A study related to the light-lanthanide tetrad effect in northeastern Atlantic (28°N 26°W) in comparison with other oceans

By Takahiro SHIOKAWA,^{*)**)} Junji SHIMODA,^{*)} and Akimasa MASUDA^{*)**,***),†)}

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Abstract: Based on the data published by Elderfield and Greaves (1982) for a water column at a site, GEOSECS station 115, of northeastern Atlantic (28°N 26°W), the light-lanthanide tetrad effect was evaluated by the method developed by Masuda and his collaborators. The extent of variation of this effect is much larger than those observed in Pacific and Indian Oceans. Meanwhile, it intrigues us that the value for the effect in question at the top of the water column is almost the same as that at its bottom. Similar facts are observed generally at water columns of other oceans studied thus far. Features of dependence of Nd concentration on depth and of dependence of Ce and Eu anomalies evaluated on the basis of the same mathematical method are also discussed. A minimum absolute value of negative aberration extremum defining the tetrad effect at station 115 can be ascribed to the outflow from the Mediterranean Sea.

Key words: Lanthanide tetrad effect; light lanthanides; AEL; Atlantic Ocean; seawater; Ce anomaly; Eu anomaly; depth profile.

Introduction. Although Masuda and Ikeuchi¹⁾ found out in 1979 the lanthanide tetrad effect in seawater based on their first successful attempts to measure lanthanides in seawater by the mass spectrometric stable isotope dilution, it was impossible to quantify this effect for a case where the precise abundance data are available just for four normally trivalent light-lanthanides, La, Nd, Sm and Gd. A method to overcome this difficulty was proposed by Masuda *et al.*²⁾ in 1994 and has been applied to ocean waters.³⁾⁻⁶⁾

This communication reports the results of calculation of light-lanthanide tetrad effect for the open North Atlantic for the first time. The calculation is carried out based on the data published by Elderfield and Greaves⁷⁾ for GEOSECS station 115 (28°01'N, 25°59'W) in the Cape-Maderia Abyssal Plain, water depth 5,250 m. It is noted here that in general, the horizontal and vertical heterogeneities in distribution of chemical components are pronouncedly recognized in Atlantic Ocean, as

compared with Pacific and Indian Oceans. Also it is known very well that the Atlantic Ocean is notably different from the Pacific and Indian Oceans in many respects of oceanography.

In our previous papers, abbreviation ABEXEL has been used to indicate the extent of tetrad effect for light lanthanides. However, a shorter abbreviation AEL will be used to replace ABEXEL in this communication.

Depth profile of light-lanthanide tetrad effect.

The depth profile of AEL for the site (Fig. 1) studied by Elderfield and Greaves⁷⁾ is shown in Fig. 2. A minimum of the absolute value of negative AEL (n-AEL) is observed at 940 m, while absolute value maxima for n-AEL are observed at 360 m and 2,140 m. Besides, it is worthwhile to note that the AEL values at the top and at the bottom of the water column are almost equal to each other, about -0.08.

In our studies, the curves are drawn by either of programs "3D-spline", interpolation, and mere connection of points, mostly by 3D-spline of KaleidaGraph. The curve in Fig. 2 is also drawn by 3D-spline.

The lanthanide concentrations in West Indian Ocean were determined by Bertram and Elderfield,⁸⁾ and calculation of the corresponding AEL values was carried out by Masuda and Shimoda.⁵⁾ It can be seen (Fig. 2) that the qualitative features of fashion of AEL variation with

^{*)} Department of Chemistry, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan.

^{**)} Department of Chemistry, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan.

^{***)} Institute of Geochemistry, Chinese Academy of Sciences, Guanshui Road 73[#], Guiyang, Guizhou 550002, China.

^{†)} Correspondence to: A. Masuda at COLGA, 449-1 Shimo-Yasumatsu, Tokorozawa, Saitama 359-0024, Japan.

Fig. 1. Location of GEOSECS Station 115 studied by Elderfield and Greaves.⁷⁾

Fig. 2. Depth profiles of AEL (extent of light-lanthanide tetrad effect; cf. Fig. 6) for northeastern Atlantic Ocean (GEOSECS Station 115)⁷⁾ and western Indian Ocean (sites 1502, 1504 and 1507).⁸⁾

depth for water columns of West Indian Ocean resemble those observed in the station 115 and that the relative scale of variation of AEL for Indian Ocean, however, appear overly reduced or compressed in comparison with that for the Atlantic station under consideration; in particular, the AEL values for the main valley are similar to

Fig. 3. Depth profiles of AEL (cf. Fig. 2) for western North Pacific Ocean.

each other between the Atlantic and Indian Oceans, but the “relative” level of AEL values for the top, the bottom and a maximum in the upper intermediate layer at station 115 is much “higher” than that for Indian Ocean. The AEL values at the top and at the bottom of West Indian Ocean are about -0.16 in contrast with -0.08 for station 115. The agreement of AEL values between the top and the bottom of water column suggests the validity of closed water column model as regards the tetrad effect of light lanthanides. The valley corresponding to the maximum of absolute value of n -AEL can be interpreted to imply the greater contribution of state of simple ion or soluble complex state related to it. Here attention is directed to the AEL-depth profile (Fig. 3) for the North Pacific; the AEL values were evaluated^{3),4)} based on the concentrations determined by Piepgras and Jacobsen.⁹⁾ The depth profiles in this diagram show the flatter patterns than those in West Indian Ocean. The AEL value at the top and at the bottom are also the same, -0.15 , for site 271-1. However, the absolute value, 0.163 of n -AEL for the top of site 39-1 ($47^{\circ}\text{N } 161^{\circ}\text{E}$) is somewhat greater than that, 0.132 , for the bottom of the same column. It may reflect high latitude effect potentially related to penetration of the polar or sub-polar waters at the bottom. At the

Fig. 4. Depth profiles of Nd content in seawater for North Pacific and Indian Oceans.

Southern Ocean (39°S 01°E) investigated by German *et al.*¹⁰⁾ for lanthanide concentration, the absolute value (0.20) of n-AEL at the top is remarkably greater⁶⁾ than that (0.12) of n-AEL at the bottom, with considerable fluctuations between the top and the bottom. Masuda and Shimoda⁶⁾ attributed the sudden decrease of absolute value immediately below the top water to the effect of melting of floating icebergs, but one cannot rule out the possibility of casual input of aeolian dust from the continents uncovered by ice. It would be adequate to divide the "Layer I" of the Southern Ocean into Layer I-U and Layer I-L.

Relation between depth and light lanthanide content. The bearings of light lanthanide content on the depth may merit some attention. In this consideration, Nd will be taken as representative of light lanthanides. Prior to investigation of station 115, our attention is paid to the Pacific and Indian Oceans. Fig. 4 shows the relation between Nd content and depth for the North Pacific and West Indian Oceans. In general, for both oceans, the relationship under consideration is rather smooth, and it can be seen that the Nd content in West North Pacific is higher than in West Indian Ocean. Here it may be worth pointing out that the seawater samples for West North Pacific Ocean are unfiltered ones,

Fig. 5. Depth profile of Nd content in seawater at GEOSECS Station 115 (thick curve). Thin curves refer to North Pacific and Indian Oceans (cf. Fig. 4).

while the seawaters for West Indian Ocean are filtered through 0.4 μ m Nucleopore membrane filters. It is conceivable that the lower Nd content in Indian Ocean than that in North Pacific Ocean is due to the process of filtration. However, taking into account the fact that the Nd content in the uppermost layer for site 271-1 of North Pacific Ocean is lower than those in Indian Ocean, it would be better to reserve the conclusion about the effect of filtration. Anyway, the observation that the AEL-depth profile for North Pacific Ocean is flatter than for Indian Ocean is considered to have something to do with the difference in contents of light lanthanides between both oceans.

Fig. 5 shows the relation between depth and Nd content for station 115 in comparison with Indian and Pacific Oceans. The samples from station 115 are 0.4 μ m filtered ones. In contrast with the Pacific and Indian Oceans, the fluctuation of Nd content with depth is notable. However, except the hump around 1 km, it is difficult to recognize the easily discernible coincidence of Nd-depth profile features with those of AEL-depth profile. The hump around 1 km can be attributed to the Mediterranean outflow. It draws our attention that the AEL values in the Mediterranean Sea samples investi-

Fig. 6. An example diagram to demonstrate the estimation of the ratios of the observed values to the normal ones for Ce and Eu. Two parabolic curves are drawn based on the mathematical method developed by us^{2),12)} and the "normal" values are evaluated at the same time. Arrows refer to AEL value. Sample is collected from the depth of 600 m at GEOSECS station 115. The abundances in Leedey chondrite¹³⁾ are taken for normalization.

gated by Greaves *et al.*¹¹⁾ range from -0.082 through -0.106 according to our evaluation.

Cerium and europium "anomalies". According to our mathematical method to evaluate the extent of light-lanthanide tetrad effect, two parabolic curves (Fig. 6) with a cusp point between Nd and Pm are obtained from "standard"-normalized values, and the "normal" values (open circles) for Ce and Eu in consistency with stably trivalent light lanthanides (La, Nd, Sm and Gd) can be evaluated. The ratios of observed values (solid triangles) to these normal ones can serve as a measure of anomaly or deviation from regularity; if the observed value agrees perfectly with the regular one, the corresponding ratio turns out to be 1.00. The ratio (Fig. 6) of the observed value (O) to the normal value (N, calculated) will be designated as ON ratio.

The ON ratios for Ce and Eu thus obtained are plotted in Fig. 7. The curves are drawn by both interpolation (thin line) and 3D-spline (thick line). First it is intriguing that the water column at station 115 appears to exhibit an anti-correlation between Ce and Eu anomalies. That is, maxima of Ce ON ratio (crossed open circle) corresponds to minima of Eu ON ratio (solid circle), and vice versa. It is natural that the extent of variation of the Eu ON ratio is smaller than that of the Ce ON ratio. The Ce ON ratio shows maxima at the top, the bottom, and at the depths of 750 m and 2,240 (3D-spline)~ 2,430 (interpolation) m. It would deserve comment that the

Fig. 7. Depth profiles of Ce ON ratio and Eu ON ratio (see text and Fig. 6).

depth of 750 m is close to the depth of 940 m which appears to be related to the Mediterranean outflow. Another interesting fact is that the AEL-depth profile exhibits a main "valley" at 2,140 m as shown in Fig. 2. An implication of the fact that the Ce ON maximum depth of 2,240~2,430 m in Fig. 7 is 100~300 m below the main valley depth of 2,140 m in Fig. 2 remains to be studied.

Let us return to the Nd-depth profile (Fig. 5). It shows maxima at the top, the bottom and around 700~1,000 m. Taken altogether, there appear to be a coincidence in maximum depth at the top, the bottom, and around 1,000 m among AEL, Ce ON ratio and Nd content as regards the column at station 115. It may not be unnatural that one cannot recognize a sharp aspect in Nd-depth profile in accordance with the depth of the main valley of AEL value around 2,140 m, whereas the AEL value indicates the chemical state(s) of stably trivalent lanthanides themselves. Nevertheless, some attention might be paid to a fact that there appears to be a slight shoulder around 2,400 m in Fig. 5. This slender shoulder and a maximum of Ce ON ratio around 2,300~2,400 m may suggest the scavenging process, producing the wide main valley in AEL-depth profile around 2,140 m.

Conclusions. The depth profile of light-lantha-

nide tetrad effect at a site of northeastern Atlantic Ocean (28°N 26°W) is quite different from those observed in the Pacific and Indian Oceans. However, most of the depth profiles of this effect have similarity that the AEL values that define the light-lanthanide tetrad effect are nearly the same at the top and at the bottom of seawater column, excepting the unusual case at the Southern Ocean.⁶⁾ The ratios of observed values for Ce and Eu to normal values calculated from the parabolic curves decided by La, Nd, Sm and Gd show intriguing aspects in bearings on depth. The ratios thus defined concerning Ce and Eu are advantageous over the anomaly indexes proposed by Elderfield and Greaves,⁷⁾ because the "normal" value is defined by the mathematical function decided by stably trivalent lanthanides and the tetrad effect is taken into account in its definition. The apparent anti-correlation between Ce and Eu ON ratios observed at the station 115 poses a problem about the behaviors of Ce and Eu under a certain condition of seawater column, although the observed phenomenon may be a special case for the column of this station.

It seems difficult to find a close simple relationship between AEL value and contents of light lanthanides in the case studied here. Nevertheless, further studies on relationship between AEL and light lanthanide content would be expected to be of significance for researches on the states of "dissolved" lanthanides, because dissolved fraction contains ultra-fine particles, colloidal material and intrinsic ions. Each of light-lanthanide content,

observed/normal ratios for Ce and Eu (Ce and Eu anomaly) and tetrad effect provides us with different quality information, and a combination of them will emerge as a new tool in oceanography and marine chemistry.

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