Depth profiles of the lanthanide tetrad effect in seawater columns, centered on a study of water column at the Cariaco Trench off the Venezuelan coast

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In 1979, Masuda and Ikeuchi found the occurrence of the lanthanide tetrad effect in the marine environments. It is observed ideally as four cyclic slight curves spanning the atomic number range of lanthanides. However, this effect was not quantified until recently. Masuda et al. (1994) devised a mathematical method to extract the extent of the lanthanide tetrad effect and gave a numerical expression to it, which is based on an application of a parabolic function to the slightly curved plotting. This value is expressed as an extremum of aberration from an rectilinear linear line assumed for a case where there is no affection of the lanthanide tetrad effect. The aberration extremum (ABEX) for light rare earth elements is designated as ABEX-l, or ABEXEL.

However note that, in order to get virtually significant values for ABEXEL, La, Nd, Sm and Gd should be determined with precisions better than 1~2%. For example, if 10% error is involved for any of them, the resultant ABEXEL value is subject to serious uncertainty, potentially leading us to erroneous assessment. According to our observation, the ABEXEL values for seawaters generally fall between ~0.0 and −0.22. Needless to say, the greater absolute values refer to the higher lanthanide tetrad effect, while ~0.0 to little tetrad effect.

Following the interpretation by Masuda (1996), the lanthanide tetrad effect in seawater is related with the internal electron condition within the lanthanide atom and the outer physico-chemical circumstance surrounding the atom concerned: the internal atomistic factor for 'free' lanthanide ion is that the atoms of lanthanides have cyclic change in steric symmetry of f electronns as well as stability about $4f$ electron configuration with atomic number and , effectively, in resultant inter-electronic repulsion between $4f$ electrons, while the outer strong biased electric field factor results from hydration of of free ions in water which gives rise to the high polarizing field due to the high polarizability of water molecules. A combination of these factors can lead to an internal slight cyclic fractionation within four adjacent lanthanides constituting a tetrad subgroup. Factors other than mentioned above can somewhat affect the effect under consideration. Virtually, the effect in question reflects the cycles of variation in steric f electron symmetry responsible for slight cycles of internal difference in chemical bonding between the lanthanide ions or atoms and ligand.

Apart from the physico-chemical arguments about the effect in question, it is phenomenologically evident that the lanthanide tetrad phenomenon takes place in presence of water, which means its occurrence in seawater as well as rocks or minerals exposed to hydrothermal solution. In this report, our attention is directed to the depth profile of the lanthanide tetrad effect in seawater column. If very interesting new implications are found in the depth profile of the lanthanide tetrad effect, it would not only erase a dubiosity conceived by traditionalists but also provide us with a new promising tool for oceanographic investigations.

We have studied the depth profiles of the lanthanide tetrad effect at several sites in oceans, and proved successfully its invaluable significance. Our current presentation is centered on the depth profile of the lanthanide tetrad effect at the Cariaco Trench off the Venezuelan coast, which intrigues us since this trench represents an oceanographically simple closed water column. De Baar et al. (1988) carefully studied this highly stagnant trench for the rare earth distribution and the marine chemistry of Mn, Fe, phosphate and silicate. They describe that the vertical mixing is restricted by the strong pycnocline at 150-300 m depth resulting from the sharp temperature gradient.The sill depth between the trench and the Caribbean Sea is 146 m, the slope of the trench dips steeply between 500 and 1400 m, and the trench site is surrounded by islets.

The depth profile of the lanthanide tetrad effect evaluated by us (Masuda et al., 1998) shows that the

maximum of the absolute value of ABEXEL (raw value = −0.192) is observed at 256 m, which coincides with the clearly defined oxic/anoxic interface at 280 m (Fig. 2b in De Baar et al., 1988). A sharp change of ABEXEL from −0.192 to −0.097 takes place in the very narrow depth range from 256 and 292 m. On the other hand, the ABEXEL value is nearly invariable (−0.104 ~ −0.110) between 697 and 1395 m. This invariability can be interpreted to reflect well the submarine topography of the trench and the developed pycnocline. Further it may suggest the resetting of the tetrad effect in the especially stagnant deep layer. The corresponding values −0.080 and −0.083 at 50 m and 150 m are quite similar to each other. These are considered to indicate the value for the surface layer of the open Caribbean Sea. The top water at depth of 5 m has the smallest absolute value (−0.023), which exhibits the immaturity of water-mass (strictly, the particles involved) at the top. That is, it indicates the greater contribution of runoff from the continental surface and/or of falling aeolian dust. Taking into account the dependences of salinity and temperature on depth, the drainage from the continental surface is judged to be greater in effect than the aeolian dust in the case under consideration.

As a summary of the studies on REE marine geochemistry and its relationship with the geochemical behaviors of Mn and Fe, De Baar et al. (1988) proposed a model of the vertical transport of strictly trivalent REE along with the cycling of Mn (or Fe) at the oxic/anoxic interface (Fig. 13 in the original paper). Important points of their model is scavenging of REE by MnO_2 and desorption of REE due to reduction of Mn(IV) to Mn(II) ion at the interface. Their model can be extended well to explain the depth profile of the lanthanide tetrad effect observed by us. This endorses the reliability of our evaluation of lanthanide tetrad effect as well as the physico-chemical qualitative arguments mentioned in the introduction.

It does not escape our notice on the other hand that the depth profile of phosphate shows the fine structure (subtle extrema) across the oxic/anoxic interface. This suggests a possibility that the phosphate takes part in enhancing the lanthanide tetrad effect in addition to a role played by Mn. Speciation of phosphate, which can be biogenic, can be a clue to this problem.

At this point some comment is necessary about the oceanographic conditions where the lanthanide tetrad effect occurs. What this study reveals is that the stagnant oxic/anoxic interface is one of the chemically favourable circumstances to promote the sharp lanthanide tetrad effect profile. The Cariaco Trench has been taken up here because of special simplicity of chemical and physical conditions of the location. However, one should not think that the lanthanide tetrad phenomenon is limited to an oxic/anoxic interface. This effect takes place in a wide variety of environment in seawaters. Very commonly, the pattern of the depth profile of the lanthanide tetrad effect appears to be related closely with the dissolved oxygen profile and sometimes potentially with the phosphate one. The lanthanide tetrad phenomenon can be developed under the oxic condition, too. A peculiarity at the oxic/anoxic interface is a sharp appearance of the developed lanthanide tetrad effect in a narrow zone. Particle/solution interactions, particle/particle interactions and so forth (Sholkovitz et al., 1994) are a part of responsible parameters, which are not discussed here.

It draws our attention that the maximum n-ABEXEL value (negative ABEXEL value), 0.192, at the Cariaco Trench is quite similar to those for the ordinary open oceans. Our previous investitations (Masuda and Shimoda, 1997) show that the maximum n-ABEXEL value for North Pacific Ocean is 0.182 and that for the western Indian Ocean is 0.199-0.205. Further piercing considerations and data accumulation would be required to draw a conclusion about this matter.

Comparison with the depth profiles of the lanthanide tetrad effect at several sites is made. The lanthanide tetrad effect will serve to advance the frontier of oceanography in both physical and chemical senses.

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