

## Three discontinuous stages in progress of lanthanides (REE) geochemistry and potential further evolution

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1. Chondrite-normalized REE pattern gives us unique valuable information for various aspects. The present author has paid basic concern to logarithmic linearity of chondrite-normalized REE pattern determined with high precisions (1~2%) using the stable isotope dilution mass spectrometry. This category is related with development of authentic magmatism. 2. However, it was found that the foregoing logarithmic linearity does not hold for products related with the water-rock reaction. This is lanthanide tetrad effect. Tetrad effect is divided to W-type and M-type. The former is observed for aqueous (high-polarity) phase, whereas the latter for low-polarity one like silicate residue. This effect occurs in presence of both phases. Thus lanthanides are divided to 1st, 2nd, 3rd and 4th subgroups. It is important that this effect remains after removal of water.

Author proposed two ways to indicate the degree of tetrad effect, assuming the parabolic function for each of subgroups, based chondrite-normalized values. (There is no difference between them in mathematical meaning.)

### Pragmatic quantitative treatment of tetrad effect:

Pm is extinct and Eu can be anomalous. Both belong to the 2nd subgroup. Thus it is assumed that the values of secondary coefficient for first and second tetrads are the same, and two parabolas intersect between Nd and Pm. Cusp point between 2nd and 3rd tetrads occurs at Gd, while that for 3rd and 4th ones is assumed to arise in the middle between Ho and Er. The degree of tetrad effect for each of 4 groups is calculated, with or without matrix of mathematics.

### Two geochemical applications of lanthanide tetrad effect:

One application is for oceanography. Depth profile of secondary coefficients for 1st and 2nd subgroups is significant to investigate the currents of seawater. Another important meaning is for genesis of hydrothermal solution and deposits from it.

3. Implications for genesis of limestone. Attention was paid to limestone rich in fusulina or corals. Fusulina shows "dislocation" factor of 1.5 in diagram showing the abundance ratio between the samples of genetically close genesis (tropical coral reef). There is a systematic difference in features between coral and fusulina.

### References

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## Arsenic behavior in the modern sediments and the controlling factors of its release into groundwater

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### Introduction

Highly arsenic contaminated groundwater causing serious toxicity widely occur in the modern sediments of the world without any anthropogenic source of arsenic. We analyzed the total and four different chemical forms of arsenic compounds (acid-soluble, oxidized, organic and sulfide compounds) with major chemical compositions of modern sediments to estimate the release process into groundwater. The sample sediments were taken from the Holocene sedimentary formation in Osaka Plain, where arsenic contaminated groundwater was occasionally observed, and from a mangrove forest in the Iriomote Island, far from highly populated areas.

### Results and Discussion

Total arsenic contents of organic-rich mangrove sediments gradually increases with depth (up to 15ppm) from the surface to 2.7m depth, the bottom of the permeable layer. Below that depth, desorbed arsenic from the iron oxyhydroxide is fixed into the newly formed pyrite under reducing condition caused by microbiological activity.

Arsenic content is higher in a 22 m thick marine clay layer (7~20ppm) than in the freshwater sediments layers (<3ppm) from the Osaka Plain. Inside of the marine clay layer, sulfur decreases in each 3 m thick portions toward the above and below freshwater sediment layers. The arsenic also decreases in the almost same portions, however, it is concentrated with iron on the inflection depths of sulfur contents.

The observation of this study suggests that arsenic tends to stay or concentrate in the sediment when iron hydroxide or pyrite is stable under a given condition. Thus, the considerable arsenic would be released into the coexisting groundwater when the stability of and/or transition rates between those arsenic fixed phases become unstable.