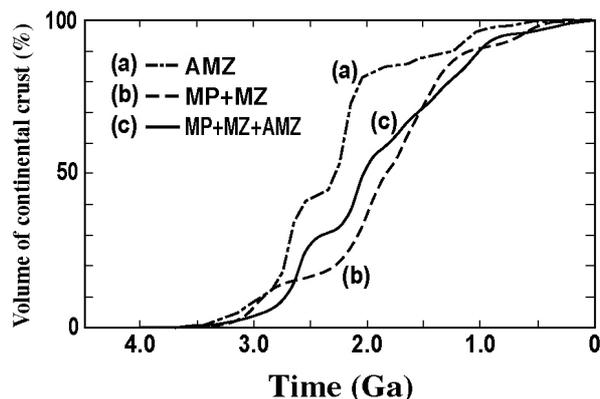
## Continental growth history of the river basin: Age distribution of detrital zircons from major rivers

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Alluvial sand of the mouth of large rivers is a mixture of the mineral grains from wide area within the river basin. It contains zircon together with predominant quartz. Zircon is known to be stable against chemical and physical weathering during fluvial transportation. Therefore, it is possible to obtain the age data directly from analysis on zircon without consideration of the effect of weathering. In a very large river of continental extension, river mouth detrital zircon should represent a huge area, sometimes covering with the entire craton. The geochronological study of detrital river mouth zircon of main continental rivers could reveal the growth history of the continental crust. Moreover, the population of zircon ages could determine the timing of major magmatic events creating igneous rocks containing zircon in the river basin, thus provide information of crustal addition rates. This study presents partial results of such a worldwide research project, applied to Mississippi, Mackenzie, and Amazon River. To achieve the purpose, the authors adopted LA-ICPMS installed at Tokyo Institute of Technology that makes very fast analysis on the isotope data.

Continental growth curves were obtained by accumulating the age distribution of zircon analyses (Fig. 1). These curves show the voluminal transition of crust with time: (a) there was a constant crustal growth in 1.3–2.2 Ga, that occupies ~70% of Mississippi and Mackenzie area in North America, (b) two major crustal growth in 2.1–2.3 and 2.6–2.9 Ga, each ~35% occupation of Amazon area in South America, (c) three major crustal growth in 0.9–1.9, 2.3–2.5, 2.5–2.8 Ga, total set of three rivers.



**Figure 1.** Crustal growth curves in the fluvial basin: MP (Mississippi), MZ (Mackenzie), AMZ (Amazon).