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SCIENTIFIC COMMENT

On cerium anomalies in the Sargasso Sea

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IN AUGUST 1980 UNFILTERED seawater was collected aboard *R V OCEANUS* in the Sargasso Sea. Throughout 1981 various surface water samples were used in developing instrumental neutron activation (INAA) methods for determining the rare earths in seawater. The first vertical profile of rare earths in seawater was reported in early 1982 and published in January 1983 (DE BAAR et al., 1982, 1983). Meanwhile Elderfield and coworkers had developed an elegant isotope dilution mass spectrometric (IDMS) method and published a vertical profile of rare earths in the eastern Atlantic Ocean (ELDERFIELD and GREAVES, 1982). The smoothly curved vertical profile of Ce (Fig. 1) in our data was very similar to that of ELDERFIELD and GREAVES (1982) and those published some years earlier for dissolved Mn, which is not unlikely given the similar oxidation-reduction thermodynamics predicted for both elements in seawater. Also, Mn was generally understood to have slow oxidation kinetics, and dissolved Mn(II) originating from reducing shelf sediments might well be allowed to transport laterally to the center of the basin. Since not much was known then about Ce oxidation kinetics in seawater (CARPENTER and GRANT, 1967), such a scenario would also appear reasonable for dissolved Ce (III) in seawater. Quite remarkably, when compared with the other rare earths, we found a positive Ce anomaly in the upper ~150 m of the water column, which had not been reported in the single samples of GOLDBERG et al. (1963) and MASUDA and IKEUCHI (1979) nor in the 11 samples of ELDERFIELD and GREAVES (1982). Similar and stronger positive Ce anomalies had, however, commonly been observed in ferromanganese nodules and crusts; i.e., both Ce and Mn appeared to be enriched in such authigenic deposits. Similar enrichments in coastal shelf sediments combined with redox dissolution might allow high signals of Mn and Ce to dissipate into the central basin. The seasonal hydrography of the August 1980 water column strongly suggested its passage through shallow Florida Straits only some months before as part of the general Gulfstream flow pattern. This Florida Straits shelf source scenario might be confirmed once positive Ce anomalies were found in anoxic environments, i.e., interstitial waters or enclosed anoxic basins.

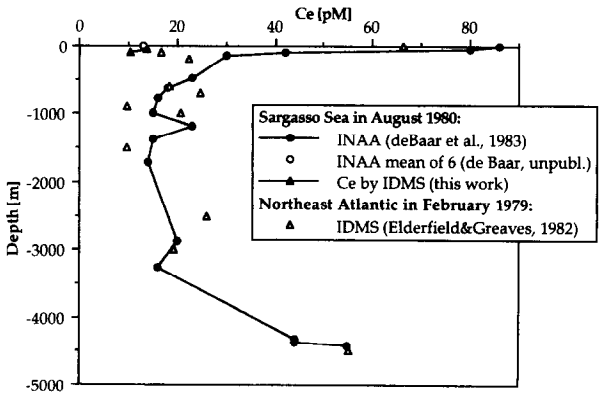

FIG. 1. Vertical profile of dissolved Ce in the Sargasso Sea (33°58'N, 58°05'W) on 23 August 1980 (DE BAAR et al., 1983). Drawn in the mean value of six replicates (DE BAAR, 1983) as well as the IDMS values for the two library samples. Also shown are the Ce levels assessed by IDMS in the NE Atlantic Ocean by ELDERFIELD and GREAVES (1982).

Since then, we produced data on Ce and other rare earths in the eastern (DE BAAR et al., 1985a) and central Pacific Ocean (DE BAAR et al., 1985b), the eastern Mediterranean (DE BAAR et al., 1990), the Indian Ocean (GERMAN et al., 1987), the Southern Ocean (SOUREN et al., 1991), and surface waters of the Carribean (DE BAAR et al., 1988), and the Black Sea (SCHIJF et al., 1991). Some of this work was in collaboration with the Cambridge group of Elderfield and coworkers who also published various other datasets (KLINKHAMMER et al., 1983; ELDERFIELD, 1988). The ongoing work of Schijf and Souren and coworkers is being done in our laboratory in Amsterdam. None of these datasets for oxygenated or low-oxygen (DE BAAR et al., 1985a) seawater showed a positive Ce anomaly. Meanwhile, Sunda and coworkers provided evidence towards *in situ* photoreduction of Mn, which may also explain the often-observed elevated Mn levels in surface waters (SUNDA et al., 1983; SUNDA and HUNTSMAN, 1988).

From investigating the anoxic Cariaco Trench basin, we observed a distinct but modest positive Ce anomaly just below the oxic/anoxic interface; however, above the interface Ce was well depleted relative to the other rare earths (DE BAAR et al., 1988). Similarly, at Cambridge the first porewater profiles of rare earths had been measured; and despite evidence for Ce mobilization, the positive Ce anomalies found were modest and restricted to waters just above and below the sediment/water interface (ELDERFIELD and SHOLKOVITZ, 1987). Recent investigations of suboxic or anoxic marine basins confirmed dramatic Ce mobilization but hardly ever a positive Ce anomaly (SHOLKOVITZ and ELDERFIELD, 1988; SCHIJF et al., 1991; GERMAN and ELDERFIELD, 1989, 1990).

Table 1. Concentrations [pM] of rare earths in seawater collected during August 1980 cruise and analyzed in 1981-1982 by INAA and 1991 by IDMS.

Depth [m]	La	Ce	Nd	Sm	Eu	Gd	Tb	Er	Yb	Lu
Station Oceanus 3 (33°58'N, 58°05'W) at 23 August 1980; INAA results (DeBaar et al., 1983):										
49	12.0	80	-.-	3.35	0.75	4.6	0.73	-.-	5.1	0.78
Surface water samples August 1980 in same general area; INAA (mean of 6 replicates; DeBaar, 1983):										
surface	13	13	13	2.6	0.7	3.7	0.6	-.-	3.4	0.54
Station Oceanus 2 (39°N, 67°01'W) at 17 August 1980; IDMS results (this work)										
47	-.-	13.7	17.9	3.8	1.0	-.-	-.-	-.-	-.-	-.-
95	-.-	10.3	16.2	3.42	0.90	-.-	-.-	4.6	4.4	-.-

More recent observations in pore waters also provided evidence for Ce dissolution, yet again only modest positive Ce anomalies in overlying waters very near the sediment (SHOLKOVITZ et al., 1989). More and more our original observation of positive Ce anomalies in oxygenated surface waters of the Sargasso Sea was becoming an oddity. The expected positive Ce anomalies (as in nodules) in anoxic waters had been found, but Ce enrichments were less than twofold as compared to the maximum enrichment of more than threefold (at 49 m depth) in our first Sargasso Sea dataset.

Recently a fine new dataset became available for rare earths in the Sargasso Sea (SHOLKOVITZ and SCHNEIDER, 1991). Despite different geographical locations and some nine years sampling interval all rare earths appear to agree nicely with our original dataset, except for Ce being considerably lower, exhibiting the negative Ce anomaly which now had been observed all around the world. Attention was drawn to one of our unpublished 1981 trial runs of six replicate surface water samples, with rather poor reproducibility since no internal ^{144}Ce tracer had been used then (DE BAAR, 1983). Otherwise those six samples by and large had the same rare earth concentrations as published in 1983 (except Ce!) and later by SHOLKOVITZ and SCHNEIDER (1991). Later authors correctly point at the likelihood of *in situ* redox chemistry of Ce as recently suggested by MOFFETT (1990), whereas it now appears that Ce which is mobilized in sediment porewaters is quite rapidly oxidized again in overlying bottom waters. Yet one cannot firmly decide for the *in situ* or the earlier margin source mechanism for Ce due to lack of observational constraints in the field.

We analyzed two library samples from the *OCEANUS* 1980 cruise by IDMS (Table 1). Despite different station locations, the values at 47 m and 95 m depth for Ce, Nd, Sm, and Eu are similar to the other now available Sargasso Sea datasets, with the exception of the much higher Ce values originally published in 1983. Later data was well scrutinized before submission; the carrier-free ^{144}Ce (produced from ^{235}U fission) internal standard had been tested for absence of stable Ce isotopes (i.e., blanks) before addition. Also two analytical blanks containing such ^{144}Ce internal standard were carried along with the overall procedure for each set of nine samples. Inadvertent production of interfering ^{141}Ce from trace amounts of ^{235}U left in a sample was monitored by checking the absence of ^{239}Np produced simultaneously from activation of ^{238}U. Random contamination would appear in contradiction with the overall smooth Ce profile (Fig. 1) and would also have affected the other rare earths. Other than the now apparently very peculiar positive Ce anomaly, we still have no reason to doubt the Ce data, unless some unnoticed systematic interference in the INAA routines has betrayed us. Here the overlap of short-lived (4.2 d) ^{175}Yb with longer-lived (32.6 d) ^{141}Ce comes to mind, but this pitfall had been well recognized and avoided by estimating the Ce (i.e., ^{141}Ce) many weeks post-irradiation in order to allow ^{175}Yb to decay away completely (DE BAAR, 1983, 1984). Nevertheless, the Ce values in the first set of nine samples of the upper 1000 m now appear to be very high. Since there is no IDMS data yet for the deep Sargasso Sea, one can only observe that in the second set of deeper samples (which were activated separately) the Ce is not unlike values found in the NE Atlantic Ocean (Fig. 1). Finally the INAA data of the East Equatorial Pacific Vertex II station generally agrees well with the IDMS

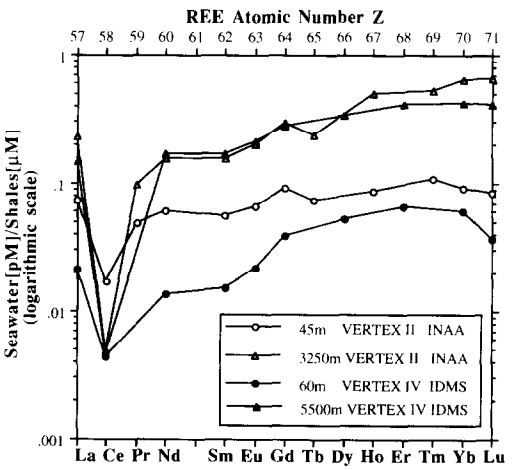

FIG. 2. Comparison of rare earth distribution patterns as measured by INAA and IDMS respectively at Vertex II (18°N, 108°W) and Vertex IV (28°N, 155°W), respectively (DE BAAR et al., 1985a,b). In the deep water the agreement is remarkable, the surface water values of nearshore station Vertex II are higher but otherwise with very similar Ce anomaly as at offshore Vertex IV.

values obtained at central North Pacific Vertex IV station (Fig. 2).

Within one decade some progress has been made and the rather unusual (if not unlikely) Ce enrichments (DE BAAR et al., 1983) appear to be the exception to the now firmly established rule that Ce is depleted in oceanic waters.

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Editorial handling: G. Faure

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