Suppression of Zr, Nb, Hf, and Ta co-precipitation during HF digestion of Ca-rich geological materials

R. TANAKA, H. KITAGAWA, A. MAKISHIMA AND
E. NAKAMURA

The Pheasant Memorial laboratory, Institute for Study of the Earth's Interior, Okayama University at Misasa, Japan (ryoji@misasa.okayama-u.ac.jp)

We have developed a new technique for the precise and accurate determination of the concentrations of high field strength elements (HFSE) Zr, Nb, Hf, and Ta in calcium-rich geological materials (e.g. carbonatite, dolomite, and augite) by ICP-MS. In order to recover sufficient Nb and Ta from a rock sample to an analyzing solution, HF-decomposition and HF-dissolution method is required (Makishima et al., 1999). This method also has the advantage that matrix elements are reduced effectively by precipitating fluorides, which has enabled the analysis of common igneous rocks. However, for Ca-enriched samples, we found sufficient recovery of HFSE cannot be obtained in the analyzing solution in their method.

We have tested recovery yields of HFSE in the synthetic Ca-Mg-Al-HF system. When the Ca/(Ca+Al) molar ratio of the matrix composition was >0.5 and >0.8, 5-100 % of Zr and Hf and 5-75 % of Nb and Ta coprecipitated with fluoride, respectively. XRD analysis confirmed that the poor recoveries of HFSE were caused by incorporation of HFSE in fluorite (CaF_2). Other Ca-bearing fluoride minerals, however, do not coprecipitate HFSE. Hence, in order to suppress fluorite precipitation, we have developed an 'Al-addition method' to change the matrix solution into an appropriate composition. In this method, an Al solution is added prior to sample decomposition with HF.

By the Al-addition method, the HFSE concentration of carbonatite [Ca/(Ca+Al)=0.99] and augite [Ca/(Ca+Al)=0.69] were analyzed. Zr-Hf and Nb-Ta were analyzed by an isotope dilution method and by an external calibration curve method, respectively (Makishima et al., 1999). To ensure full recovery of Nb and Ta, the Ca/(Ca+Al) had to change to <0.7 for the carbonatite, but no Al-addition was required for the augite. On the other hand, when the Ca/(Ca+Al) was >0.4 for carbonatite and >0.3 for augite, recovery yields of Zr-Hf spike were always higher than that from samples, resulting in isotopic disequilibria between sample and spike. Lower recovery yields of Zr-Hf from the sample were caused by increasing Ca/Al in the HF-solution during sample decomposition, which would be controlled by decomposition rate. Therefore, it is necessary to suppress fluorite precipitation during HF decomposition not only to get the full recovery of Nb and Ta, but also to achieve Zr and Hf isotope equilibrium using the isotope dilution method.

Reference

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Sorption of rare earth elements by *Bacillus subtilis*

T. TANAKA,[1] Y. TAKAHASHI,[1] X. CHATELLIER,[2]
K. H. HATTORI,[3] AND D. FORTIN[3]

[1] Department of Earth and Planetary Systems Science, Hiroshima University, Hiroshima, Japan (takahasi@geol.sci.hiroshima-u.ac.jp)
[2] Geosciences Rennes, CNRS-University of Rennes 1, Rennes, France
[3] Department of Earth Sciences, Ottawa University, Canada

The behavior of rare earth elements (REE) in natural waters is important because relative abundances of REE provide information relevant to their sources. Many studies have shown factors affecting the behavior of REE, such as soluble complexes with a variety of ligands and the sorption on inorganic particulate matter. However, few studies have been conducted on the interactions between REE and bacteria, although the role of bacteria has been well recognized in the migration of trace elements. In this study, the sorption of REE onto *Bacillus subtilis,* a Gram positive bacterium, was examined. *B. subtilis* suspensions washed with 1.0 mM NaCl solutions were exposed to REE (initial concentration: 100 ppb each of REE) in PTFE vessels. REE contents in the aqueous phase separated by filtration (0.20 μm) was determined by ICP-MS. Sorption of REE on PTFE can be ignored below pH 6. The results summarized in Fig. 1 show that the bacteria preferentially sorb heavy REE (Tm, Yb, Lu) and the distribution coefficients (K_d) between bacteria and aqueous phase are greater at lower REE/bacteria ratio. The REE pattern of the distribution coefficients is very distinct. Such a REE pattern in geological material may be used as a signature of possible involvement of bacterial activities. The enrichment of heavy REE by *B. subtilis* was also enhanced at lower REE/bacteria ratio (i.e., a larger number of binding sites are available). This suggests that there are at least two binding sites onto the cell wall of *B. subtilis,* which are able to sorb REE. Such binding sites likely correspond to phosphate and carboxylate groups (e.g., Daughney and Fein, 1998). Our proposed interpretation is supported by the estimated REE pattern of distribution coefficients between bacteria and aqueous solution based on the complex-forming constants of REE with phosphoric acid and D-gluconic acid.

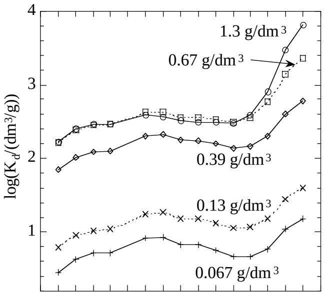

Fig. 1: Distribution coefficient (K_d) of REE between *B. Subtilis* and aqueous phase at various concentrations of bacteria (g/dm^3).

Reference

Daughney C. J. and Fein J. B., (1998), *J. Colloid Interface Sci.* **198**, 53-77.