

## Distributing behaviors of rare earth elements upon the formation of Na/K-REE double sulfates

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Sulfurous-acidic spring waters in the Manza hot spring area, Japan, show a wide variety of rare earth element (REE) compositions. Some show flat chondrite-normalized REE patterns similar to that of the bedrock of this area. The others show patterns depleted in light REEs (LREEs) although they were different from each other in details [1]. The depletion of LREEs in the REE pattern may be caused by the formation of alunite group minerals, which show the patterns enriched in LREEs. It is suggested that the enrichment of LREEs in alunite group minerals is associated with solubility of double sulfates of REEs and potassium [2]. We thus carried out (Na, K)-REE double sulfates synthesis experiments and examined salt-solution distributing behaviors of REEs upon the formation of the double sulfates.

REE sulfates solution was reacted with Na<sub>2</sub>SO<sub>4</sub> and/or K<sub>2</sub>SO<sub>4</sub> solution in PTFE sealed containers at designated temperatures for predetermined periods. We then separated the solution and precipitates by filtration, and analyzed REEs in the filtrates by the ICP-AES.

The experimental results reveal that the distributing behaviors of REEs upon the formation of the double sulfates are affected by the reaction temperature and the Na/K ratio. The formation of the double sulfates with Na was an endothermic reaction, while that with K was exothermic. The distribution patterns of REEs in Na-K mixed systems under some conditions could be reproduced by the combination of the distribution patterns observed in single systems of Na and K. Under other conditions, however, LREEs were precipitated more excessively than the prediction based on the combination of the single systems.

An application of the salt-solution distribution ratios of REEs to the REE composition of the spring waters with the flat REE pattern can reproduce the REE patterns depleted in LREEs found in other spring waters.

[1] Y. Kikawada *et al.* (2013) *Procedia Earth Planet. Sci.*, **7**, 428-431. [2] Y. Kikawada *et al.* (2004) *J. Radioanal. Nucl. Chem.*, **261**, 651-659.