NOTE

Lanthanide tetrad effect observed in marine environment

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We have found that lanthanide tetrad effect (PEPPARD *et al.*, 1969) is operative for heavy rare-earth elements (REE) in a phosphorite sample (GOLDBERG *et al.*, 1963). Also it has been evinced that the similar effect is observed for REE in sea waters. However, in the case where the plot (Masuda-Coryell plot) is void of the points for Tb, Ho and Tm, the resultant joint-line pattern is to have the common characteristics that the zigzag pattern is pointed downward at Dy and Yb and upward at Er. That is, the zigzag pattern with phase coincidence in breaking and its direction is a partially cut-off reflection of lanthanide tetrad effect.

Employing the stable isotope dilution technique, we could determine REE in one-liter sample of sea water, with errors less than 2~3%.

INTRODUCTION

In studies of liquid-liquid (aqueous-benzene) extraction involving H[DOP], di n-octyl phosphinic acid, $(n-C_8H_{17})_2PO(OH)$ and DEH[CIMP], di 2-ethyl hexyl chloromethyl phosphonate, $(ClCH_2)PO(OC_6H_{12} \cdot C_2H_5)_2$, PEPPARD *et al.* (1969) recognized tetrad effect on lanthanides (III). According to their observation, when the concentration ratios between the aqueous phase and the organic phase is plotted on semi-logarithmic diagram against the atomic number of the lanthanide, the plot consists of four separate curves, encompassing four points, La-Ce-Pr-Nd, Pm-Sm-Eu-Gd, Gd-Tb-Dy-Ho and Er-Tm-Yb-Lu, with Gd being an element common to the second and the third tetrad. The results for one of two systems investigated by them are cited in Fig. 1.

The above authors suggested that the first, second and third cusps correspond to "one-quarter-filled", "half-filled" and "three-quarters-filled" shell effects, respectively. That is, three discontinuities occur respectively between the third and the fourth, just at the seventh, and between the tenth and eleventh 4f electron filling. (As is well known, the maximum number for 4f electron orbitals is fourteen, and it was theoretically argued that a discontinuity in properties should occur at Gd, because of a predicted half-filled shell effect.)

NUGENT (1970) advanced an explanation that the tetrad effect in question originates

mainly from the quantum mechanical inter-electronic repulsion energy of the q electrons in $4f^q$ electronic configuration. The tetrad effect is observed in the changes of the unit cell volumes, the standard free energy of complex formation (SIEKIERSKI, 1971; SIEKIERSKI and FIDELIS, 1972) and free enthalpy of hydration (GUILLAUMONT and DAVID, 1974).

Well it is an interesting problem whether the lanthanide tetrad effect can be observed in nature. As mentioned below, we have noticed that the effect under consideration is found in materials associated with marine environment.

Fig. 1. Example of the tetrad effect (PEPPARD *et al.*, 1969). Variation of $\log K$ with atomic number Z where K is the equilibrium distribution constant between an aqueous solution of 1.1F LiBr + 0.5F HBr and the solution of 0.6F di(2-ethylhexyl) chloromethyl phosphonate in benzene, at $22^\circ \pm 2^\circ C$.

EXAMINATION OF DATA BY GOLDBERG *et al.*

GOLDBERG *et al.* (1963) analyzed a surface sea water, a phosphorite and a manganese nodule for rare-earth elements, REE, i.e., lanthanides, employing the technique of neutron activation analysis. According to their description, the data on phosphorite is of highest quality, good to about $\pm 3\%$. It is understood (GOLDBERG *et al.*, 1963) that the REE found in the oceanic phosphorite are very probably precipitated directly from sea water. It grasps and retains our attention that, as seen in Fig. 2, the phosphorite REE determined with best accuracies exhibit two arcuate curves comprising two tetrads, Gd-Tb-Dy-Ho and Er-Tm-Yb-Lu. (For normalization, REE abundances in Leedey chondrite (MASUDA *et al.*, 1973; MASUDA, 1975) are employed in this paper.) It is of great significance that these two tetrads are in complete agreement with the third and fourth tetrads pointed out by PEPPARD *et al.* (1969). However, it is hard to recognize tetrad effect on REE lighter than Gd.

Chondrite-normalized REE pattern for a surface sea water from 100 meter depth, 15 km west of San Diego, is shown in Fig. 3. It is less easy to discern tetrad effects in Fig. 3 than in Fig. 2. But, since Tm determination is subject to relatively great uncertainties, little attention may be paid to Tm in drawing a smooth curve. Thus it can be said that the same tetrad effect as observed in phosphorite (Fig. 2) is found also in sea water (Fig. 3). It is noted here that if the abundance data are available for Gd, Dy,

Fig. 2. Chondrite-normalized REE pattern of a phosphorite investigated by GOLDBERG *et al.* (1963).

Fig. 3. Chondrite-normalized REE pattern of a sea water sample, 15 km west of San Diego, investigated by GOLDBERG *et al.* (1963).

Er, Yb and Lu and the points for these elements are connected by straight lines, apparently zigzag patterns as indicated by broken lines in Figs. 2 and 3 will be obtained. Those zigzag patterns should have common features that they are pointed downward at Dy and Yb and upward at Er. Emphasis must be placed on that apparently zigzag patterns shown by broken lines in Figs. 2 and 3 are reflection of tetrad effect shown by smooth solid lines. This must borne in mind, because it is impossible for usual stable-isotope dilution technique to determine monoisotopic REE such as Tb, Ho and Tm.

DETERMINATION OF REE IN SEA WATER

To check the ubiquity of tetrad effect on heavy REE in sea water, we have determined REE in sea water from 1,690 meter depth in Pacific Ocean $32^{\circ}28'N$, $138^{\circ}49'E$. As mentioned above, since Tb, Ho and Tm cannot be determined by mass spectrometric stable isotope dilution technique, our criterion for the examination of tetrad effect under consideration is based on zigzag pattern with phase coincidence in positions of up-and-down pointings.

GOLDBERG *et al.* (1963) and HØGDAHL *et al.* (1968) used a 10 liter sea water sample for each of their determinations of REE, but we succeeded in determination of REE using a one-liter sample, with errors of 2 ~ 3%, in which stable isotope dilution was employed; both GOLDBERG *et al.* and HØGDAHL *et al.* employed neutron activation.

Table 1. REE concentrations (ppt) in seawater sample from 1,690-m depth, 32°28'N, 138°49'E

La	5.09	Eu	0.156	Er	0.974
Ce	2.84	Gd	0.908	Tm	0.131*
Pr	—	Tb	0.147*	Yb	0.935
Nd	3.53	Dy	0.984	Lu	0.165
Sm	0.658	Ho	0.306*		

* Estimated from Fig. 5.

A sample of about one-liter was acidified by 3 ~ 4ml of 6N HCl to be stored. In separation of REE, about 20mg of purified Fe in solution were added together with REE spike solution, then 2ml of concentrated NH_4OH was added to co-precipitate REE with $\text{Fe}(\text{OH})_3$ at $\text{pH} = 10 \sim 11$. After hydroxides were centrifuged, they were dissolved by 3ml of 0.5N HCl. REE fraction was separated by cation-exchange column (8mm $\times$ 50mm). Impurities of REE in reagents used were subtracted.

Our results are presented in Table 1 and the corresponding chondrite-normalized REE pattern is shown in Fig. 4. Like sea water analyzed by GOLDBERG *et al.* (1963), our sample shows large negative Ce anomaly. Compared with the value Ce^* estimated to fall on the La-Nd join, the depletion factor for the observed Ce value is $3.34 (= \text{Ce}^*/\text{Ce})$. The corresponding factor for the sample studied by GOLDBERG *et al.* is 4.35.

Fig. 4. Chondrite-normalized REE pattern of sea water, from 1,690-m depth, 32°28'N, 138°49'E, analyzed by us. Open circles refer to values estimated from Fig. 5.

Fig. 5. Concentration ratios of a phosphorite (GOLDBERG *et al.*, 1963) to our sea water sample (cf. Table 1).

Our deepest attention is engaged to the zigzag phase coincidence of our sea water pattern (Fig. 4) with the patterns shown by broken lines in Figs. 2 and 3. It can be said that the zigzag pattern for heavy REE is ubiquitous with common up-and-down effect and that this effect is essentially an interrupted reflection of lanthanide tetrad effect on heavy REE.

Effectively close relationship between phosphorite (GOLDBERG *et al.*, 1963) and our sea water is shown in Fig. 5. Based on this relationship, we can estimate the concentrations of Tb, Ho and Tm for our sample; estimated values are presented in Table 1. Open circles in Fig. 4 represent the estimated values for Tb, Ho and Tm, and curves drawn with broken line display the presumed tetrad effect.

DISCUSSION

It has been evinced that there is a tetrad effect operative for heavy REE in marine environment. As pointed out above, it is hard to recognize the similar effect on light REE. It is true that the situation is complicated by the natural absence of Pm and the possible anomalous valencies of Ce and Eu. Nevertheless, an effect presumably related with the tetrad effect does not seem tangible for light REE span in Figs. 2, 3 and 4. Perhaps a reason for this might be that light REE are larger in ionic radii and more soluble than heavy REE. Also some attention might be paid to that the points for La, Nd and Sm in Fig. 1 happen to fall on a

straight line passing through them.

A general trend for La, Nd and Sm obviously suggests a discontinuity at Gd. To a much lesser extent, Gd discontinuities are recognized for chondrite-normalized REE patterns for deep-sea cherts and siliceous microfossils (SHIMIZU and MASUDA, 1977). Very careful scrutiny of their data would enable us recognize that most of deep-sea siliceous materials reserve the hyperfine zigzag features with similar effect to that mentioned above. Findings reported here are expected to raise new intriguing problems not only with marine chemistry and geology but also with biological chemistry.

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