The tetrad effect, a general effect in partitioning of *REE* between aqua and solid

T. Akagi *Laboratory of Chemistry, Tokyo University of Agriculture and Technology, Fuchu, Tokyo 183, Japan*

S. Nakai *Laboratory for Earthquake Chemistry, Tokyo University, Bunkyo-ku, Tokyo 113, Japan*

A. Masuda *Department of Chemistry, The University of Electro-communications, Chofu, Tokyo 182, Japan*

Introduction

A tetrad effect of a *REE* mineral and seawater has first been convincingly demonstrated by our careful analysis (Akagi *et al*., 1993). This is the first step to provide a method to view the partition of elements from an effect different from mere 'ionic radius effect', which has been a kind of golden rule to geochemists.

The tetrad effect has been observed so far in waters, kimuraite (a *REE* carbonate mineral), leucogranites and kuroko ore deposits (Akagi *et al*., 1993; Masuda *et al*., 1987). There are two conjugate types in the effect, W and M types; W type usually in waters and M type in rocks. From the empirical and theoretical studies, W and M type effects are understood to appear as the results of partition between water and solid, respectively, in water and solid phases.

In this paper, we will present some data which imply that this effect could operate widely in the hydrosphere and earth surfaces.

Method

Samples analysed here are apatite, galena, bastnaesite and monazite. They are typical *REE*-rich minerals. Some samples show only slight tetrad effect. The most precise and accurate data are required in order to discern the effect. An acceptable precision is obtained only by the isotope dilution mass spectrometry (IDMS), with which we obtained the data. The accuracy of IDMS is independent from the recovery of elements, which is another important advantage. (Any preconcentration and separation procedures are subjected to slight variation of recovery obeying the tetrad effect, as any chemical separations are based on the strengh of chemical bonds.)

Monoisotopic elements can not be measured with IDMS. To compensate for this disadvantage, we sometimes used ICP-MS along with appropriate preconcentrations. However, preconcentration and separation of REE limit the use of ICP-MS in this sort of study for the reason stated before. Only samples, which show a 'more than moderate' tetrad effect, can be measured by ICP-MS.

Results and discussion

The *REE* patterns are shown in Figure 1 along with that of kimuraite (Akagi *et al*., 1993). Because the abundance of monoisotopic elements can not be measured by IDMS, the tetrad effect will appeared as a zig-zag pattern. In the patterns of the allanite and apatite, zig-zag patterns are seen obviously, but those of the monazite and bastnaesite are exhibited as almost simple curves. From the chondrite normalised patterns, we calculated the deviation in normalised values of Ce, Sm, Eu, Dy and Yb from the neighbouring elements. The deviations are shown in figure 2. If we ignore anomalous Ce and Eu, it is clear that there is a deviation common to all samples in the same direction. The simplest reason to explain the deviation is the tetrad effect.

We have used the normalising values reported by Masuda. There are different sets of normalising values reported by different scientists. The shape of the normalised pattern is affected by the choice of normalising values, and the choice is very important especially when discussing a very faint tetrad effect pattern of this sort. However the similar changes in the pattern of kimuraite are observed, whichever normalising value is used. In addition, the changes are the same, if we use the sets of normalised values obtained by IDMS-ID analysis, the most reliable method. Therefore it can be concluded that the tetrad-effect-like pattern is not an artefact produced by the choice of normalising values. We also think that the set of normalising values we have used are reasonably accurate.

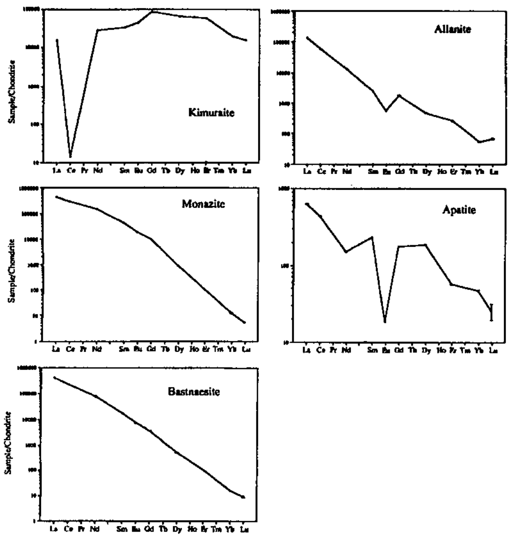

FIG. 1. Chondrite normalised patterns of *RE* elements.

So far we have considered that the tetrad effect can be seen only in aqueous samples and in some special solid material, in which the association of water has been very important in their genesis. The appearance of the 'faint' tetrad effect in some of the very common REE minerals implies that the tetrad effect is rather a ubiquitous effect.

Mineralogically, the appearance of the tetrad effect will provide us with some useful information. Most of the minerals show the W type tetrad effect, which indicates the accumulation of *REE* in aqueous media in the mineral's genetic history. The M type tetrad effect observed in the pattern of the apatite reflects the accumulation of *REE* onto solid from an aqueous medium. The extent of the tetrad effect is affected by the physicochemical condition of the environment where REE had accumulated. Hopefully, from the laboratory experiment simulating natural conditions, we will be able to estimate the conditions of the accumulation.

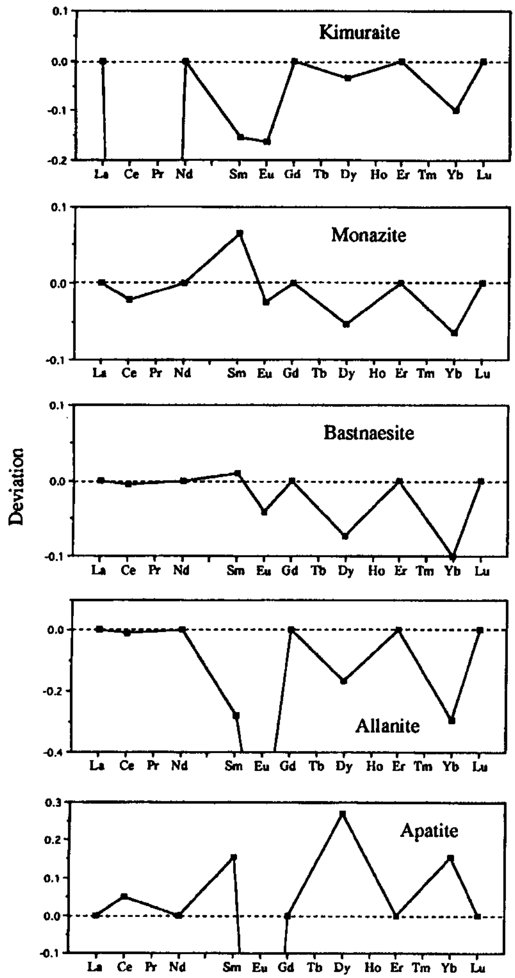

FIG. 2. Deviations of normalised values of Ce, Sm, Eu, Dy and Yb from those of neighbouring elements.

References

Akagi, T. *et al.* (1933) *Geochim. Cosmochim. Acta*, **57**, 2899–905.

Masuda *et al.* (1987) *Geochem. J.*, **21**, 119–24.