Rare earth and trace element biogeochemistry of white clam in off Hatsushima cold seepage

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In order to understand the control of the activities of biological communities over the seepage flow chemistry, and effect of biological and biogeochemical processes on oceanic chemistry, the white clams (*Calytogena soyoae*) collected from off Hatsushima cold seepage, western part of Sagami Trough, were measured for their trace element concentrations. Rare earth and other trace element concentrations of the clam in their organs, such as gills and foot were measured, and trace metal abundance of other specific coastal bivalves and biological community (e.g. octopus) were determined as a reference. The results permit us to discuss the varied concentration distribution and composition in different species and organs of the clam, and the fractionation between seepage fluids and the creature. The REE concentrations of different organs of the white clam show no significant differences with other species and communities. As compared with the bulk seawater, the organs of the clam show depletion in heavy REEs, indicating that the biological processes may fractionate the light and heavy REEs in seawater to some extents. The shale-normalized REE patterns showing no Eu anomaly suggest that the geochemistry of Hatsushima white clam crowed region is principally controlled by pore water and/or continental underground water, not by hydrothermal fluid. Alternatively, the REE compositions of the organs of the clam simply reflect the composition of the seepage water. Ho/Y ratios have the large variation compare with the bulk seawater, which agrree with the consideration that biological process fractionates Ho/Y ratio in coastal water and enriches Y in seawater.

Key word : REE, white clam, cold seepage, off Hatsushima

希土類および微量元素の生物地球化学
ー初島沖湧水域におけるシロウリガイを例にとってー

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本研究は熱水噴出孔・冷水湧出域など深海底の比較的還元的な環境に生息するシロウリガイを対象生物種として，海洋生物試料のICP質量分析法による希土類元素の測定に関する試料の前処理方法および分析の高感度化を検討した。また，生体の希土類元素濃度分布と海水の溶存希土類濃度（0.22μm 以下)との比較から，希土類をはじめとする多くの微量元素の海洋における分布と生物活動との関わりだけではなく，サンプリングされた海域の地球化学的特徴などを明らかにした。シロウリガイの希土類元素濃度には部位ごと（足やエラなど）に顕著な濃度差が見られ，Shaleで規格化した希土類パターンはいずれの部位においても中希土を富んだCeに正のアノーマリを持つ曲線を示した。また，Ho/Y 比は部位別の変化より各種二枚貝の間において大きく変動し，このことから，これまで問題となっていた海水で観測されるHoと Y の分別の一部は，生物の選択的な摂取／吸着過程で起こる可能性が大きいことが推測される。更に，他の海域の生物体の濃度との比較から，この海域のシロウリガイ群集の希土類はプレートの沈み込みに起因する熱水性の湧水ではなく，陸起源の地下水や間隙水の可能性が大きいと推測した。

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1. Introduction

Since cold seepage biological communities have been found in tectonically active subduction zones [e.g. off Oregon (Suess et al., 1985; Kulm et al., 1986a), off Peru (Kulm et al., 1986b), the Nankai Trough and Japan Trench (Pichon et al., 1987; Sibuet et al., 1988)] and in tectonically passive areas [e.g. Florida Escarpment (Paull et al., 1984), Louisiana slope (Kennicutt et al., 1985), Northern California (kennicutt et al., 1989), and the Laurentian Fan (Mayer et al., 1988)], their activities in association with their habitat have largely and increasingly concentrated interests of biologists and geochemists. The related studies show that such activities are due to support of microbial chemosynthesis which oxidizes dissolved compounds in a manner similar to that occurring in deep-sea hydrothermal communities (Cavanaugh et al., 1987; Childress et al., 1986). Recently, several studies investigated the chemistry of seep flow to understand the sources of the fluids, and their contribution to the oceanic chemistry (Sakai et al., 1987; Gamo et al., 1988; Tsunogai et al., 1996).

The cold seepage have been revealed in off Hatsushima located at western Sagami Bay (Fig.1), central Japan in 1984 by the submersible *Shinkai 2000*, which characterized in dense deep-sea biological communities dominated by the white clam *Calyptogena soyoae* (Okutani and Egawa, 1985). The clam communities stretch for 7 km along the foot of a steep escarpment off Izu Peninsula at water depths of 900-1200 m (Tanaka and Hashimoto, 1991). The area is located near the convergence front of the northern tip of the Philippine Sea Plate, which is subducting beneath the Eurasian and North American plates. Although a numerous of studies have become active around this region since 1986, most of previous works focused on biology, geology and physics, the geochemical data is extremely limited. For example, the source of the cold seep fluid is not well known depending on their various possibility, such as pore water in accreted sediments compacted by plate subduction, hydrocarbon in sediments and land-derived groundwater. In order to understand the control of the activities of biological communities over the seepage flow chemistry, and effect of biological and biogeochemical processes on oceanic chemistry, we collected the clam samples and measured concentrations of the trace elements, like rare earths and others, in their organs, gills and feet. The results permit us to discuss the concentration distributions and compositional variations in different organ of the clam, and the fractionation between seepage fluids and the creature.

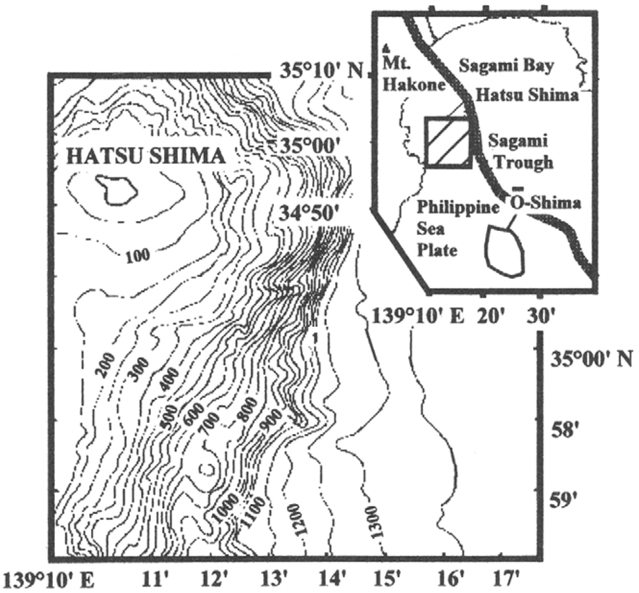

Fig. 1 Topographic map of the Hatsushima site in western Sagami Bay, central Japan, which is reproduced from the bathymetric chart (1:100,000) published by Japan Maritime Safety Agency in 1983. A broken line encircles the area of cold seepage, dominantly densified by white clam.

2. Sampling and Analytical method

The white clams, *Calyptogena soyoae* were collected by using the submersible R/V *Shinkai 2000* and an unmanned sampler *Dolphin 3K* of the Japan Marine Science and Technology Center (JAMSTEC), in 1991, 1994 and 1996. After collection, the clams were immediately stored in a freezer under -80ºC and transported to the laboratory on land. After defrozen and washed with Milli-Pure water, the freeze-dried (-30ºC) gills and feet were digested with super-high purity nitric and perchloric acids (TAMA PURE AA-100) for machine-analysis (Ishii et al., 1989). As a reference, the trace metal abundance of other specific coastal bivalve and biological community (e.g. octopus) were determined also.

The trace elements, such as cadmium, sodium, potassium, magnesium, cobalt, iron, molybdenum, strontium and nickel etc., were determined by using ICP-AES (Shimadzu ICPQ-1012W). Rare earth elements and Y were preconcentrated by Bio-Rad AG-50W-X8 cation exchange resin (100-200 mesh), and then introduced into

ICP-MS (Yokogawa PMS-2000) for concentration measurement. Radioactive yttrium (^{88}Y) was added to the sample solution as a yield monitor for the chemical procedure and indium was used as an internal standard for ICP-MS detection. The blanks of the entire procedure and reagents were ~1% for Y and HREEs, ~4% for MREEs, ~8% for LREEs except Ce (~15%). The analytical errors of 5 replicate measurements were about ± 6%, and the yield of REEs for the chemical procedure was quantitative (~ 90%).

3. Results and discussion

There is no an aged deterioration and almost no differences in the major and trace metal concentration factor patterns both in gills and feet (Fig. 2), showing the exceedingly high concentration factor ($>10^5$) in cadmium, iron, magnesium, phosphate and zinc compared with others, such as calcium, sodium and strontium (<10). Only cadmium concentrated one order higher in the white clam than other bivalve, which correspond to sulfur. It may be explained by the ecological and geochemical setting of the white clam. Peculiarly, the gills of these clams, contain bacteriocytes which are densely packed with prokaryotic cells of presumably symbiotic chemoautotrophic sulfur bacteria. It can be briefly described that sulfate, supplied from the overlying bottom water, is microbially reduced by the methane, which is supplied from the deeper layers to the sediments (Hashimoto et al., 1989). Clams take the microbial hydrogen sulfide by using their feet, which extend to a depth of ca. 10-12cm below the sediment-water interface, and transfer it to their gills (Masuzawa et al., 1992).

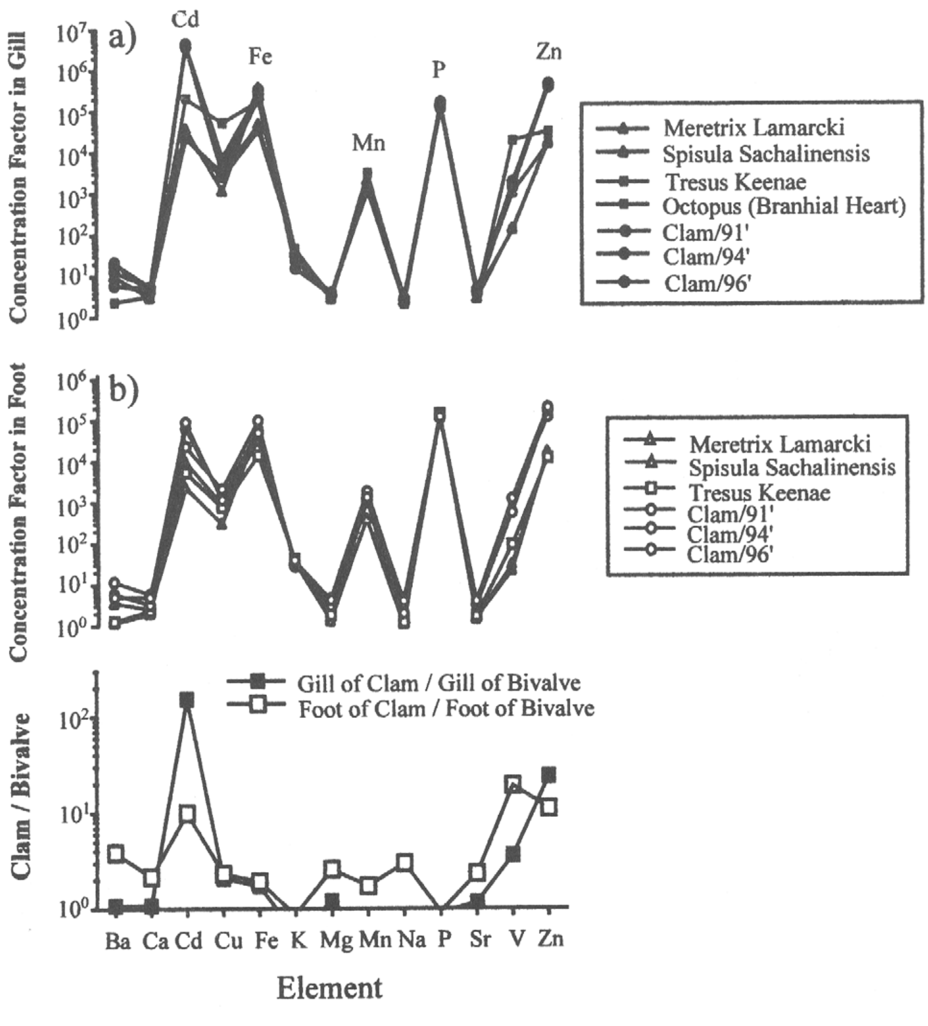

Fig. 2 Major and trace metal abundances of the bivalve, including white clam collected during different year and *Meretrix Lamarcki, Sprsula Sachalinensis, Tresus Keenae* which were collected from the eastern coast of central Japan normalized by bottom sea water respectively in their gills (a) and feet (b).

The shale-normalized REE abundances of the feet and gills of the clam show clear enrichment in middle REEs and deficiency in heavy REEs, with negative Ce and slight positive Gd anomalies. It is of importance that no Eu positive anomalies display in these REE patterns, suggesting that the geochemistry of Hatsushima white clam crowed region is principally controlled by pore water and continental underground water, not by hydrothermal fluid (Mills and Elderfield, 1995; Haas, et al., 1995). This is an assent to the suggestion of the pore water from the near region reported by Tsunogai recently (1996). Alternatively, the REE compositions of the organs of the clam simply reflect the composition of the seepage water. Rare earth element compositions of different species and communities (Fig. 3, a: white clam, b: other bivalves and c: octopus) present aged generation, while normalized by subbottom seawater (1180m) from central Sagami Bay (Zhang and Nozaki, 1998). And their concentration factors account quite high up to 10^5 fold both in gills and feet, which agree with the major metal abundance. As compared with the bulk seawater, the organs of the clam show depletion in heavy REEs and REEs are concentrated largely in their gills than in food, indicating that the biological processes may fractionate the light and heavy REEs in seawater to some extents.

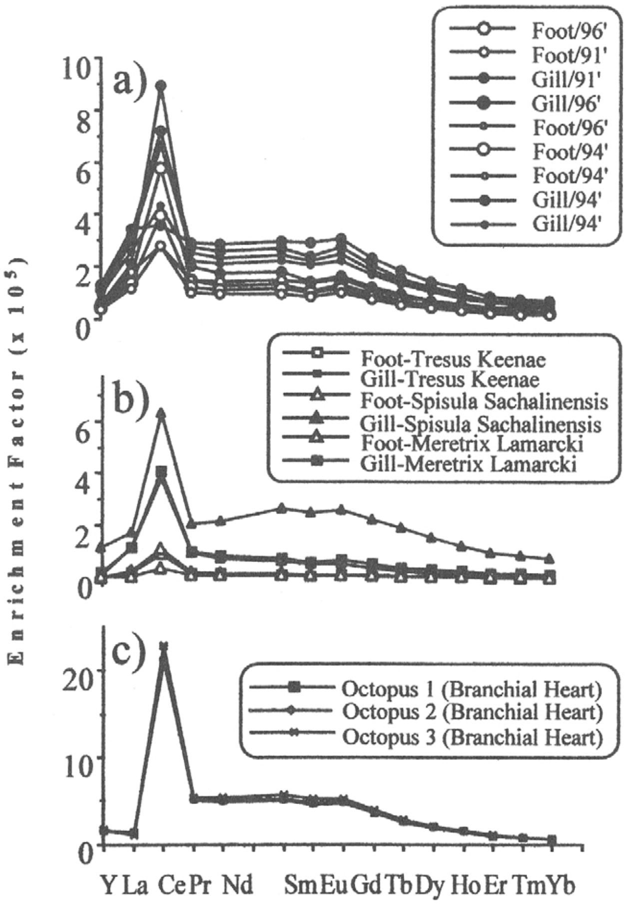

Fig. 3 REE patterns of different species and communities (a: white clam, b: other bivalves and c: octopus). The abundances were normalized by subbottom seawater (1180m) from central Sagami Bay.

The light REEs, for white clams from Hatsushima cold seepage, bivalves and octopus from the eastern coast of central Japan, fractionate to heavy REEs showing the LREE/HREE ratios of from 10 to 60. As exception of octopus, a high correlation coefficient ($R^2>0.9$) between Er/Nd and La/Yb were obtained both of white clam and other bivalves (Fig. 4). It suggests that the fractionation between light and heavy REEs of bivalves those living in cold seep region is possibly controlled by the similar mechanism with those in general sea floor, such as adsorption by particle and biochemical reaction. Gd anomalies (Gd/Gd*) distribute no significant character ranging from 1.0 to 1.4 scatteredly for all the samples (Fig. 5). Respectably, Ho/Y have the large variation distributing meaniful between average seawater (ca. 1.0 x 10^{-2}, Zhang, et al., 1994; Zhang and Nozaki, 1996) and continental crust (1.8 x 10^{-2}). Moreover, Ho/Y distinguish in varied species and organs, which agree with the consideration that biological process fractionates Ho/Y ratio in seawater and enriches Y in seawater. The speciation of the REEs in the organs of the clam and the mechanisms to extract the REEs from seawater into the organs have not been known, and will be the main objective of such studies in future.

4. Summary

The white clams (*Calytogena soyoae*) were collected from off Hatsushima cold seepage and rare earth and other trace element concentrations of the these clam in their organs, such as gills and feet were determined. The following results permit us to understand the control of the activities of bivalve communities over the seepage flow chemistry, and effect of biological and biogeochemical processes on the oceanic chemistry.

1. The geochemistry of Hatsushima white clam crowed region is principally controlled by pore water and/or continental underground water, not by hydrothermal fluid.

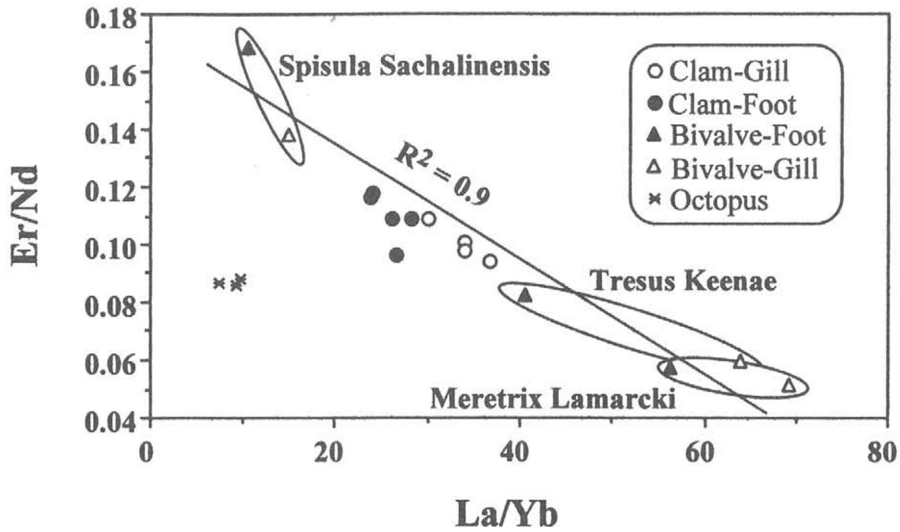

Fig. 4 Er/Nd vs. La/Yb for white clams from Hatsushima cold seepage, bivalves and octopus from the eastern coast of central Japan.

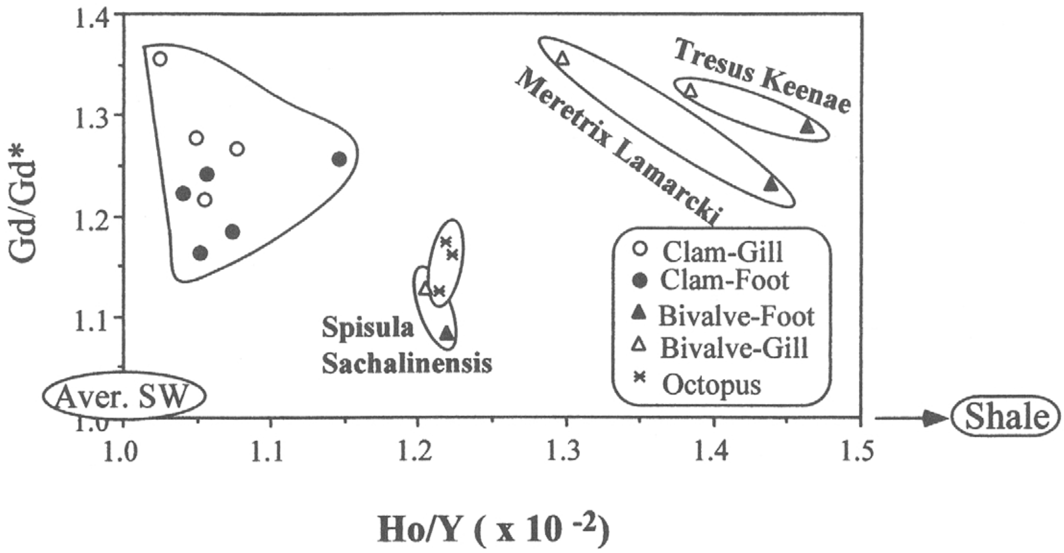

Fig. 5 Gd/Gd* vs. Ho/Y for white clams, other bivalves and octopus.

2. The major ion and trace metal, such as REEs etc. of the bivalves were concentrated approximately 10^5 fold comparative to the bulk seawater.

3. LREEs are enriched over HREEs, showing LREEs/HREEs ranging from 10 to 60. The fractionation between light and heavy REEs probably depend on the absorption and biological reaction.

4. Ho/Y ratios distinguish in varied species and organs. It suggest that fractionation between Ho and Y is induced possibly by biochemical processes.

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