Evolution of the yttrium-holmium systematics of seawater through time

M. Bau   *GeoForschungsZentrum Potsdam, PB 4.3 Lagerstättenbildung,*
P. Dulski   *Telegrafenberg A-50, D-14473 Potsdam, Germany.*

Introduction

Extension of rare-earth element (*REE*) to combined *REE* and Y (REY) studies by considering, for example, shale-normalised REY (REY$_{SN}$) patterns in which Y is inserted between Dy and Ho, may provide new insights into REY speciation in aqueous solutions. Since differences in speciation result in dissimilar behaviour during scavenging, which is one of the processes that control the REY distribution in seawater (e.g., Byrne and Kim, 1990), REY systematics may allow us to distinguish between organic and inorganic complexation of Y and *REE*s on surfaces of marine particles. This may provide a means to qualitatively asses the relative importance of organic and inorganic ligands in the marine environment. In this contribution we will focus on the evolution of the Y-Ho systematics of seawater through time.

Modern seawater

Although the *REE* geochemistry of seawater has gained broad attention over the last decades and is rather well known by now (e.g., Elderfield, 1988), almost nothing is known about the behaviour of Y in the marine environment. Only one single vertical seawater profile for dissolved Y is available (Bau *et al.*, 1994), which suggests a nutrient-type distribution with depletion in surface waters (50 pmol/kg) and concentrations which increase with depth to a maximum value of 205 pmol/kg at 2250 m. All along the profile REY$_{SN}$ patterns display a positive Y$_{SN}$ anomaly and non-chondritic Y/Ho weight-ratios between 47 and 77. These results are supported by data for individual samples from the North Atlantic (Høgdahl *et al.*, 1968), the Japan Sea (Shabani *et al.*, 1990) and the Mediterranean Sea (P. Möller, pers. comm.). From comparison of data for dissolved and total Y and Ho abundances in seawater, Bau *et al.* (1994) suggest that Ho (and the other *REE*s) are considerably more particle-reactive than Y.

Modern chemical sediments

Considering modern chemical sediments, we have to distinguish between those that reflect the composition of ambient seawater and those that preferentially scavenge Y or individual *REE*s.

Ferromangenese (Fe-Mn) crusts, for example, may either be hydrogenetic or hydrothermal in origin. The former usually show high abundances of Y and *REE*s, positive Ce$_{SN}$ and negative Y$_{SN}$ anomalies, whereas the latter commonly display low REY abundances, negative or no Ce$_{SN}$ anomalies and positive Y$_{SN}$ anomalies. The prominent difference between the two types appears to be their growth rate. Hydrogenetic Fe-Mn crusts represent slow precipitation of Fe-Mn-oxihydroxides which leaves enough time for Ce^{III} oxidation and preferential scavenging of Ce^{IV} species, and which allows enough time to reach an exchange equilibrium for trivalent Y and *REE*s between seawater and Fe-Mn-oxihydroxide surfaces. In contrast, hydrothermal Fe-Mn crusts represent rapid precipitation which does neither allow significant Ce^{III} oxidation which is kinetically slow nor induces REY fractionation. Thus, the REY$_{SN}$ pattern of the seawater-dominated mixture of hydrothermal fluid and seawater is not modified during the precipitation event, and hydrothermal Fe-Mn crusts, i.e. rapidly precipitated Fe-Mn-(hydr)oxides, can be used as indicators of the Y$_{SN}$ anomalies in seawater.

Comparing alumosilicate-free marine phosphorites or even more so, pure carbonate fluorapatite and seawater, we observe large similarities in their REY$_{SN}$ patterns such as negative Ce$_{SN}$ anomalies, *HREE*$_{SN}$ enrichment and positive anomalies of La$_{SN}$, Gd$_{SN}$ and, most important, Y$_{SN}$. Though Ce$_{SN}$ anomalies are redox-related and do not necessarily reflect similar sized anomalies in seawater (e.g., German and Elderfield, 1990), we suggest that the Y$_{SN}$ anomalies in marine phosphorites which otherwise show all the features typical of the seawater REY distribution most probably reflect similar Y$_{SN}$ anomalies in seawater.

Commonly, REY$_{SN}$ patterns of alumosilicate-

free marine limestones resemble those of seawater, suggesting that they too can be used as indicators of the Y_{SN} anomalies in seawater.

Ancient chemical sediments

A compilation of ICP-MS determined Y/Ho ratios of chemical sediments is shown in Fig. 1 which comprises data from iron-formations (IFs), manganese-formations, phosphorites and limestones. The samples considered cover the complete geological history from the Archaean (3.8 Ga-old Isua IF) to the present. As evidenced by Fig. 3, the Y/Ho ratios of pure marine precipitates have remained virtually the same since the onset of formation of marine chemical sediments, suggesting that seawater has always been characterised by positive Y_{SN} anomalies.

Discussion

Assuming negligible differences between carbonato-Y- and -Ho-complexes in solution, Byrne and Lee (1993) ascribed Y-Ho fractionation in seawater exclusively to the formation of organic surface-complexes with functional groups of carboxylic acids. If this hypothesis is correct and no other processes are able to generate positive Y_{SN} anomalies in seawater, this suggested that even in the Archaean ocean enough organic material was available to dominate surface-complexation of Y and REEs. Consequently, the amount of organics present in seawater might have been constant throughout geological history, supporting similar interpretations derived from carbon-isotope studies (e.g., Schidlowski and Aharon, 1992).

To check whether or not inorganic surface-complexes are able to generate positive Y_{SN} anomalies in seawater, we studied Y and REE

partitioning between seawater and hydrogenetic Fe-Mn crusts. In contrast to ambient seawater, these crusts display negative Y_{SN} anomalies. Results of applying the scavenging model of Byrne and Kim (1990) suggest that Ho and neighbouring REEs form considerably stronger surface-complexes on these precipitates than Y does, and thereby increase the Y/Ho ratio of seawater. Experimental results obtained from semiquantitative REY scavenging by Fe-hydroxides support these conclusions. Data from the Sargasso Sea (Sholkovitz et al., 1994) show that REE partitioning between sub-surface seawater (> 200 m depth) and marine particles (mainly Mn-oxides or Mn-oxide-coatings) is indistinguishable from that between seawater and hydrogenetic Fe-Mn crusts. Apparently, inorganic and organic (-ally coated) marine particles both initiate similar Y and REE fractionation trends that eventually result in positive Y_{SN} anomalies in seawater: The occurrence of positive Y_{SN} anomalies in Precambrian seawater, therefore, cannot be used to argue in favour of the presence of constant amounts of organics in seawater throughout geological time.

References

Bau, M., Dulski, P., and Möller, P. (1994) Yttrium and holmium in South Pacific seawater: Vertical distribution and possible fractionation mechanisms. Chem. Erde, (in press).

Byrne, R.H. and Kim, K.-H. (1990) Geochim. Cosmochim. Acta, 54, 2645−56.

Byrne, R.H. and Lee, J.H. (1993) Mar. Chem., 44, 121−30.

Elderfield, H. (1988) Phil. Trans. Roy. Soc. London, A325, 105−26.

German, C.R. and Elderfield, H. (1990) Paleoceanography, 5, 823−33.

Høgdahl, O.T., Bowen, B.T., and Melson, S. (1968) Advan. Chem. Ser., 73, 308−25.

Schidlowski, M. and Aharon, P. (1992) Carbon cycle and carbon isotope record: Geochemical impact of Life over 3.8 Ga of Earth history. In Early organic evolution (M. Schidlowski et al, eds.), Springer, Berlin, 147−75.

Shabani, M.B., Akagi, T., Shimizu, H., and Masuda, A. (1990) Anal. Chem., 62, 2709−14.

Sholkovitz, E.R., Landing, W.M., and Lewis, B.L. (1994) Geochim. Cosmochim. Acta, 58, 1567−79.
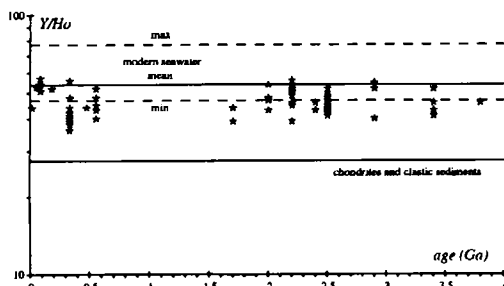
FIG. 1. Variation of Y/Ho ratios of marine chemical sediments during geological history (details on samples are available from the authors upon request).