Distributions of Rare Earth Elements in Japanese estuaries

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Introduction and Methods

Direct determination using ICP-MS for rare earth elements (REEs) in seawater, which are presumably present at less than the detection limit, is a difficult analytical task in the presence of seawater matrix. A simple and rapid method to separate and concentrate REEs in seawater was developed using a new chelating resin, NOBIAS chelate-PA1, which is a polyamino-polycarboxylic acid type resin. The resin was then used in an investigation of the geochemical behaviors of REEs in Japanese estuaries which are reported here.

Results and Discussion

The REEs were recovered at more than 90% for a pH ranging between 5 and 6 in spiked seawater samples which were diluted in a salinity value ranged from 0 to 34. Total procedural blanks for REEs for the present study were lower than 0.1 ppt. It was concluded that the chelating resin can be applied for the preconcentration of REEs in estuarine water samples.

The determined REE concentrations in the natural water samples indicated geochemical properties in the Japanese estuaries. These concentrations increased rapidly at low salinity (~1). Such a trend has been observed in some rivers [1, 2]. The increase in REEs concentrations was attributed to the salt-induced desorption from resuspended particles in river waters [3]. The concentrations of the REEs were constant at high salinity (>20) near the mouth of the rivers, indicating the removal of REEs during mixing in the estuary at a salinity value less than 20, as has been reported in other estuaries [2]. The REE concentrations slightly decreased with distance from the mouth of the rivers.

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[1] Nozaki *et al.* (2000) *GCA* **64,** 3975–3982. [2] Nozaki *et al.* *GCA* **64,** 3983–3994. [3] Elderfield *et al.* (1990) *GCA* **54,** 971–991.

Experimental study on the mechanism of metasomatism in the system between Scheelite↔Ferberite

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Experiments on metasomatism were carried out in the tungstates (scheelite and ferberite) - aqueous solutions ($Fe[NH_4]_2[SO_4]_2$ and $CaCl_2$) system. We changed duration (1 to 2016 hours), concentration of aqueous solution (0.01 to 1.0 mol/l) and temperature (130 to 170 °C). The starting materials were powdered sample (100 µm) and chipped sample (1.5×2.0×3.0 mm).

The peaks of ferberite and scheelite were detected from reacted samples by X-Ray diffraction analysis in the scheelite - $Fe[NH_4]_2[SO_4]_2$ and ferberite - $CaCl_2$ aqueous solution system, respectively. The metasomatism is easy to proceed as the concentration of the reaction solution is higher and the reaction temperature is higher. It is considered that the reaction rate occurring in initial stage was high due to the wide contact area between solution and unreacted material and the presence of fine particles on the surface of starting material which rapidly dissolved. The replacement textures were observed by SEM and reflected light microscope. SEM observation shows the euhedral crystal of scheelite formed in the ferberite - $CaCl_2$ aqueous solution system due to slow growing of the crystal.

Ferberite crystals grow toward the inside of starting material (scheelite) accompanying a lot of pores in the scheelite - $Fe[NH_4]_2[SO_4]_2$ aqueous solution system, since molar volume of ferberite (40.40 cm^3) is smaller than that of scheelite (47.05 cm^3). The tendency in the thickness variation of chipped sample with time could not be recognized in the metasomatism from scheelite to ferberite. The replacement texture is classified into the pseudomorphic replacement texture [1-3]. On the contrary, small amount of scheelite was precipitated on the surface of starting material (ferberite) in the ferberite - $CaCl_2$ aqueous solution system. The size of the sample increases with time so that the replacement texture grows not only toward the inside of samples but also on the surface of starting material. The texture is categorized into rim replacement texture.

[1] Edwards (1960). [2] Bastin (1969). [3] Craig & Vaughan (1981).