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Low cerium among the dissolved rare earth elements in the central North Pacific Ocean

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Abstract

Seawater samples were collected at the Vertex IV site at 28°N, 155°W in the central North Pacific Ocean. The very old deep waters show low concentrations of dissolved Ce, and the lowest values worldwide of dissolved Ce relative to the other REE, as defined by either the Ce/Nd ratio or the Ce anomaly Ce/Ce^* . The very old deep waters in the central North Pacific show the highest concentrations of dissolved strictly trivalent REE, i.e. except for Ce. Within the thermocline region there exist very close linear relations of the REE series with the nutrients PO_4 and NO_3 , but curvature versus nutrient SiO_4 . This and the general about twofold enrichment of deep Pacific versus deep Atlantic of REE and PO_4 , NO_3 , would support the notion that ocean biogeochemical cycling of the REE is coupled with the ocean cycling of organic matter. Multiple regressions of Nd, representing the LREE, and Er, representing the HREE, versus both phosphate and silicate are significant. Nevertheless there is room for the hypothesis of invoking additional net deep water scavenging of mostly the LREE (i.e. Nd) but also the HREE (i.e. Er). There is a trend of increasing REE abundance with increasing atomic number, when the dissolved seawater data at Vertex IV site are normalized versus PAAS reference. This trend is consistent with stabilization in seawater due to stronger inorganic complexation with carbonate ion with increasing atomic number from La to Lu. There are indications for a positive Gd anomaly at Vertex IV site and also in other datasets of dissolved REE in other oceans. Inter-oceanic comparison between the North Pacific and the Northwest Atlantic shows for the deep Pacific an up to 2.5-fold relative enrichment for the strictly trivalent REE, that is parallel with enrichment of phosphate and nitrate, suggesting REE-cycling along with the ocean cycle of organic matter. The Pacific/Atlantic concentration ratio does not increase with increasing atomic number along the REE series. The deep Pacific shows an up to 3-fold relative Ce depletion versus the deep Atlantic. The deep North Pacific is enriched with Eu relative to the deep Northeast Atlantic, likely due to more emissions of Eu-enriched hydrothermal fluids in the Pacific basin.

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Keywords: Cerium; Rare earth elements; North Pacific Ocean

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1. INTRODUCTION

The Rare Earth Elements (REE) are a unique series of 15 chemical elements ranging from atomic number 57 element $_{57}\text{La}$ and the 14 elements that follow, up to $_{71}\text{Lu}$. In seawater all REE exist in the REE^{3+} ion state with identical electron configurations of the outermost 5s and 5p electron shells (2 and 6 electrons respectively) causing very similar chemistry. With increasing atomic number (i.e. protons in the nucleus), the inner 4f shell is gradually filled from zero electrons for La to 14 electrons for Lu. This gives rise to gradual trends in their chemistry, notably with increasing atomic number (and 4f shell electrons) the REE^{3+} ion tends to be more strongly bound to inorganic complexing agents in seawater (Goldberg et al., 1963; Turner et al., 1981; Cantrell and Byrne, 1987; de Baar et al., 1991). Total dissolved La exists for 52% as LaCO_3^+ ion and 36% $\text{La}(\text{CO}_3)_2^-$ ion, and some other inorganic complexes such that only 4.8% exists as the truly “free” La^{3+} ion (Schijf et al., 2015, their Table 3). This inorganic speciation gradually changes along the series up to Lu which exists for 88% as $\text{Lu}(\text{CO}_3)_2^-$ ion, 11% as LuCO_3^+ ion and merely 0.1% as the free Lu^{3+} ion (Fig. 1). Similarly such trends along the REE series have been studied for sorption of the REE on model organic and inorganic surfaces that are assumed to be the major constituents of marine particles (Schijf et al., 2015; their Fig. 5; and citations therein).

At any given location in the oceans, the vertical profiles of the REE and many other elements are dominated by the

circulation and mixing of ocean water masses (de Baar et al., 2017a, 2017b). In general, the circulation and mixing tends to lead to an averaging of more local effects, such that the resulting vertical and/or lateral distributions of a chemical element tend to be quite smooth. Therefore the hydrography does play a very important role in the ocean distribution of the REE (Zheng et al., 2016; Behrens et al., 2018). Superimposed on this hydrography, the ocean biogeochemical cycling of the REE is closely linked with the biological cycle of the major biological elements C, N, P and Si, Ca. Here adsorption of the REE on biogenic particles is deemed to play a major role, but more intrinsic incorporation of the REE in biogenic particulate matter has also been suggested in the literature.

The free REE^{3+} ion is thought to be the most reactive species, notably for adsorption onto biogenic particles in the upper water layers where plankton is most abundant. This adsorption is deemed to lead to “fractionations” along the REE series akin to fractionations of stable isotopes of one element, for example Cd stable isotopes (de Baar et al., 2017c; and references therein). For the REE series such fractionation trend with increasing atomic number is the result of a balancing act between (i) the concentrations and REE-affinities of inorganic complexes in the seawater, and (ii) the concentrations and REE-affinities of the adsorbing agents on the surface of marine particles.

Some ~10% portion of the biogenic particles in the surface ocean escapes to deeper water layers. This settling of biogenic particles debris, often as larger aggregates also comprising biogenic hard parts (siliceous opal, CaCO_3) and lithogenic mineral particles, is enhanced by the latter biogenic hard parts and lithogenic minerals that are much heavier (higher density) than organic matter and the surrounding seawater medium. This is known as the ballast effect (Ittekkot et al., 1991; Ittekkot, 1993; Klaas and Archer, 2002, and references therein). As a result the adsorbed REE also settle down into the deep sea. Next upon respiration and remineralization and hence dissolution of most of the particles, the adsorbed REE have lost their carrier and are released again into deep waters. This ocean biogeochemical cycling of the REE (except Ce) is in the current article reported to be apparently related with the world ocean cycling of major nutrient elements N and P, i.e. the ocean cycling of organic matter. The deep mineralization of biogenic debris in combination with circulation of deep waters (de Baar et al., 2017a, 2017b), causes a steady increase of both the major nutrients nitrate and phosphate and the REE going from relatively young deep waters in the North Atlantic Ocean to the oldest deep waters in the North Pacific Ocean. However observed relations of the REE (except Ce) with the nutrient silicate also have to be taken into account, both at our study site in the North Pacific Ocean (this work) and elsewhere (de Baar et al., 1983, 1985a; Elderfield, 1988; Garcia-Solsona et al., 2014; Hathorne et al., 2015; Zheng et al., 2016; and several others). This makes sense because the siliceous opal acting as ballast will upon deep dissolution cause increasing deep concentrations of both dissolved silicate and dissolved REE. Multivariate regressions of the REE versus both phosphate and silicate are significant (this work). Neverthe-

Fig. 1. The inorganic chemical speciation of the REE series in seawater at chosen standard salinity $S = 35$ and $\text{pH} = 8.2$. Shown are the major inorganic complexes $\text{REE}(\text{CO}_3)^+$, $\text{REE}(\text{CO}_3)_2^-$, the summation of these carbonate species, and the free REE^{3+} ion. Latter free REE^{3+} ion is plotted at tenfold vertical scale to better see the decreasing trend with increasing atomic number along the REE series. This decreasing trend is thought to represent decreasing susceptibility to adsorptive scavenging on suspended particles. The summation of carbonate species increases steadily from 89% for La up to 99% for Lu and largely explains the increasing stabilization in seawater solution with increasing atomic number. The relatively minor inorganic complexes with Cl^- , SO_4^{2-} , OH^- and HCO_3^- are not shown. Graph after Schijf et al. (2015), their Table 3, but original non-rounded values that better show the gradual trend of the free REE^{3+} species.

less there is room for the hypothesis of additional net deep water adsorptive scavenging of the REE. Indeed similarity of the REE with deep water scavenging removal of Cu has previously been suggested (de Baar et al., 1985a; their Figs. 1 and 5). The trivalent element Al(III) is an extreme case of reactivity to such deep water scavenging, as it subject to very intense net removal from deep waters by adsorptive scavenging on settling debris particles (Van Hulten et al., 2013, 2014; Middag et al., 2015; de Baar et al., 2017b).

Parallel to observed relations of the REE with silicate, there exist relations of the REE with Alkalinity (after adjustment) (de Baar et al., 1983, 1985a; Elderfield, 1988; Garcia-Solsona et al., 2014; Hathorne et al., 2015; and several others). Briefly, upon adjustment for a minor contribution of dissolved nitrate (Brewer and Goldman, 1976) and normalization to salinity $S = 35$ (Brewer, 1978), the thus derived Alkalinity_{adjusted} is an indicator of addition of Ca^{2+} ions to deep waters due to remineralization of biogenic CaCO_3 . Overall relations of the REE with major nutrients phosphate, nitrate, or silicate, and Alkalinity_{adjusted} clearly show that, one way or another, the REE world ocean cycling surely is linked to biological cycling.

However some minor portion of settling biogenic particles and their associated REE do escape mineralization within the water column, and become buried in the seafloor. In this removal from surface waters, remineralization in deep waters, and some burial, the La with 4.8% free La^{3+} ion is comparatively more reactive than the Lu with merely 0.1% free Lu^{3+} ion (Fig. 1). As a result the seawater in the oceans tends to become gradually enriched with the ‘heavy’ elements (HREE) relative to the light elements (LREE). (*The HREE and LREE wording is commonly used, but in fact the mass itself of each element does not play a role in the oceans.*)

There are two REE that can have different oxidation states in the marine environment. Firstly dissolved Ce^{3+} tends to oxidize to solid Ce(IV) state and as such is removed from seawater (de Baar et al., 1988; Schijf et al., 1991). It is now believed that Ce oxidation is catalytic on the surface of bacterially formed Mn-oxyhydroxides and Ce(IV) does not form a separate mineral (see Schijf et al., 2015). This net removal of Ce gives rise to a negative anomaly of Ce in seawater relative to its neighbours in the REE series, that is further presented and discussed in text Section 5.1. Secondly Eu(III) can become reduced to the Eu(II) state in the processes of formation of mid-ocean ridges (Michard et al., 1983; Klinkhammer et al., 1983, 1994a, 1994b; Sverjensky, 1984; Wood, 1990; Bau, 1991; Mitra et al., 1994; and others). This is the cause of a positive Eu anomaly in the hot ($\sim 380^\circ\text{C}$) and strongly reducing environment of hydrothermal vents at mid-ocean ridges, as discussed in Section 5.5.4.

With regard to the gradual filling of the inner 4f electron shell, there are fine details associated with the empty 4f shell of La, the exactly half-filled 4f shell of Gd and completely filled shell of Lu. In theory this may give rise to, in itself quite small, anomalies of La, Gd and Lu relative to the other REE in the series. For Gd such an anomaly can be defined by comparison with “normal” Gd^* , interpolated

between two of its neighbours in the REE series. This is further presented and discussed in Section 5.3.

For La and Lu at the beginning and the end of the REE series, definition of a “normal” La^* or Lu^* is feasible, in principle, either by extrapolation or by a polynomial fitting of the complete REE series pattern (Möller et al., 2002). However the purported anomalies of both La and Lu will not be treated here. Similarly the complete “tetrad” effect including anomalies not only of La, Gd and Lu but also at 1/4 and 3/4 positions of the f-shell, i.e. in between Nd and Pm, and in between Ho and Er, respectively, is not treated here. In a previous assessment by McLennan (1994) no evidence for complete tetrad effects in geochemistry was found. Mathematical methods exist for defining the tetrad effect of the REE series (Monecke et al., 2002). Tetrad effects are known in certain liquid/liquid partition coefficients, and have been suggested for seawater (Masuda and Ikeuchi, 1979), yet are even more of a challenge to observe in seawater, also because Pm does not exist as a stable element (de Baar et al., 1985b; their Fig. 7; McLennan, 1994, their Fig. 1).

For intercomparisons along the complete REE series there is another complication. Briefly in the processes of nucleosynthesis (*still taking place in stellar evolution elsewhere in the universe*), there are two major features. These are (i) strong predominance of elements with even atomic number over elements with odd atomic number (*the Oddo-Harkins rule*), and (ii) systematic decrease in abundance with increasing atomic number (Oddo, 1914; Harkins, 1917). Planet Earth represents the results of these processes, such that in any rock type, and in seawater, there is a prominent even/odd predominance as well as the decreasing trend. Both dominant effects can, in principle, be removed by normalization versus a geochemical reference (Elderfield, 1988). The REE abundance in continental rocks is suitable as such a normalization reference, because it is deemed to represent the REE pattern of external input into the oceans either via rivers or via aeolian dust transport. Nowadays the average REE composition of Post Archean Australian Shale (PAAS) is commonly used (McLennan, 1989) and listed in Table 1, below the seawater values. Notice that the concentrations in PAAS are 6–7 orders of magnitude higher than in seawater.

Finally, the element ^{61}Pm (Promethium) can be seen as an ultimate case of the Oddo-Harkins rule. Promethium, with odd atomic number 61, has no stable isotopes. Therefore in the various figures in this article there is a gap between Nd and Sm. (*Otherwise negligible amounts of short-lived Pm isotopes can be produced naturally by rarely occurring fission of ^{238}U . The radioisotope ^{147}Pm ($t_{1/2} = 2.6$ year) has also been re-introduced as fallout of nuclear bomb testing and the Chernobyl nuclear accident.*)

Since the pioneering studies of REE in seawater by Goldberg et al. (1963) and Masuda and Ikeuchi (1979), there was a new interest, at first independently by Harry Elderfield and Mervyn Greaves in Britain using Fe co-precipitation followed by Isotope Dilution Mass Spectrometry (IDMS) yielding 10 of the 14 naturally occurring REE (Elderfield and Greaves, 1982), and the current lead author, then in the U.S.A., using Chelex-100 column separation fol-

Table 1

Concentrations [$\mu\text{mol}\cdot\text{kg}^{-1}$] of the dissolved REE at Vertex IV site. Also listed are the concentrations [$\mu\text{mol}\cdot\text{kg}^{-1}$] of REE in other geochemical reservoirs, notably the PAAS reference for shales (McLennan, 1989) that commonly is presumed to represent typical global abundance of the terrestrial source for REE in the oceans. Prior to definition and use of the PAAS reference, the (global) average shale reference (a mixture of North Atlantic Shale Composite NASC, and European shales and Russian platform shales) was used for normalization (Haskin and Haskin, 1966). Shales representing the crustal abundance of REE are relatively enriched in LREE compared to chondrites, the latter deemed to be representative for the REE composition of the bulk earth (Evensen et al., 1978). Also listed are various estimates of the average REE content of rivers as a source of REE supply into the oceans. Amazon(3) is river end-member, average of 3 samples (1 sample of Elderfield et al., 1990, and 2 samples of Sholkovitz, 1993). Only Sm, Gd and Dy for assessment of Gd anomaly in rivers: Amazon(18) is river end-member, average of 18 samples (Barroux et al., 2006); 12 Rivers is average of 18 samples of 12 rivers (Elderfield et al., 1990).

Depth [m]	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
All REE concentrations in [$\mu\text{mol}\cdot\text{kg}^{-1}$]														
25	5.3	3.78		4.59	0.98	0.23	1.45		1.83		1.49		1.12	0.125
60	6.31	2.56		3.57	0.756	0.23	1.57		1.785		1.494		1.25	0.128
100	5.48	2.51		3.47	0.73	0.21	–		2.22		1.61		1.18	–
150	4.6	2.69		4.06	0.85	0.25	1.54		2.49		1.83		1.46	0.34
200	8.0	2.55		4.29	0.89	0.26	1.77		2.37		1.88		1.54	–
300	10.6	2.39		6.70	1.30	0.37	2.6		3.45		2.69		2.54	–
400	13.4	1.71		9.25	1.83	0.52	–		3.80		3.62		3.37	0.55
500	19.5	1.45		11.8	2.29	0.63	3.93		4.83		4.37		4.09	0.73
600	25.0	2.41		15.6	2.89	0.79	4.70		5.76		5.18		6.68	0.89
750	33.6	2.56		18.7	3.40	0.93	5.24		6.44		5.98		4.55	1.02
900	35.0	2.67		18.9	3.44	0.95	5.65		6.62		6.41		6.61	1.00
1100	–	2.76		17.1	3.10	0.87	5.16		6.72		6.27		6.88	1.91
1500	36.2	2.39		20.5	3.64	1.05	6.05		8.20		7.79		8.17	1.81
1750	–	2.41		20.9	3.77	1.07	6.43		7.78		7.73		8.24	–
2000	39.0	2.37		26.0	4.19	–	7.84		7.74		–		10.2	1.82
3000	45.0	2.17		43.9	8.22	1.38	–		13.3		11.4		12.7	2.07
4000	56	2.52		49.8	9.70	2.40	12.71		14.1		11.8		12.3	2.16
4500	57	2.26		41.6	8.56	2.26	11.7		13.0		9.43		8.44	1.34
5000	–	4.33		49.5	9.94	2.52	10.9		14.3		11.4		12.7	2.07
5500	43	2.72		45.1	8.50	2.22	11.2		11.3		9.19		8.70	1.44
Reservoir	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Shales PAAS: [$\mu\text{mol}\cdot\text{kg}^{-1}$]	275	568	62.7	235	36.9	7.1	29.6	4.9	28.8	6.0	17.0	2.4	16.3	2.5
Shales (Haskin & Haskin, 1966): [$\mu\text{mol}\cdot\text{kg}^{-1}$]	295	592	71.7	263	49.9	10.6	40.4	7.74	33.8	8.12	22.4	3.73	20.4	3.49
Chondrites (Evensen et al., 1978): [$\mu\text{mol}\cdot\text{kg}^{-1}$]	1.716	4.55	0.684	3.285	1.024	0.382	1.30	0.236	1.564	0.344	0.992	0.152	0.954	0.145
River sources into the oceans for assessment of Gd anomaly in rivers														
[$\mu\text{mol}\cdot\text{kg}^{-1}$]	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Amazon(3)	344	844		540	138	33	158		121		66		53	6.9
Amazon(18)					188		185		151					
12 Rivers					270		300		199					

lowed by Instrumental Neutron Activation Analysis (INAA; de Baar, 1984) yielding 12 of the 14 REE (de Baar et al., 1983, 1985a, 1985b). Further joint efforts at Cambridge (U.K.), combining Chelex-100 with IDMS, led to studies on REE in the anoxic Cariaco Trench (de Baar et al., 1988) and the current study in the central North Pacific Ocean originally presented in 1986 at a conference (de Baar et al., 1985c) and, 32 years later, now finally published. Several more studies of the REE in the oceans followed in the period from the late 1980's to today (e.g. Klinkhammer et al., 1983, 1994a, 1994b; Elderfield, 1988; German et al., 1990, 1995; Schijf et al., 1991, 1994, 1995; Sholkovitz, 1993; Bertram and Elderfield, 1993; Sholkovitz et al., 1994; Shimizu et al., 1994; Zhang and Nozaki, 1996; Bau et al., 1997; Nozaki et al., 1999;

Amakawa et al., 2000, 2004a, 2004b; Nozaki and Alibo, 2003a, 2003b; Alibo and Nozaki, 2000, 2004; Wang and Yamada, 2007; Zhang et al., 2008; Hara et al., 2009; Oka et al., 2009; and several others). Most recently, exciting results of all the 14 natural REE in seawater have been reported by final measurements with ICP Mass Spectrometry (ICP-MS), with pre-concentrations either by the more classical Fe co-precipitation (Zhang and Nozaki, 1996; Grenier et al., 2013; Jeandel et al., 2013; Zheng et al., 2014, 2016; and others), or by novel chemical separation methods (Hathorne et al., 2012, 2015; Pahnke et al., 2012; van de Flierdt et al., 2012; Rousseau et al., 2013; Garcia-Solsona et al., 2014; Hatje et al., 2014, 2016; Haley et al., 2014; Molina-Kescher et al., 2014; Osborne et al., 2015, 2017; Behrens et al., 2016, 2018; and several others). While

appreciating the wealth of REE data in all this fine work and the interpretations in many resulting articles of several admired colleagues, an exhaustive review of all the literature on REE in seawater is beyond the scope of the current article. Here we are focusing on the dissolved REE at the Vertex IV site in the central North Pacific Ocean, and will only make a few comparisons with a few examples of published REE data at a few other ocean sites.

2. METHODS

2.1. Sampling and filtration

Seawater samples were collected on 14 July 1983 at the Vertex IV site at 28°N, 155°W, using 30-liter, Teflon-coated, modified Go-Flo bottles (General Oceanics) on Dacron sheathed, Kevlar hydroline (Bruland et al., 1979), similar as described by de Baar et al. (1985a). Briefly, upon recovery the bottles were placed outside a clean air laboratory and connected via tubings with filter assemblies inside the clean laboratory, for filtration through acid-cleaned, 0.3 µm pore size Nuclepore membrane filters, with a slight overpressure of 0.4 µm filtered nitrogen gas on the Go-Flo bottles. Water samples were stored in hot-acid-cleaned polyethylene containers and acidified to pH 2 with double quartz distilled 8 N hydrochloric acid.

2.2. Extraction, purification and mass spectrometry

The samples were analyzed in 1984 using the Isotope Dilution Mass Spectrometry (IDMS) method as described previously (de Baar et al., 1988). The IDMS method requires at a minimum two stable isotopes for an isotope ratio, therefore the mono-isotopic elements Pr, Tb, Ho and Tm could not be analyzed at the time and are not reported. Briefly all extractions and purifications were done at the University of Cambridge, inside a Class-100 laminar flow bench in a clean room, using hot-acid-cleaned Teflon FEP and polyethylene labware. The isotopically enriched REE spike solution comprises a mixture of each of the 10 REE that have multiple stable isotopes. An exact mass corresponding to 2 L seawater was weighed out accurately, and a known amount (weight) of spike solution was added. The isotopically enriched seawater was passed over a Chelex-100 column, and after washing off the seasalt component, the REE were stripped off the column. The sample was further purified on a cation exchange column (AG50WX8) and stripped off the column in two separate fractions, one comprising all La plus about half of the Ce, the second comprising the other half of the Ce and all other REE. These fractions were then loaded on a triple filament bead for mass spectrometry, the La and half of the Ce on the Rhenium (Re) centre filament, the other half of the Ce and all other REE on the two Tantalum (Ta) side filaments. Isotope dilution mass spectrometry was performed at Cambridge with an Isomass 54E mass spectrometer. By heating of the centre Re filament, the $_{57}\text{La}$ was analyzed as an oxide, upon which the centre filament was heated and used as

normal for enhanced ionization of the other multi-isotopic REE ($_{58}\text{Ce}$ to $_{71}\text{Lu}$) from the Ta side filaments. The emitted REE isotope ions are counted by the mass spectrometer. The more abundant REE (i.e. with even atomic number, and lower atomic number, e.g. $_{58}\text{Ce}$, $_{60}\text{Nd}$) have longer emission time, longer isotope counting, and hence better counting statistics. Afterwards the concentrations of 10 REE in the original seawater sample were calculated offline. Counting statistics indicate a precision better than 1% for the more abundant elements, where the less abundant REE (uneven atomic numbers and/or higher numbers, e.g. $_{71}\text{Lu}$) tend to have less precision but still better than 2%. Gravimetric errors of both the seawater sample and the spike addition are relatively minor, but would somewhat deteriorate the overall precision. Intercalibration of accurate standards representative of the previous Vertex II dataset (de Baar et al., 1985a) with the Cambridge IDMS method showed excellent agreement (de Baar et al., 1985b; their Table 1). Overall accuracy is around 2%. The REE dataset of Vertex IV was first presented in a conference in 1986 (de Baar et al., 1985c) and is listed in Table 1.

3. HYDROGRAPHY, DISSOLVED OXYGEN AND MAJOR NUTRIENTS

3.1. Hydrography

The Vertex IV station at 28°N, 155°W is in the longitudinal center (155°W) of the large Subtropical Gyre of the North Pacific Ocean (Fig. 2) and was sampled on 14 July 1983. The surface waters at 28°N latitude are part of the eastward flowing North Pacific Current, and separated by a strong thermocline in the ~100 to 600 m depth range (Fig. 3) from the underlying North Pacific Intermediate Water (NPIW; Talley, 1993). The core of the North Pacific Intermediate Water is commonly defined as the salinity minimum, with a potential density surface of $\sigma_\theta = 26.8$ (Amakawa et al., 2004a). At the Vertex IV site this is at 600 m depth with salinity minimum $S = 33.99$ (Fig. 3A) and $\sigma_\theta = 26.81$. This salinity minimum of the NPIW is clearly visible in the diagram of potential temperature θ [°C] versus salinity (Fig. 4). Below the core of the NPIW lies the transition zone with the extensive, nearly homogeneous North Pacific Deep Water (NPDW) layer, the latter situated between about 2000 and 4000 m (Talley, 2000). The origin of the NPDW is upwelling of the southern source bottom waters, Antarctic Bottom Water (AABW; in the North Pacific known as Lower Circumpolar Deep Water, LCDW). Indeed with increasing depth there is a steady increase of salinity (Fig. 3), the LCDW being more saline due to the influence of more saline North Atlantic Deep Water (NADW) on Antarctic source waters. The NADW in turn has obtained its higher salinity signal from mixing in the Atlantic with very saline Mediterranean Overflow Water (MOW).

The Vertex IV hydrography dataset (Broenkow and Reaves, 1985) goes down to 1500 m and is listed in Table 2. The nearby WOCE P16 station 050 (28°N, 152°W) provides data in the 1485–5506 m depth interval (Table 3).

Fig. 2. Chart of O₂ minimum zone in the northeast Pacific Ocean and worldwide station positions indicated by small dots under the letter symbols A–M. The contour lines in the northeast Pacific represent the dissolved oxygen (O₂) minimum situated at the $\sigma_\theta = 27.30$ neutral density surface, with O₂ at 10 $\mu\text{mol}\cdot\text{kg}^{-1}$ intervals for only the 10–40 $\mu\text{mol}\cdot\text{kg}^{-1}$ range. Dissolved O₂ after database of [Lauvset et al. \(2016\)](#). Stations A–M and their positions are as follows: (A) VERTEX IV station (14 July 1983) at 28°N, 155°W in the central North Pacific Ocean (this work); here the dissolved O₂ minimum is 22 $\mu\text{mol}\cdot\text{kg}^{-1}$ at $\sigma_\theta = 27.31$ at 900 m depth. (B) SAFe intercalibration station (cruise in May 2009) GEOTRACES at 30°N, 140°W for which REE data at 3000 m depth after [Behrens et al. \(2016\)](#). (C) VERTEX II station (09 Nov 1981) at 18°N, 108°W ([de Baar et al., 1985a](#)); here the O₂ minimum is in the 3–10 $\mu\text{mol}\cdot\text{kg}^{-1}$ range, at σ_θ in the 25.84–27.30 range, in the 110–800 m depth interval. (D) EUC-Fe 14 station (10 Sep 2006) at 0°N, 180°W after [Grenier et al. \(2013\)](#). (E) SA5 station at 0°N, 150°E (cruise in September–October 1992) after [Zhang and Nozaki \(1996\)](#). (F) SA12 station at 27°S, 175°E (cruise in September–October 1992) after [Zhang and Nozaki \(1996\)](#). (G) Bermuda Atlantic Time Series (BATS) station (cruise in June–July 2008) GEOTRACES at 31°40'N, 64°10'W after [Pahnke et al. \(2012\)](#); and (13 June 2010) at station 21 (31°45'N, 64°06'W) of GEOTRACES section GA02 for CO₂ data of [Fig. 6](#) and [Fig. 22](#). (H) CoFeMUG station 4 at 11.5°S, 22.5°W (cruise in November–December 2007) after [Zheng et al. \(2016\)](#). (K) BonusGoodHope station S3 at 47.55°S, 04.37°E (cruise in February–March 2008) after [Garcia-Solsona et al. \(2014\)](#); GEOTRACES in International Polar Year 2008. (M) North Madagascar Basin station 1504 (cruise in August–September 1986) at 27°00.5'S, 56°58.0'E ([Bertram and Elderfield, 1993](#)).

Fig. 3. Vertical distributions of Salinity (A) and Potential Temperature θ (B) in the upper 1500 m at Vertex IV site (28°N, 155°W). Data of [Broenkow and Reaves \(1985\)](#). The salinity minimum at $S = 33.99$ at 600 m depth represents the core of the NPIW.

Fig. 4. Relationship of Salinity and Potential Temperature θ [°C] in the upper 1500 m at Vertex IV site (28°N, 155°W). Data of Broenkow and Reaves (1985). The salinity minimum at $S = 33.99$ at 600 m depth represents the core of the NPIW. Above this salinity minimum is the mixing line versus surface waters, below the salinity minimum is the mixing line versus North Pacific Deep Water down to 1500 m depth. At greater depth this mixing line continues, red line for 1485 m to 5506 m depth interval (Table 3) of WOCE P16N, Leg 2, station 050 (28°N, 152°W). (RV T.G. Thompson, R.A. Feely and C.L. Sabine; <https://cchdo.ucsd.edu/cruise/325020060213>). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Dissolved oxygen

The dissolved oxygen (O_2) dataset (Table 2) shows a minimum of $29 \mu\text{mol}\cdot\text{kg}^{-1}$ at 900 m depth (Fig. 5A) that is situated at the $\sigma_\theta = 27.26$ neutral density surface. Just below at 950 m depth the O_2 is virtually the same at $30 \mu\text{mol}\cdot\text{kg}^{-1}$ at the $\sigma_\theta = 27.30$ surface that is depicted for the entire Northeast Pacific Ocean in Fig. 2. For example in the easternmost North Pacific at Vertex II station at 18°N, 108°W, the $\sigma_\theta = 27.30$ surface (not shown; see Broenkow and Krenz, 1982) shows much lower $O_2 = 10 \mu\text{mol}\cdot\text{kg}^{-1}$ and an overlying intense O_2 minimum zone (OMZ) with O_2 values in the $3\text{--}10 \mu\text{mol}\cdot\text{kg}^{-1}$ range for depths between 110 and 800 m (Fig. 5A). The Northeast Pacific Ocean is well known for the very low OMZ conditions, as shown also in Fig. 2. For example at Geosecs station 343 (16°31'N, 123°01'W), near the Vertex II site (18°N, 108°W), dissolved O_2 is not detectable in the 226–324 m depth range and very low $<10 \mu\text{mol}\cdot\text{kg}^{-1}$ across the 196–690 m depth range (Fig. 5B). The other station near the Vertex II site, Geosecs 345 (22°31'N, 122°12'W), shows a less extreme O_2 minimum, comparable to the one at Vertex II (Fig. 5B).

Lateral mixing along isopycnal surfaces (e.g. Fig. 2) is believed to transfer the low O_2 signature originating in the eastern region towards the center of the North Pacific

basin. The eastern equatorial Pacific Ocean experiences local upwelling of nutrient rich subsurface waters; this upwelling supports plankton blooms, that upon senescence and settling lead to strong O_2 deficiencies in underlying waters. In contrast the Vertex IV site is oligotrophic and believed to support little plankton growth. Therefore the O_2 minimum at our Vertex IV site is likely to be mainly the result of such lateral mixing (and perhaps some advection as well), and much less, if at all, the result of *in situ* oxygen consumption. This notion is supported by the Vertex study of dissolved manganese (Mn) that also is controlled by lateral transport (Martin and Knauer, 1985; Martin et al., 1985).

3.3. Major nutrients

The dataset of the major nutrients is listed in Table 4. The major nutrients nitrate and phosphate are depleted in the surface waters (Fig. 6A, B). The center of the Subtropical North Pacific Gyre is oligotrophic, i.e. the growth of phytoplankton is limited due to lack of these nutrients. Within the thermocline both nitrate and phosphate increase strongly with depth to maxima at 900 m depth coinciding with the oxygen minimum. Below this both nutrients steadily decrease with depth to lowest values in the LCDW near the seafloor. Silicate is also depleted in surface waters, hence limiting for growth of diatoms (Sarhou et al., 2005). In the thermocline there is a strong increase with depth to $128 \mu\text{M}$ at 900 m, followed by more modest increase to a maximum of $170 \mu\text{M}$ at 3000 m that is representative of the core of the NPDW. Below this the silicate decreases with depth due to mixing of the NPDW with the underlying LCDW that contains $153 \mu\text{M}$ at 5500 m depth.

The steep increase of nutrients in the 200–900 m depth range shows a very significant ($R^2 = 0.998$ for $n = 7$ samples) linear relation between nitrate and phosphate (Fig. 7A; Table 5). However for the same depth range there is a slightly negative curvature of silicate versus phosphate (Fig. 7B). Similarly there is a negative curvature of silicate versus nitrate (Fig. 7C). As a result a curve fitting power function yields a better fit to the 7 data points than a simple linear regression. Most likely this curvature is due to vertical mixing between three end-member water masses: the North Pacific Intermediate Water (NPIW) with its core at 600 m depth, mixing with overlying surface waters and underlying North Pacific Deep Water (NPDW). Although this vertical mixing extends both above 200 m and in a transition zone extending well below 900 m (Fig. 4), a dotted line is depicted in Fig. 7B and C connecting the more or less two end-members at 200 m and 900 m depth. The sample at 600 m depth represents the third end-member NPIW. Thus apparently the NPIW comprises slightly less dissolved silicate relative to phosphate and/or nitrate than the overlying and underlying water masses. For phosphate and nitrate their relative proportions are identical in the NPIW and the overlying and underlying water masses (Fig. 7A).

Within the O_2 minimum zone there is some deficiency of nitrate due to microbial nitrate reduction. The expected

Table 2

Hydrography in the upper 1450 m at Vertex IV site. Sal. is Salinity (dimensionless); Temp. is Temperature; θ is Potential Temperature; L.T. is Light Transmission only in upper 300 m; Pigments also only in upper 300 m, but below 300 m depth no Light Transmission and Pigments. Data of [Broenkow and Reaves \(1985\)](#).

Depth [m]	Sal.	Temp [°C]	θ [°C]	O ₂ [$\mu\text{mol}\cdot\text{kg}^{-1}$]	L.T. (%)	Pigments [$\text{mg}\cdot\text{m}^{-3}$]
0	35.26	23.7	23.7	204	84.9	0.05
5	35.27	23.69	23.69	205	85.6	0.05
10	35.25	23.69	23.69	202	86.7	0.06
15	35.27	23.69	23.69	200	86.5	0.06
20	35.25	23.69	23.69	200	86.5	0.06
25	35.24	23.67	23.66	202	86.5	0.07
30	35.3	22.67	22.66	203	85.5	0.07
35	35.17	22.32	22.31	201	85.1	0.07
40	35.15	21.97	21.96	200	85.8	0.11
45	35.21	21.76	21.75	198	85.9	0.11
50	35.15	21.58	21.57	195	86.4	0.12
55	35.18	21.42	21.4	194	86.5	0.16
60	35.16	21.21	21.2	190	86.6	0.18
65	35.16	21.09	21.08	189	86.7	0.22
70	35.16	20.97	20.96	189	86.3	0.25
75	35.16	20.85	20.84	191	86.1	0.30
80	35.18	20.57	20.55	196	85.7	0.39
85	35.13	20.32	20.31	193	85.0	0.48
90	35.14	20.2	20.19	190	84.9	0.46
95	35.14	19.94	19.93	189	84.7	0.42
100	35.11	19.72	19.71	186	85.4	0.37
110	35.1	19.32	19.3	205	87.2	0.25
120	35.06	18.8	18.78	199	87.8	0.24
130	34.95	18.22	18.2	184	88.7	0.15
140	34.94	17.92	17.9	198	89.2	0.09
150	34.94	17.68	17.65	195	88.5	0.14
160	34.9	17.38	17.35	198	88.5	0.19
170	34.86	17.06	17.03	201	89.0	0.15
180	34.84	16.91	16.88	205	89.2	0.13
190	34.82	16.7	16.67	209	89.2	0.12
200	34.77	16.19	16.16	202	89.5	0.07
210	34.68	15.75	15.72	201	89.9	0.07
220	34.64	15.38	15.38	205	89.9	0.07
230	34.6	14.98	14.95	207	89.9	0.06
240	34.55	14.52	14.48	207	90.0	0.07
250	34.48	14.16	14.13	208	90.1	0.07
260	34.44	13.81	13.78	203	90.0	0.07
270	34.4	13.35	13.31	202	90.0	0.07
280	34.35	12.93	12.89	204	89.9	0.07
290	34.3	12.47	12.43	210	89.8	0.07
300	34.26	12.01	11.97	199	89.8	0.07
Depth [m]	Sal.	Temp [°C]	θ [°C]	O ₂ [$\mu\text{mol}\cdot\text{kg}^{-1}$]		
310	34.23	11.78	11.74	203		
320	34.2	11.47	11.43	206		
330	34.2	11.32	11.27	206		
340	34.16	10.97	10.93	204		
350	34.17	10.85	10.8	205		
360	34.14	10.73	10.69	206		
370	34.13	10.5	10.45	205		
380	34.14	10.34	10.3	208		
390	34.16	10.08	10.03	207		
400	34.11	9.66	9.62	203		
410	34.09	9.5	9.46	203		
420	34.1	9.36	9.32	203		
430	34.07	9.11	9.07	203		
440	34.1	8.91	8.86	199		
450	34.05	8.72	8.67	194		
460	34.03	8.62	8.57	190		

Table 2 (*continued*)

Depth [m]	Sal.	Temp [°C]	θ [°C]	O ₂ [$\mu\text{mol}\cdot\text{kg}^{-1}$]
470	34.03	8.4	8.35	187
480	34.04	8.28	8.23	179
490	34.04	8.01	7.96	174
500	34.03	7.7	7.71	167
550	34.01	6.58	6.53	134
600	33.99	5.59	5.54	102
650	34.05	5.03	4.98	077
700	34.08	4.69	4.63	058
750	34.15	4.51	4.45	042
800	34.21	4.34	4.28	035
850	34.26	4.18	4.11	030
900	34.34	4.09	4.03	029
950	34.36	3.91	3.83	030
1000	34.39	3.77	3.7	032
1050	34.42	3.64	3.56	034
1100	34.45	3.48	3.41	038
1150	34.47	3.39	3.31	042
1200	34.49	3.27	3.19	046
1250	34.5	3.18	3.09	048
1300	34.51	3.11	3.02	051
1350	34.53	3.01	2.91	054
1400	34.54	2.92	2.82	057
1450	34.56	2.82	2.72	058

4. RESULTS

Table 3

Hydrography in 1485–5506 m depth interval at WOCE P16 station 050 (28°N, 152°W) (<https://cchdo.ucsd.edu/cruise/325020060213>). Sal. is Salinity (dimensionless); Temp. is Temperature; θ is Potential Temperature.

Depth [m]	Sal.	Temp. [°C]	θ [°C]
1485	34.56	2.75	2.65
1683	34.59	2.42	2.30
1879	34.61	2.16	1.95
2099	34.63	1.95	1.80
2345	34.65	1.78	1.62
2590	34.66	1.66	1.48
2838	34.67	1.58	1.37
3080	34.67	1.53	1.30
3399	34.68	1.50	1.24
3790	34.69	1.48	1.18
4228	34.69	1.49	1.14
4715	34.69	1.50	1.09
4909	34.69	1.50	1.07
5200	34.70	1.52	1.05
5506	34.70	1.56	1.05

nitrate (Fig. 5D) is calculated as $15 \times \text{PO}_4$ after Broecker and Peng (1982), utilizing the global average N/P ratio = ~ 15 (Fanning, 1992). The difference with the measured nitrate yields the apparent deficiency due to nitrate reduction (Fig. 5C). There is a maximum deficiency at 400 m depth, and another, stronger deficiency maximum at 1300 m depth. The Eastern Pacific with stronger OMZ also shows stronger nitrate deficiency. At the Vertex II site there is a stronger nitrate deficiency than at Vertex IV (Fig. 5C, D), nicely consistent with stronger O₂ minimum at Vertex II relative to Vertex IV (Fig. 5A, B). Note that Dr. Eden Rue previously published a similar figure for Vertex II station (Rue et al., 1997, their Fig. 3A).

4.1. Vertical profiles

The vertical profiles of the REE, except Ce, show a general increase of concentration with increasing depth (Fig. 8). The highest concentrations are found in the sample at 4000 m depth. Below this, there is a distinct decrease of concentration in the samples at 4500 m and 5500 m depth. This decrease is ascribed to the influence of Lower Circumpolar Deep Water (LCDW) of Antarctic origin, which is younger and hence has accumulated less dissolved REE due to overall less input by remineralization of settling biogenic particles. This is consistent with lower dissolved silicate (Fig. 6C) in the lowermost 5000 m and 5500 m samples, a well known observation throughout the North Pacific Ocean, caused by inflow of LCDW that contains lower silicate due to less overall remineralization. The LCDW signal is also apparent in the higher salinity at nearby GEOSECS stations (not shown) as discussed in Section 3.1. Notice that the REE maximum (4000 m) is found at a different depth than the maximum of silicate (3000 m), and those of phosphate and nitrate (900 m). Therefore, the general trend of association of the REE with the ocean biological cycle is obvious, yet not straightforward.

In the surface waters, all REE show concentrations distinctly above zero. This is different from the nutrients which are severely depleted in these oligotrophic surface waters (Fig. 6). The elevated REE in surface waters are ascribed to a combination of (i) supply from more inshore REE-enriched waters off Asia along with the Kuroshio Current feeding into the North Pacific Current, with (ii) additional supply by partial dissolution of aeolian dust input also derived from Asia, and (iii) slow removal due to uptake in or adsorption on biogenic particles. Finally, the very different distribution of Ce will be discussed in Section 5.1.

Fig. 5. (A) Vertical profiles of dissolved oxygen (O₂) in the upper 1500 m at Vertex IV site (28°N, 155°W) and at Vertex II site (18°N, 108°W). Data of Broenkow and Reaves (1985), and Broenkow and Krenz (1982), respectively. (B) Same as (A) at expanded horizontal concentration scale in the 0–30 μmol.kg⁻¹ range. Also shown are O₂ for Geosecs stations 343 (16°31'N, 123°1'W) and 345 (22°31'N, 122°12'W) that are nearby the Vertex II site (Broecker et al., 1982). (C) Vertical profiles of nitrate deficiency (=measured nitrate – expected nitrate) at Vertex IV site, as well as at Vertex II site. (D) Vertical profiles of expected nitrate (=15 × PO₄) and measured nitrate (NO₃) at Vertex IV site, as well as at Vertex II site. (Vertex II data: nitrate after Rue et al., 1997, their Table A1; phosphate PO₄ after Cutter and Bruland, 1984, their Fig. 4C. See also Rue et al., 1997, their Fig. 3A for similar graph but expected nitrate calculated from the nitrate/phosphate relationship in the water column above and below the suboxic zone).

4.2. Sm-Nd relationship

Within the REE-series the element Nd (number 60) is 2 positions below Sm (number 62); there are no data for the element between them, because Pm has no stable isotopes. Upon plotting the relation between Sm and Nd (Fig. 9) at a variety of different locations, two observations can be made. Firstly for all these datasets, all of filtered seawater, there is a generally good agreement of the regression slopes. This provides confidence in the precision, if not accuracy, of these datasets, that had been produced by different final analytical methods, i.e. INAA (Vertex II; de Baar et al., 1985a), IDMS (North Madagascar Basin, Bertram and Elderfield, 1993; Vertex IV, this work), and novel Isotope Dilution ICP-MS producing data for all 14 REE using isotope spike addition (Pahnke et al., 2012; Garcia-Solsona et al., 2014; Behrens et al., 2016).

Secondly, a detailed look at the regression slopes of the different datasets shows that these slopes seem to tend to slightly increase with the general increase of the age of the water masses at the various stations. Going from the relatively young waters in (i) the Northeast Atlantic (BATS) the slope increases to intermediate age waters of (ii, iii) the Southern Ocean (BonusGoodHope) and the Indian Ocean (North Madagascar Basin) and finally the oldest waters in (iv, v) the North Pacific (Vertex II and Vertex IV). This is consistent with the trend of relative enrichment of higher atomic number REE that are more stable in seawater due to stronger inorganic complexation (Fig. 1), i.e. with increasing age of deep waters the Sm appears to be relatively more enriched versus Nd. Because ⁶²Sm is only two atomic numbers higher than ⁶⁰Nd the difference is quite small, therefore below comparisons for more distant ⁷⁰Yb and ⁶⁸Er versus ⁶⁰Nd are presented.

Table 4

Concentrations [μM] of the major nutrients at Vertex IV site. In the main text we use both the symbols for the anions NO₃, SiO₄ and PO₄ and the words nitrate, silicate and phosphate. In seawater at typical pH ~7.9 to ~8.1 these exist as the fully dissociated NO₃⁻ ion, the undissociated H₄SiO₄ silicic acid, and the predominant HPO₄²⁻ ion with minor amounts of PO₄³⁻ and H₂PO₄⁻ ions.

Depth [m]	NO ₃ [μM]	SiO ₄ [μM]	PO ₄ [μM]
25	0.02	1	0.027
40	–	1.5	0.02
50	–	1.9	–
60	0.02	1.6	–
75	0.02	1.7	–
100	0.01	2.4	0.037
125	2.8	2.9	0.186
150	2.4	3.3	0.231
175	4.6	4.9	0.344
200	7.2	7.5	0.597
300	12	13.9	0.968
400	20.3	28.4	1.541
500	26.7	48.2	1.928
600	36.3	78.1	2.602
750	42.7	111.2	3.149
900	44.3	128	3.268
1100	43.7	134	3.308
1300	42.7	142	3.311
1500	42.1	154	3.085
1750	41.3	151	3.131
2000	42	158	3.167
2500	41.6	162	3.104
3000	39.1	170	2.915
3500	37.7	160	2.718
4000	37.8	165	2.775
4500	37.1	162	2.697
5000	36.6	157	2.636
5500	36.3	153	2.616

Fig. 6. Vertical profiles of concentrations [μM] of dissolved major nutrients and of the dissolved carbonate ion at Vertex IV site (filled black dots) and for interocean comparison also at the BATS site (open blue squares). Figures are: (A) nitrate; (B) phosphate; (C) silicate; (D) carbonate ion [CO_3^{2-}]. The Pacific nutrients data (A, B, C) are of Vertex IV station at 28°N , 155°W . The Pacific carbonate data of (D) is based on CO_2 system data at WOCE Station 50 at 28°N , 152°W nearby Vertex IV station at 28°N , 155°W . The Atlantic data at BATS station is of station 21 at $31^\circ45.92'\text{N}$, $64^\circ04.95'\text{W}$ of GEOTRACES GA02 section (IDP 2014, www.geotraces.org; from this the carbonate data was calculated). The Pacific/Atlantic concentration ratio in deep waters is on the order of about twofold for nitrate (A) and phosphate (B). For silicate (C) the Pacific/Atlantic concentration ratio is much higher from fourfold at 4500 m to tenfold at 1000 m depths. For the carbonate ion (D) the Pacific/Atlantic concentration ratio is in the 0.4–0.6 range in the 1000–3000 m depth interval, and ~ 0.75 for the deepest 4500 m samples. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

4.3. Yb-Nd and Er-Nd relationships in the North Pacific and the North Atlantic

In old deep waters of the North Pacific, the slope value 0.40 of regression of the relationship between heavy element Yb and light rare earth element Nd (Fig. 10A) is 3.4-fold the slope value 0.13 in younger waters of the Northwest

Atlantic. Due to stronger inorganic complexation the HREE, i.e. here Yb, tend to be more stabilized in seawater than the LREE, i.e. here Nd. The linear regression for the North Pacific is only for the upper 2000 m samples. When including the two Pacific samples at 3000 m and 4000 m the linear regression (not shown) would tend to have a lower slope value ($\text{Yb} = 0.26\text{Nd} + 1.09$) albeit with lower

Fig. 7. Relations among the major nutrients in the 200–900 m depth interval. (A) Nitrate as a function of phosphate. (B) Silicate as a function of phosphate. (C) Silicate as a function of nitrate.

$R^2 = 0.90$ for $n = 15$ samples. The lower slope value still is twice that in the Northwest Atlantic. The two deepest samples (4500 m and 5500 m) in the North Pacific tend to follow more the Atlantic trend. This, and also the lowered trend at 3000 m and 4000 m, is deemed to be due to significant portions of relatively younger water of Antarctic origin. For the two deepest samples this is clearly visible also in the vertical profiles (Fig. 7) where both Nd and Yb are lower, but Yb more so than Nd.

Similarly the somewhat less heavy element Er still belongs to the HREE and the slope value 0.34 versus Nd (Fig. 10B) is, as expected given the smaller gap versus light element Nd, somewhat lower than the above slope value 0.44 for Yb versus Nd. However the slope value 0.10 for the Northwest Atlantic is also lower, as expected for the same reason. As a result, for Er versus Nd the Pacific slope value is 3.4-fold the Atlantic slope value, i.e. the same as for Yb versus Nd. When including the two Pacific samples at 3000 m and 4000 m the linear regression (not shown) would tend to have a lower slope value ($\text{Er} = 0.24\text{Nd} + 1.34$) albeit

with lower $R^2 = 0.94$ for $n = 15$ samples. This lower slope value still is more than twice that in the Northwest Atlantic.

4.4. Shale-normalized patterns

Four samples illustrate the two dominant features that exist in the shale-normalized graphs (Fig. 11). Firstly, there is a strong depletion of Ce, that is further discussed in Section 5.1. Secondly, with increasing atomic number (from La to Lu) there is a steady increase in abundance for all REE, except Ce. This is the well known enrichment of the ‘heavy’ elements (HREE) versus the ‘light’ elements (LREE). As mentioned above this is due to stronger inorganic complexation with increasing atomic number (Fig. 1), that tends to prevent removal by notably adsorption of the ‘free’ (i.e. the uncomplexed) REE^{3+} ion.

4.5. Good agreement at 3000 m depth

The article of Behrens et al. (2016) reports on an excellent novel method for measuring all 14 natural existing REE, but also comprises results for an ultraclean collected and filtered seawater sample at 3000 m depth at the site (30° N, 140°W) of the SAFE intercalibration (Fig. 2). This SAFE 3000 m sample was analyzed by 4 different laboratories, and the average REE concentration values (Behrens et al., 2016; their Table 7) are shown here (Fig. 12). The pattern of all 14 REE of this SAFE sample agrees very well with the 9 REE of the Vertex IV sample at 3000 m (unfortunately there is no Gd data for this sample), as well as the 12 REE of the Vertex II sample at 3000 m (Fig. 11). At closer look, for the HREE Dy to Lu there appears to be a trend of somewhat decreasing concentrations going from inshore (Vertex II) via SAFE site to the offshore Vertex IV site. However the differences are small. Note the strong Ce anomaly as well as the more modest Gd anomaly (SAFE and Vertex II), which both are further discussed below.

5. DISCUSSION

5.1. Cerium

5.1.1. Vertical distribution of cerium

The vertical profile at Vertex IV shows very low dissolved Ce around $2 \text{ pmol}\cdot\text{kg}^{-1}$ that is lower than at almost all other locations in the world oceans (Fig. 13). Only at the Pacific equator very low dissolved Ce was also found (Grenier et al., 2013; red diamonds in Fig. 13A, B and insert). Grenier et al. (2013; their Table 2) also found very low Ce (e.g. $\text{Ce} < 2 \text{ pmol}\cdot\text{kg}^{-1}$) at several more stations in the region, where generally only the upper water column was sampled. Looking in more detail at Vertex IV (Fig. 13B and insert) there is a surface maximum of $3.8 \text{ pmol}\cdot\text{kg}^{-1}$ not very different from other open oceans, and here likely due to aeolian dust input from Asia. Dust supply is indicated by high Al in surface waters at the same Vertex IV site; Al is the key tracer for dust supply (Orians and Bruland, 1986). A more modest surface maximum exists for Nd, Sm and Eu but not for the others. Dust is generally

Table 5

The equations of linear regressions and/or curve fitting power functions of major nutrients among each other (as shown in Fig. 7) where nitrate as dependent variable of independent variable phosphate; and silicate as dependent variable of independent variables either phosphate or nitrate; and of REE as dependent variable of the independent variable of the nutrients for 7 samples in the 200–900 m depth zone (see Fig. 17 for only Nd). For Nd, Sm, Eu, Gd, Dy, Er versus SiO_4 the curve fitting power functions are more significant than the linear regressions. Coefficients are rounded to 3 decimals, also the R^2 is rounded to 3 decimals because rounded to 2 decimals would in some cases yield $R^2 = 1.00$ that is deemed to be less informative, if not misleading as if perfect.

$\text{NO}_3 = 14.06 \text{ PO}_4 + 1.15$	$R^2 = 0.998$ for $n = 7$ samples
$\text{SiO}_4 = 15.86 \text{ PO}_4^{1.683}$	$R^2 = 0.993$ for $n = 7$ samples
$\text{SiO}_4 = 44.74 \text{ PO}_4 - 30.49$	$R^2 = 0.963$ for $n = 7$ samples
$\text{SiO}_4 = 0.307 \text{ NO}_3^{1.556}$	$R^2 = 0.990$ for $n = 7$ samples
$\text{SiO}_4 = 3.164 \text{ NO}_3 - 26.32$	$R^2 = 0.954$ for $n = 7$ samples
$\text{Nd} = 5.531 \text{ PO}_4 + 1.073$	$R^2 = 0.998$ for $n = 7$ samples
$\text{Nd} = 0.393 \text{ NO}_3 + 1.539$	$R^2 = 0.997$ for $n = 7$ samples
$\text{Nd} = 1.608 \text{ SiO}_4^{0.517}$	$R^2 = 0.994$ for $n = 7$ samples
$\text{Nd} = 0.119 \text{ SiO}_4 + 5.119$	$R^2 = 0.960$ for $n = 7$ samples
$\text{Sm} = 0.9621 \text{ PO}_4 + 0.3599$	$R^2 = 0.998$ for $n = 7$ samples
$\text{Sm} = 0.0684 \text{ NO}_3 + 0.4392$	$R^2 = 0.999$ for $n = 7$ samples
$\text{Sm} = 0.360 \text{ SiO}_4^{0.475}$	$R^2 = 0.995$ for $n = 7$ samples
$\text{Sm} = 0.0206 \text{ SiO}_4 + 1.071$	$R^2 = 0.948$ for $n = 7$ samples
$\text{Eu} = 0.258 \text{ PO}_4 + 0.119$	$R^2 = 0.999$ for $n = 7$ samples
$\text{Eu} = 0.0183 \text{ NO}_3 + 0.140$	$R^2 = 0.999$ for $n = 7$ samples
$\text{Eu} = 0.109 \text{ SiO}_4^{0.453}$	$R^2 = 0.996$ for $n = 7$ samples
$\text{Eu} = 0.0055 \text{ SiO}_4 + 0.309$	$R^2 = 0.951$ for $n = 7$ samples
$\text{Gd} = 1.357 \text{ PO}_4 + 1.153$	$R^2 = 0.990$ for $n = 6$ samples
$\text{Gd} = 0.0966 \text{ NO}_3 + 1.258$	$R^2 = 0.990$ for $n = 6$ samples
$\text{Gd} = 0.866 \text{ SiO}_4^{0.387}$	$R^2 = 0.989$ for $n = 6$ samples
$\text{Gd} = 0.0298 \text{ SiO}_4 + 2.062$	$R^2 = 0.946$ for $n = 6$ samples
$\text{Dy} = 1.357 \text{ PO}_4 + 1.153$	$R^2 = 0.990$ for $n = 7$ samples
$\text{Dy} = 0.109 \text{ NO}_3 + 1.799$	$R^2 = 0.986$ for $n = 7$ samples
$\text{Dy} = 1.247 \text{ SiO}_4^{0.348}$	$R^2 = 0.980$ for $n = 7$ samples
$\text{Dy} = 0.0328 \text{ SiO}_4 + 2.806$	$R^2 = 0.936$ for $n = 7$ samples
$\text{Er} = 1.606 \text{ PO}_4 + 1.081$	$R^2 = 0.994$ for $n = 7$ samples
$\text{Er} = 0.114 \text{ NO}_3 + 1.216$	$R^2 = 0.993$ for $n = 7$ samples
$\text{Er} = 0.865 \text{ SiO}_4^{0.414}$	$R^2 = 0.993$ for $n = 7$ samples
$\text{Er} = 0.0344 \text{ SiO}_4 + 2.264$	$R^2 = 0.948$ for $n = 7$ samples
$\text{Yb} = 1.649 \text{ PO}_4 + 0.886$	$R^2 = 0.787$ for $n = 7$ samples (2 outliers at 600 m and 750 m)
$\text{Yb} = 1.851 \text{ PO}_4 + 0.056$	$R^2 = 0.996$ for $n = 5$ samples (2 outliers removed)
$\text{Lu} = 0.258 \text{ PO}_4 + 0.193$	$R^2 = 0.966$ for $n = 5$ samples (no data at 200 m and 300 m)

shale-like and therefore LREE-enriched relative to seawater, notably for Ce.

There is a subtle yet distinct minimum of the dissolved LREE Ce, Nd and Sm at 100 m depth that coincides with a pigment maximum around 85 m depth (Fig. 14). This suggests that the LREE are removed from solution by uptake into and/or adsorption on plankton particles. Such a fairly deep pigment maximum or Deep Chlorophyll Maximum (DCM) is common under oligotrophic gyres (Cullen, 1982; Mackey et al., 1995). The light level is low, but nutrients are available such that phytoplankton can grow. In the overlying waters there is more light but nutrients are very low and limiting for growth.

Further down there are distinct Ce minima of $1.7 \text{ pmol}\cdot\text{kg}^{-1}$ and $1.5 \text{ pmol}\cdot\text{kg}^{-1}$ at 400 m and 500 m depth respectively (Fig. 13B). At first glance this corresponds with the broad salinity minimum zone (Fig. 3A) of the North Pacific Intermediate Water (NPIW), yet somehow there is a higher Ce of $2.4 \text{ pmol}\cdot\text{kg}^{-1}$ in the NPIW core at 600 m

depth (Fig. 13B). The Ce concentration then increases steadily to maximum values of $2.67 \text{ pmol}\cdot\text{kg}^{-1}$ in the core of the O_2 minimum ($\text{O}_2 = 29 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$) and below that Ce is $2.76 \text{ pmol}\cdot\text{kg}^{-1}$ at 1100 m depth where O_2 also is low at $38 \text{ }\mu\text{mol}\cdot\text{kg}^{-1}$. The relation of these Ce maxima with the O_2 minimum is further discussed in Section 5.1.3. Further down the dissolved Ce decreases to $2.4 \text{ pmol}\cdot\text{kg}^{-1}$ in the 1500–2000 m depth range, a minimum of $2.2 \text{ pmol}\cdot\text{kg}^{-1}$ at 3000 m that is the core of the very old North Pacific Deep Water (NPDW), and then slightly increasing again towards the seafloor, ascribed to somewhat higher Ce in the relatively younger LCDW. This is matched by the lower concentrations of all other (strictly trivalent) REE in the same LCDW which has accumulated less REE than the very old NPDW.

5.1.2. Oxidative removal of Ce from seawater

5.1.2.1. Chemical thermodynamic equilibrium considerations.

Exact reaction mechanisms for the oxidation in seawater of

Fig. 8. Vertical profiles of concentrations [pmol.kg^{-1}] of the REE at Vertex IV site.

Ce^{3+} to solid Ce(IV) state are subject of research and debate, but the reaction equation:

is useful to begin with for this discussion. Other solid states, e.g. Ce(OH)_4 or $\text{CeO}_2 \cdot 2\text{H}_2\text{O}$ may also be envisioned (Hayes et al., 2002; Yu et al., 2006). Next the more refined and realistic reaction mechanisms involving Mn are discussed below.

An equilibrium equation informs about the permitted direction of the reaction, but not on the actual kinetic rate. Kinetics are further discussed in Section 5.1.2.2. Also the Ce(IV) oxidation state is presented as an ideal pure oxide, but in the real ocean this is most likely not the case, instead

an association with other biogeochemical components is more likely, as discussed below.

Nevertheless, for this simple reaction (Eq. (1)) the inorganic thermodynamic stability diagram of Ce in seawater was developed carefully by Dr. van Gaans (de Baar et al., 1988; their Fig. 11) based on existing knowledge at the time. Given adequate O_2 (Fig. 5; Table 2), this leads to a predicted equilibrium concentration of Ce(III) in seawater on the order of 10^{-15} to 10^{-14} mol per liter with some dependence within this range on the pH and O_2 in the seawater. This is some 2–3 orders of magnitude lower than the here reported dissolved Ce concentrations in deep waters (1500–5500 m) at Vertex IV site in the 1.5–2.7 pM range, i.e. $1.5\text{--}2.7 \times 10^{-12}$ mol per liter (Fig. 13, Table 1). Deep

Fig. 9. Relationships of adjacent even atomic number elements ^{60}Nd (horizontal axis) and ^{62}Sm (vertical axis) in filtered seawater at various stations worldwide by various authors with different analytical methods in the home laboratory. The linear regressions are for Sm as the dependent variable as a function of Nd as the independent variable. The generally good agreement provides confidence in the various analytical methods. Shown are all data of complete water column depth profiles at stations: BATS ($n = 10$ samples in 20–4500 m depth range) after Pahnke et al., 2012, their Table 5; BonusGoodHope ($n = 10$ samples in 40–5300 m depth range) after Garcia-Solsona et al., 2014, their Table 1, station S3; North Madagascar Basin site 1504 ($n = 33$ samples in 11–5220 m depth range) after Bertram and Elderfield, 1993; SAFe ($n = 1$ sample at 3000 m depth) after Behrens et al., 2016; Vertex II ($n = 17$ samples in 15–3250 m depth range) after de Baar et al., 1985a; Vertex IV ($n = 19$ in 25–5500 m depth range) this work.

waters in other oceans, notably the younger deep waters (depths > 2000 m) in the Northwest Atlantic (BATS site) contain higher Ce concentrations in the 4–7 pmol.kg⁻¹ range (Fig. 10). The dissolved O₂ in the old deep North Pacific waters is on the order of 50–160 μmol.kg⁻¹ (depth range 1500–5380 m, GEOSECS station 204; Broecker et al., 1982) and still adequate for the above oxidation reaction (Eq. (1)). In the generally younger deep waters of all other oceans, both the dissolved O₂ and the pH tend to be higher. Thus the well oxygenated deep waters of the world oceans all appear to be oversaturated with Ce³⁺ versus solid CeO₂. There may be several reasons for this apparent oversaturation.

Firstly the reaction mechanism is now known to be different from the above Eq. (1) as discussed in Section 5.1.2.2. Secondly the net rate of oxidation of Ce³⁺ in seawater may be very slow, see also Section 5.1.2.2. The age difference of deep waters between the Northwest Atlantic BATS site and the North Pacific Vertex IV site is on the order of about 1000 years on the basis of various approaches for age determination (Matsumoto, 2007; Khatiwala et al., 2012; Gebbie and Huybers, 2012). The Ce concentration in the deep Pacific Vertex IV site is some 2–4 pmol.kg⁻¹ lower than at the

Northeast Atlantic BATS site. Thus the net removal rate of Ce by its oxidation would be some 2–4 pM during the ~1000 years.

Thirdly, there is a wide range of small suspended particles in seawater, ranging from very fine colloids and viruses to larger intact plankton and agglomerates. Conceivably small colloid size particles are not retained by the nominal 0.3 μm size cutoff of the membrane filters in our samples at Vertex IV site. In other words the operationally defined dissolved fraction may in fact contain fine colloids. For example Nishioka et al. (2001) found that small colloids may represent 13–50% of dissolved Fe (<0.2 μm filtered) in the depth interval between 200 and 600 m at several sites in the Northeast Pacific Ocean. Until recently no such study existed for Ce and the other REE in ocean seawater samples, yet it is conceivable that some of the ‘dissolved’ Ce may in fact be fine colloids. If so then some portion of Ce-colloids would, at least partly, bridge the gap of 2 orders of magnitude between the thermodynamic predicted dissolved Ce and the actually measured dissolved Ce. Recently Fröllje et al. (2016) reported colloid size fractionation of 3 samples collected in upper waters of the central North Pacific (nearby our Vertex IV site), but found no discernible colloid fraction of the REE, given the analytical uncertainty of the measurements in each size fraction.

Finally, the predicted thermodynamic equilibrium concentration of Ce³⁺ was, at the time in 1988, based on the then best and relevant stability constants. New experimental work may lead to adjustments of the stability diagram of Ce in seawater medium as function of redox state (expressed as p_e or E_H) and pH (e.g. Hayes et al., 2002; Yu et al., 2006). However, extrapolation of laboratory experiments that were done at high Ce concentrations and quite low pH, to the very low Ce concentrations and high pH ~8.1 of seawater, is beyond the scope of the current article.

Moreover the above prediction is versus pure crystalline CeO₂ phase. In the real ocean this would more likely be a mixture with other oxides, notably Mn-oxides and Fe-oxides, or oxyhydroxides of Mn and/or Fe, and Fe-Mn oxyhydroxide mixtures, and that would lead to a different solubility of Ce in seawater. Also some of these forms may be amorphous and/or include organic moieties, and hence would be somewhat at the edge, or outside the scope, of thermodynamic equilibrium prediction. Nevertheless there is a distinct Ce depletion in seawater relative to the other REE (see further in Section 5.1.4) and this can only be due to oxidation of dissolved Ce³⁺ to a solid Ce(IV) state.

5.1.2.2. Biogeochemical kinetics rate considerations for Ce oxidation. The oxidation rate of Ce is most likely related to the well-studied microbial oxidation of dissolved Mn (e.g. Tebo, 1991; Tebo et al., 2005). For efficient biogeochemical oxidation of dissolved Mn to solid Mn-oxide state, microbes likely are able to enhance the rate of oxidation relative to strictly inorganic oxidation.

The Cariaco Trench has a distinct boundary interface between oxic (detectable O₂ > 0) upper waters and anoxic (detectable H₂S > 0, non-detectable O₂ = 0) deep waters.

Fig. 10. Yb-Nd and Er-Nd Relationships in North Pacific and Northwest Atlantic Oceans. (A) Dependent variable Yb plotted as function of independent variable Nd for Vertex IV in the upper 2000 m of the North Pacific Ocean (filled black dots; $n = 13$ samples in 25–2000 m depth range) and BATS in the Northwest Atlantic Ocean (filled blue squares; $n = 10$ samples in 20–4500 m depth range), with linear regressions. Open black dots for 4 deep Pacific samples (3000–5500 m depths) not part of linear regression. (B) Dependent variable Er plotted as function of independent variable Nd for Vertex IV in the upper 2000 m of the North Pacific Ocean (filled black dots; $n = 14$ samples in 25–2000 m depth range) and BATS in the Northwest Atlantic Ocean (filled blue squares; $n = 10$ samples in 20–4500 m depth range), with linear regressions. Open black dots for 4 deep Pacific samples (3000–5500 m depths) not part of linear regression. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Latter deep waters are strongly enriched with dissolved Mn versus the oxic upper waters (Jacobs et al., 1987). Upward vertical diffusion of dissolved Mn leads to the formation of large amounts of fresh Mn-oxyhydroxide particles at 278 m depth just above the oxic/anoxic interface. These freshly formed Mn-oxyhydroxides act as scavenging agent for adsorption of the complete REE series that have strong maxima on the particles, with Ce anomaly $Ce/Ce^* = 1.81$, in conjunction with minima of dissolved REE and dissolved $Ce/Ce^* = 0.2$ (de Baar et al., 1988). The Ce/Mn concentration ratio in these suspended particles at 278 m depth is 0.15 pmol/ μ mol, in other words 1 Ce for every ~ 6500 Mn. From the vertical distributions of dissolved Mn and REE, the net turnover rate of Mn was thought to be much faster than that of the REE. Among the REE, the turnover rate of Ce, as well as the Ce anomaly Ce/Ce^* , was found to be a factor 2–3 higher than the other LREE Nd and Sm. In other words there appears to be a mechanism of first adsorption of Ce^{3+} and all other REE^{3+} to the freshly formed Mn-oxide particles, followed by oxidation of Ce (III) to the Ce(IV) state. Moreover, redox cycling of Fe in the Cariaco Trench is similar to that of Mn but less pronounced. Nevertheless the freshly formed oxyhydroxides contain both Mn and Fe as major components, as well as many trace elements that are scavenged by adsorption i.e. the REE, of which Ce(III) is further oxidized to the Ce (IV) state.

The O_2 minimum zones at Vertex IV and Vertex II both still contain some dissolved O_2 , but there is a nitrate depletion (due to nitrate reduction) yet no H_2S is present. Presumably suboxic ($O_2 < \sim 5 \mu\text{mol.kg}^{-1}$ and $H_2S = \text{zero}$)

conditions elsewhere produce signals of O_2 minimum and nitrate depletion, that by lateral transport become visible in the O_2 minimum zones in the water column of the Vertex IV and Vertex II sites. The extended suboxic zone (50–100 m depth) of the Black Sea is an ideal natural laboratory to study the effect of suboxic conditions on REE cycling. Here the suboxic/anoxic transition depth zone was found to be the location for active cycling of the REE (Schijf et al., 1991). The vertical gradients of the REE were the strongest for Ce. Hence the authors envisioned a reaction sequence where first dissolved Ce(III), and all other REE(III), are adsorbed on the Mn oxides particle maximum, and next there is oxidation to Ce(IV). Moreover, mixing experiments did show an initial rapid removal of dissolved Ce and Nd, with a slightly more rapid removal of Ce versus Nd, but this rate difference perhaps not significant (Schijf et al., 1994). The removal rate of Ce was found to be almost two orders of magnitude faster than an estimate of the Ce oxidation rate in studies by Moffett (1990, 1993). Otherwise Moffett (1990, 1993, 1994) also emphasizes the major roles of microbes and Mn cycling for the Ce oxidation and cycling.

These observations and concepts are consistent with a more recent study of the role of Mn dioxide ($\delta\text{-MnO}_2$) and Fe oxyhydroxide in the oxidation of Ce(III) to Ce (IV) (Ohta and Kawabe, 2001). Once adsorbed, the Ce (III) is further oxidized to the Ce(IV) state where the MnO_2 acts as the oxidizing agent. Ohta and Kawabe (2001) envision the following redox reactions:

Fig. 11. REE patterns normalized versus PAAS of 4 different samples. Among 14 REE there were 10 analyzed by IDMS and here reported. Vertical axis of left hand graphs is of seawater/PAAS concentration ratio in $[\text{pmol}\cdot\text{kg}^{-1}]/[\mu\text{mol}\cdot\text{kg}^{-1}]$ at regular scale. Right hand graphs is of same seawater/PAAS but at 10^{Log} scale.

Fig. 12. Good agreement of REE patterns between Vertex IV, Vertex II and SAFe, all samples at 3000 m depth. Horizontal axis Pm in *italics* and in brackets has no stable isotopes and as such does not exist in nature. Vertical axis is at ^{10}Log scale for the concentration ratio in $[\text{pmol.kg}^{-1}]/[\mu\text{mol.kg}^{-1}]$ of seawater/PAAS. All 14 natural existing REE were reported for SAFe (Behrens et al., 2016). This SAFe 3000 m sample was analyzed by 4 different laboratories, and the average REE concentration values (Behrens et al., 2016; their Table 7) are shown here. For Vertex IV only the 10 REE that have multiple stable isotopes can be measured. No Gd data at 3000 m sample of Vertex IV, hence only 9 REE here shown. For Vertex II there were 12 REE reported, Dy and Er were not measured. SAFe after Behrens et al., 2016; Vertex II after de Baar et al., 1985a; Vertex IV this work.

or

for reduction of $\text{MnO}_{2(c)}$ to Mn(III) or Mn(II), respectively. Several other studies tend to confirm the key role of Mn-(oxyhydr)oxides in the oxidation of Ce(III) to Ce(IV) state (e.g. Bau, 1991; Bau and Koschinsky, 2009; among others). Given the several orders of magnitude lower concentration of Ce relative to Mn, obviously these reactions (Eqs. (2) and (3)) have a no discernable effect on the overall amount of $\text{MnO}_{2(c)}$.

Estuarine mixing between river water and seawater is well known to act as a major removal mechanism of high concentrations of trace elements from river water. In the Amazon river and estuary system, the large majority (>90%) of dissolved REE is removed in the initial mixing zone at salinity <6.56 (Sholkovitz, 1993). The Ce concentration decreases from 930 pmol.kg^{-1} in the river end-member to $15.6 \text{ pmol.kg}^{-1}$ in the most oceanic sample end-member at $S = 36.64$. This ocean end-member is comparable to Ce in the $15\text{--}25 \text{ pmol.kg}^{-1}$ range in the O_2 minimum zone at Vertex II, but much higher than the about 2 pmol.kg^{-1} at the Vertex IV site (Fig. 12). The estuarine removal is stronger for Ce than for the other REE, such that throughout the Amazon estuary a negative Ce anomaly Ce/Ce^* develops from ~ 0.7 at low salinity to ~ 0.4 at high salinity. Oxidation

of Ce(III) to Ce(IV) is taking place in the estuarine waters, and this is already responsible for at least part of the negative Ce anomaly in the oceans.

5.1.3. Reductive mobilization of Ce

Under reducing conditions in the suboxic ($\text{O}_2 < \sim 5 \text{ μmol.kg}^{-1}$ and $\text{H}_2\text{S} = \text{zero}$) realm, Ce(IV) is remobilized into seawater. In general, reducing conditions develop in some special semi-enclosed ocean basins with poor ventilation of deep and bottom waters, and mostly in pore water of marine sediments worldwide, due to microbial decomposition of organic matter that requires an oxidant. Examples of semi-enclosed basins where REE have been studied are the Black Sea (Schijf et al., 1991), the Cariaco Trench (de Baar et al., 1988) and the hypersaline Bannock and Tyro basins in the Mediterranean (Schijf et al., 1995). Once the energetically more favorable O_2 is depleted, other oxidants are reduced in sequence of Gibbs free-energy change. This sequence of early diagenesis is nitrate reduction, reductive dissolution of Mn-oxides, reductive dissolution of Fe-oxides, and reduction of sulphate leading to accumulation of sulphide (H_2S). (Once H_2S becomes detectable this is defined as anoxic conditions, i.e. far more reducing than suboxic conditions.)

The diagenetic sequence exists in all marine sediments over vertical depth scales of millimeters to at most a few meters. The Black Sea is an ideal natural laboratory to study this diagenetic sequence at much higher vertical resolution between 50 and 100 m depth of the water column. Here it was found that the reduction of Ce(IV) to Ce(III) occurs well below nitrate reduction, just below Mn reduction, and above Fe reduction (Schijf et al., 1991). Moreover, because the solid Mn-oxides are a crucial carrier of particulate Ce and all other REE, due to the Mn dissolution all other REE also are mobilized into solution in the suboxic seawater. Overall this implies that reductive mobilization of Ce(IV) to Ce(III) only occurs in O_2 -depleted suboxic zones. Therefore in any ocean waters that still contain detectable O_2 , there should be no *in situ* Ce reduction. At the Vertex IV site the O_2 minimum at 900 m depth still contains O_2 at 29 μmol.kg^{-1} and below that at 1100 m depth O_2 at 38 μmol.kg^{-1} . Therefore *in situ* Ce reduction cannot take place at Vertex IV site. Instead the dissolved Ce(III) maxima at 900 m and 1100 m depth of 2.7 pmol.kg^{-1} and 2.8 pmol.kg^{-1} , respectively, are likely due to lateral transport from a suboxic source region. This lateral transport of dissolved Ce(III) goes along with lateral transport of the O_2 depletion as discussed in Section 3.2. and also lateral transport of high concentrations of dissolved Mn (Martin and Knauer, 1985; Martin et al., 1985). In the eastern Pacific, the source region of mobilization of Ce and Mn in suboxic conditions may occur in the water column itself, for example the zero- O_2 zone in between 226 m and 324 m of GEOSECS station 343 (Fig. 5B, green line). In shallower waters, such suboxic zones may exist in pockets of suboxic bottom water. Moreover the suboxic zone of underlying sediments would also be a source of mobilized Ce and Mn. Between these source regions and the far offshore Vertex IV site, there would be a lateral gradient of dissolved Ce and Mn along with the reverse gradient of dissolved O_2

Fig. 13. (A) The vertical profile of dissolved Ce at Vertex IV (filled black dots; this work) and at equatorial Pacific station EUC-Fe 14 (filled red diamonds) at 0°N, 180°W after Grenier et al. (2013). Left hand graph also shows BATS (open blue squares) after Pahnke et al., 2012, their Table 5; BonusGoodHope (open green diamonds) after Garcia-Solsona et al., 2014, their Table 1, station S3; North Madagascar Basin site 1504 (purple symbols) after Bertram and Elderfield, 1993; SAFe (black cross) after Behrens et al., 2016; Vertex II (open red triangles after de Baar et al., 1985a). Right hand graph at expanded horizontal concentration scale for only Vertex IV and EUC-Fe 14 stations. Insert same for only the upper 400 m depth interval. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 14. At Vertex IV site, there is a subtle yet distinct minimum of the dissolved LREE Ce, Nd and Sm (sixfold plotted) at 100 m depth that coincides with a pigment maximum around 85 m depth. This suggests that the LREE are removed from solution by association with plankton particles. This association is deemed to be by adsorption on the outside surface of plankton particles, but more intrinsic uptake into plankton may perhaps also take place.

(Fig. 2). For example, at the Vertex II site in the eastern Pacific, the stronger O_2 minimum as low as $3\text{--}10\ \mu\text{mol.kg}^{-1}$ in the broad 110–800 m depth range (Fig. 5A, B) also shows a much stronger dissolved Ce maximum as high as 25 pM (Fig. 13). Latter O_2 minimum and Ce maximum at Vertex II is also accompanied by a distinct maximum zone of dis-

solved Mn concentrations up to $\sim 4\text{ nM}$ (de Baar et al., 1985a; their Fig. 8). In contrast, at Vertex IV, there is a distinct maximum of dissolved Mn in the O_2 minimum zone, but at much lower $0.4\text{--}0.55\text{ nM}$ concentrations (Martin et al., 1985; their Table 5). In summary the dissolved maxima of both Ce and Mn decrease from east nearshore to west offshore, in parallel with the opposite increasing trend of O_2 minimum concentrations (Fig. 2).

5.1.4. Rapid or slow removal of Ce from ocean waters?

There is an apparent paradox between the ~ 1000 years time it apparently takes for net removal of some $2\text{--}4\text{ pmol.kg}^{-1}$ dissolved Ce going from deep Atlantic to deep Pacific (see above Section 5.1.1), and the much faster experimental oxidation/removal rates reported by Moffett (1990) and Schijf et al. (1994). This paradox or gap may largely be explained by the virtual absence of reactive particles in the deep ocean. Moreover the experimental oxidation/removal rates are gross oxidation rates whereas the interocean difference is due to a net rate of oxidative removal. Re-mobilization of Ce(IV) into dissolved Ce(III) in suboxic waters such as the OMZ underlying the Namibian upwelling (Zheng et al., 2016) and the OMZ at Vertex II site underlying the eastern Pacific upwelling (de Baar et al., 1985a), would continuously re-supply dissolved Ce to ocean waters. Hence such re-mobilization effectively causes a slower net removal rate of dissolved Ce. Such very

Fig. 15. Left hand graph (A) shows the lowest element concentration ratio Ce/Nd at Vertex IV site. This demonstrates the very strong Ce depletion versus the regular REE(III). Also shown are equatorial Pacific station EUC-Fe 14 (filled red diamonds) at 0°N, 180°W after Grenier et al. (2013); BATS (open blue squares) after Pahnke et al., 2012, their Table 5; BonusGoodHope (open green diamonds) after Garcia-Solsona et al., 2014, their Table 1, station S3; North Madagascar Basin site 1504 (purple symbols) after Bertram and Elderfield, 1993; SAFe (black cross) after Behrens et al., 2016; Vertex II (open red triangles after de Baar et al., 1985a). Right hand graph (B) at expanded horizontal concentration ratio scale for only Vertex IV and EUC-Fe 14 stations. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

active redox cycling is well studied and known for Mn and Fe in the oceans. By analogy, and also due to the strong associations of Ce removal with Fe-Mn-oxyhydroxides, an active redox cycling of Ce, Mn and Fe together is thought to occur within the suboxic depth zone of marine sediments and special suboxic zones in the water column. Once the remobilized, reduced forms of Ce, Mn, Fe, and Co as well (Noble et al., 2012), diffuse out again into O₂-containing waters, there will be oxidation and precipitation trapping most of the diffusive flux, but some Ce, Mn and Fe escapes and may be transported long distances along isopycnal surfaces. Similarly, hydrothermal vents can support plumes of elevated Mn, Fe (and presumably Ce as well) over very long distances of hundreds of kilometers (Middag et al., 2011a, 2011b, 2015; Klunder et al., 2011, 2012; Wu et al., 2014; Resing et al., 2015).

Some portion of the total volume of ocean deep waters is affected by effluxes from suboxic regimes and hydrothermal vents, that lead to formation of fresh Mn-Fe-oxyhydroxides acting as scavengers of Ce and the other REE, as well as some escape of Mn, Fe and Ce into adjacent deep waters. However, another portion of even larger volume of deep ocean waters, is not affected and has always been well oxygenated. Remarkably, van Hulten et al. (2017) have noticed a quite uniform background concentration of dissolved Mn in the 0.10–0.15 nM range in the deep oceans. This is close to equilibrium with the solid phase pyrochroite. If so, then there is very little chemical reactivity of Mn in this major portion of deep ocean waters, i.e. very little formation of fresh Mn-oxides, i.e. not much scavenging of the REE, and not much further oxidation of adsorbed Ce(III) to the Ce(IV) state. If so, then this would perhaps be some

part of the explanation for the overall very low effective net removal of dissolved Ce during the ~1000 years travel time of deep waters from the North Atlantic to the North Pacific Ocean.

5.1.5. Ce/Nd ratio and Ce/Ce* anomaly

Ideally the depletion of Ce compared to the other REE is defined relative to its direct neighbours La and Pr in the series, as follows:

$$\text{Ce}/\text{Ce}_{\text{La,Pr}}^* = 2(\text{Ce}/\text{Ce}_P)/(\text{La}/\text{La}_P + \text{Pr}/\text{Pr}_P) \quad (4)$$

where Ce_P and La_P and Pr_P are the concentrations in the PAAS reference. However because La itself may have an anomaly due to its empty 4f shell, and because in our IDMS-based dataset there is no data of mono-isotopic Pr, it is deemed more reliable to simply calculate the elemental ratio Ce/Nd (Fig. 15). This shows lowest Ce/Nd ratio values for Vertex IV compared to the other sites. In comparison with the Ce profile (Fig. 13B) the Ce/Nd values of Vertex IV deep samples (Fig. 15B, black dots) are lower than the Ce/Nd at the equatorial Pacific (Fig. 15B, red diamonds). This is due to the fact that the older deep waters at our 28°N site have accumulated somewhat more strictly trivalent REE, i.e. here Nd, than the somewhat younger deep waters at the equator. In summary, the Vertex IV site not only shows low Ce concentrations but also the strongest depletion of Ce relative to Nd.

Lacking Pr data at Vertex IV, we define the Ce anomaly relative to the next element Nd instead, as follows:

$$\text{Ce}/\text{Ce}_{\text{La,Nd}}^* = 3(\text{Ce}/\text{Ce}_P)/(2\text{La}/\text{La}_P + \text{Nd}/\text{Nd}_P) \quad (5)$$

This is shown in Fig. 16 for Vertex IV site, for the equatorial Pacific, for the SAFe 3000 m sample, and for the Atlantic BATS site. These Ce anomalies largely confirm the trends of Ce/Nd in preceding Fig. 15.

As a matter of fact, for the equatorial Pacific, SAFe and for BATS there is Pr data available. Hence the ‘ideal’ Ce anomaly has also been calculated as per above Eq. (4). This $Ce/Ce_{La,Pr}^*$ is almost identical to the $Ce/Ce_{La,Nd}^*$ but $Ce/Ce_{La,Pr}^*$ is not shown in Fig. 16 to avoid clutter.

In summary the depletion of Ce compared to the other REE can be defined either (i) as Ce/Nd ratio (Fig. 15) or (ii) as $Ce/Ce_{La,Nd}^*$, or (iii) (for equatorial and SAFe and BATS only) as $Ce/Ce_{La,Pr}^*$. Firstly the relative Ce depletion (Figs. 15 and 16) is systematically always the lowest at Vertex IV, and secondly always more distinct at Vertex

Fig. 16. Vertical profile of the Ce anomaly Ce/Ce^* as defined versus La and Nd shown as black filled dots for Vertex IV site. Dotted line in 1000–1500 m and 1500–2000 m depth intervals because values are missing for samples at 1100 m and 1750 m due to lack of La values for these two depths. Also shown are Ce/Ce^* at the equatorial Pacific (red diamonds), at the 3000 m depth at SAFe site (blue cross), and Ce/Ce^* at Northwest Atlantic BATS site (filled blue squares). The datasets of the equator (EUC-Fe 14), the SAFe sample and the BATS site also contain data of Pr such that the Ce anomaly is also calculated versus La and Pr. The latter Ce/Ce^* values versus La, Pr are not shown to avoid clutter, but are virtually the same as the Ce/Ce^* defined versus La and Nd. Equatorial Pacific after Grenier et al. (2013); their station EUC-Fe 14; BATS after Pahnke et al., 2012, their Table 5; SAFe after Behrens et al., 2016. (Not shown to avoid clutter, are Ce/Ce^* values for Vertex II, Bonus Good Hope, and North Madagascar Basin.) Insert is upper 500 m depth interval at expanded vertical scale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

IV from the other stations than the Ce concentration alone (Fig. 13).

5.2. Relations of the strictly trivalent REE with the major nutrients

5.2.1. Preceding observations of Zn, Cd, Ni, Cu and nutrients

For understanding the concepts and observations of REE relations with the major nutrients, it is useful to be informed about the preceding concepts and observations for other trace metal elements. Bruland (1980) reported some of the first vertical profiles of dissolved transition metal elements Zn, Cd, Ni and Cu in the North Pacific Ocean. Among their 3 stations one station H77-17 is situated at 32°41'N, 145°W in the very oligotrophic central North Pacific gyre, very close to our Vertex IV station at 28°N, 155°W. In the surface waters the dissolved Zn and Cd were extremely low, depleted just like the depletions of major nutrients silicate, nitrate and phosphate in these oligotrophic waters. Quite remarkably the dissolved Zn has a very strong linear correlation ($r = 0.996$) with major nutrient silicate. Dissolved Cd has a very strong correlation ($r = 0.992$) with major nutrient phosphate, i.e. also with major nutrient nitrate. However dissolved Ni and Cu are different. Firstly in surface waters there still is significant dissolved Ni and Cu present. Secondly within the upper 800 m the Ni was found to increase linearly with phosphate, while at depths below 800 m the Ni tends to follow silicate. A plot of Ni versus silicate exhibits positive curvature at depths less than 800 m indicative of Ni being regenerated to a greater degree than silicate at these shallow depths (Bruland, 1980). Based on this dual behavior of Ni versus both phosphate and silicate, Bruland (1980) derived a significant ($r = 0.995$ for 47 samples, of which 38 duplicate analyses, i.e. overall 85 data values) expression in which Ni correlates with both phosphate and silicate. Finally dissolved Cu tends to increase with depth but less so than the major nutrients, such that for the deep waters a combination of nutrient-like regeneration and adsorptive scavenging removal of Cu was suggested (Bruland, 1980).

The West Atlantic Ocean comprises the ‘Great Ocean Conveyor’ (Broecker, 1991) of the North Atlantic Deep Water (NADW; in the 2000–4000 m depth range) flowing southwards, above which the northwards flowing Antarctic Intermediate Water (AAIW at typically ~1000 m depth). Below the NADW is the Antarctic Bottom Water (AABW) also flowing northwards. The vertical distributions of major nutrients and nutrient-type trace metals (e.g. Al, Cd) are strongly dominated by this lateral transport and the vertical mixing between the AAIW and NADW and the NADW and AABW (van Hulst et al., 2013, 2014; Middag et al., 2015, 2018). Local biogeochemistry plays a minor role (Zheng et al., 2016; Behrens et al., 2018). For example in the Northwest Atlantic the distribution of silicate is considered ‘conservative’ i.e. affected only by hydrographic transport and mixing (de Baar et al., 1983).

The Antarctic Ocean, comprising all waters south of the circumpolar Antarctic Polar Front (APF, situated at ~50° S), is very different from the oligotrophic central gyres such as the central North Pacific Ocean. Surface waters of the

Antarctic Ocean comprise ample major nutrients. Quite remarkably dissolved “nutrient-type” trace metals Zn, Cd, Ni and Cu show the same trend with higher concentrations in Antarctic surface waters (de Baar et al., 2017c; their Table 1). Notably dissolved Zn and Cd are much higher in Antarctic surface waters than in the surface waters of the oligotrophic central North Pacific Ocean, but Ni and Cu are elevated as well when compared with the central North Pacific.

5.2.2. Prior observations of REE and major nutrients in the world oceans

These above existing concepts for transition metals Zn, Cd, Ni and Cu served as guidelines for interpretation of the first reported vertical profiles of the REE in the oceans. For example in the North Atlantic Ocean the vertical profiles of strictly trivalent REE (i.e. excluding Ce) show a fairly linear increase with depth that bears a faint resemblance to the distribution of nutrients, especially silicate (Elderfield and Greaves, 1982; de Baar et al., 1983). However dissimilarities were obvious, notably in the upper waters the REE diverge appreciably from the nutrients, with significant REE concentrations towards the surface where nutrients are depleted. Nevertheless for depths below 1000 m a significant ($r = 0.997$) linear relation of Lu with silicate was found (de Baar et al., 1983). Because silicate is deemed dominantly conservative in the North Atlantic, the Lu also behaves dominantly conservatively. Hence the linear relationship of Lu and silicate may be seen as largely the result of water mass mixing between endmembers (AAIW, NADW, AABW), where regional biogeochemistry hardly contributes, if at all. In the Brazil basin in the south-west Atlantic, the deep waters (>2000 m) also show a linear relation of REE with silicate, also due to predominantly conservative mixing, rather than from local biogeochemical processes (Zheng et al., 2016; their Fig. 11). However in the eastern South Atlantic (Angola Basin) there is no relationship between the REE and dissolved silicate (Zheng et al., 2016; their Fig. 11). In the deep Pacific similar trends versus silicate were found for heavy elements Er and Lu, but with a major offset due to very high silicate values (de Baar et al., 1985a, their Fig. 4; Elderfield, 1988, his Fig. 6; Zhang and Nozaki, 1996). In summary, these studies showed that the REE in some locations resemble the distribution of silicate. However: “the REE are not coupled tightly with silicate in their oceanic behaviour” (wording cited from Elderfield, 1988). The REE were considered to be affected by both a nutrient-like regeneration and by scavenging in deep waters, and as such deemed similar to the vertical distribution and its underlying processes of dissolved Cu (de Baar et al., 1985a; their Fig. 5).

The Antarctic Ocean shows elevated REE in surface waters, following the trend of elevated major nutrients and trace metals (de Baar et al., 2017c, their Table 1). For example, stations S4 and S5 of Garcia-Solsona et al. (2014) are situated south of the Antarctic Polar Front (APF) and REE concentrations (excluding Ce) in the upper 1000 m waters of S4 and S5 generally are higher than in their stations S1, S2 and S3 north of the APF. Similar stations 113–193 of Hathorne et al. (2015) are all situated

south of the APF and in the upper 1000 m of the water column show significantly higher REE concentrations than in the upper 1000 m of their stations 101 and 104 situated north of the APF. Because of these ‘High Nutrient’ conditions in upper waters of the Antarctic Ocean, the Antarctic relationships of the trivalent REE with the major nutrients are not necessarily suitable for comparison with the extremely oligotrophic (nutrient-depleted) conditions in upper waters of the central North Pacific Ocean.

This being stated, it is noticed that Garcia-Solsona et al. (2014) reported strong linear correlations of the REE with dissolved silicate with R^2 coefficients in the 0.88–0.98 range. No distinction was made between the true Antarctic stations and the sub-Antarctic stations. Similar results were reported for Nd concentrations in the same region, with $R^2 = 0.87$ (Stichel et al., 2012). Other dissolved nutrients, such as NO_3 and PO_4 , were reported to be less correlated with REE and correlations hold only in the first 1000 m of the water column (Garcia-Solsona et al., 2014), but no R^2 coefficients for the latter 1000 m depth range for REE versus NO_3 or PO_4 were reported.

Hathorne et al. (2015) report correlation coefficients (R^2) between phosphate concentrations and the REEs (excluding Ce) in their dataset ranging from 0.47 to 0.66 for the LREE and MREE (from La up to and including Dy), but increasing to 0.71–0.81 for the HREEs (Ho to Lu). A very similar pattern was reported for the correlations with nitrate concentrations. The linear correlation coefficients of REE with silicate were higher with reported R^2 values ranging from 0.88 to 0.95.

In addition to the oceanic Si cycle of formation of diatom opal frustules in surface waters, and their dissolution in deep waters, there also is the cycle of CaCO_3 hard shells. Here Alkalinity, after adjusting for nitrate and normalized to salinity $S = 35$, serves as a tracer for net increase of the dissolved Ca^{2+} concentration in seawater due to deep dissolution of CaCO_3 shells. For Lu in the deep Pacific a similar offset was found of deep Alkalinity_{adjusted} as for silicate (de Baar et al., 1985a, their Fig. 4). Given this major offset, the cycling of the REE is not coupled tightly with CaCO_3 in their oceanic behaviour either.

5.2.3. Relations of REE with major nutrients in the upper 1000 m at Vertex IV site

In the thermocline region (~200–900 m) there is a steep increase with depth of both the major nutrients (Fig. 6) and the REE series, except Ce (Fig. 8). Plots of Nd as a function of PO_4 in this depth range show a very good linear correlation (Fig. 17A). The same is true for Nd versus NO_3 (Fig. 17B), but for Nd versus SiO_4 there appears to be a slight positive curvature (Fig. 17C) indicative of Nd being regenerated to a greater degree than silicate at these shallow depths. As a result the curve fitting power function of Nd versus SiO_4 is more significant than a linear regression. For the other REE, except Ce, the linear regressions versus PO_4 and NO_3 are listed in Table 5, and also very significant, albeit less so for Yb and Lu. Moreover the obvious curvatures of the relations of Sm, Eu, Gd, Dy, Er with SiO_4 (Table 5) are just like that for Nd and together indicative of Nd, Sm, Eu, Gd, Dy, Er being regenerated to a greater

Fig. 17. Relations of Nd versus the major nutrients, with linear regressions. Coefficients are not rounded, the R^2 is not rounded because rounded $R^2 = 1.00$ would be less informative. See also Table 5 for linear regression relationships and curve fittings of Nd and other REE. (A) Nd versus phosphate (PO₄) in the 200–900 m depth range at Vertex IV site, with linear regression. (B) Nd versus nitrate (NO₃) in the 200–900 m depth range at Vertex IV site, with linear regression. (C) Nd versus silicate (SiO₄) in the 200–900 m depth range at Vertex IV site shows a distinct curvature. Hence a simplistic linear regression, while still highly significant, is less tight than for Nd versus nitrate and phosphate.

degree than silicate at these shallow depths. These positive curvatures of REE versus silicate are due to the relatively less regeneration of silicate also versus phosphate (Fig. 7B) and nitrate (Fig. 7C) whereas regeneration of phosphate and nitrate is equal (Fig. 7A). The lesser regeneration of silicate appears most significant at the 600 m depth sample representing the core of the North Pacific Intermediate Water (NPIW) as mentioned in Section 3.3. Hence the overall curvatures as listed in Table 5 are seen as the result of relatively more regeneration of the REE together with phosphate and nitrate within the NPIW, versus less regeneration of silicate within the NPIW, and this in relation to vertical mixing of the NPIW with overlying (~200 to ~400 m) and underlying (~700 to ~900 m) waters.

These very good correlations of the REE with both PO₄ and NO₃ would support the concept of association of the REE with the organic matter soft tissue of biogenic particles, that upon settling and remineralization lead to the here reported strong increase of concentrations of PO₄, NO₃ and the dissolved REE in the upper 1000 m thermocline region. For one element Nd, such coupling of its cycling with remineralization of organic matter has been reported in the eastern North Atlantic by Stichel et al. (2015; their Fig. 5) relying on the Apparent Oxygen Utilization (AOU) that is well known to have a distribution parallel to that of PO₄ and NO₃, due to the fact that all result from mineralization of organic matter. Moreover, Lambelet et al. (2016) present a section plot of Nd including contours of AOU (their Fig. 2b) in the western North Atlantic, and discuss this using a plot of Nd concentrations versus AOU (their Fig. 10). More nearby our Vertex IV station, at stations in the Northwestern Pacific, Behrens et al. (2018) also report a gradual increase in Nd concentration along with an increase in AOU in two water masses. This indicates Nd release from sinking organic particles through mineralization.

5.2.4. Relations of REE with silicate in deep waters

At the Vertex IV site in the central North Pacific, the deep (1100–5500 m) water concentrations of the Nd representing the LREE do not show a convincing trend versus dissolved silicate (Fig. 18A, filled black dots). Linear regression (not shown) of deep Nd versus silicate is not significant ($R^2 = 0.47$ for $n = 9$ datapoints). For deep water concentrations of Er representing the HREE, there is a more significant linear regression ($R^2 = 0.73$ for $n = 8$) with dissolved silicate (Fig. 18B, filled black dots). The better linear fit of Er compared to Nd is deemed to be due to Er being a more conservative element, by its much lower percentage free ion (Fig. 1) the Er is less prone to adsorptive scavenging removal. In other words, once Nd and Er have become dissolved together with silicate, there is less chance of disturbance of the Er-Si trend than for the Nd-Si trend.

The weak trends, if at all, of the REE with silicate in the deep central North Pacific are in contrast with the more significant, or highly significant, trends in the deep Atlantic Ocean (Fig. 18). Near Bermuda (32°N, 64°W), for 7 samples at 5 sampling depths (1000–4500 m) i.e. 2 duplicate samples, the R^2 is 0.86 for Nd and 0.88 for Er (Fig. 18A, B, blue filled squares and regression line). In one example station in the Southwest Atlantic (12°S, 23°W) for 8 samples in the 1499–5002 m depth range the R^2 is 0.996 for Nd and 0.994 for Er (Fig. 18A, B, green filled triangles and regression line). However in the southeast Atlantic there was no relationship of REE and silicate (not shown; see Zheng et al., 2016; their Fig. 11).

As an example for the deep Southwest Pacific (27°S, 175°E) for 8 samples in the 1238–4519 m depth range both Nd and Er show more (Nd) or less (Er) distinct curvature versus dissolved silicate (Fig. 18A, B, red filled diamonds). For the deep equatorial Pacific (0°S, 150°E) similar curvatures are observed (Fig. 18A, B, purple filled triangles). In general the deep trends at 27°S and at the equator tend to steadily approach the trend of the generally higher concen-

Fig. 18. (A) Nd, representing the LREE, plotted versus silicate. (B) Er, representing the HREE, plotted versus silicate. Vertex IV deep waters in 1100–5500 m depth range (black filled dots); BATS deep waters in 1000–4500 m depth range (blue filled squares) also shown linear regression; after Pahnke et al. (2012); South Atlantic St. 4 deep waters in 1499–5002 m depth range (filled green triangles), also shown linear regression, after Zheng et al. (2016); South Pacific St. SA12 in 1238–4519 m depth range (filled red diamonds) after Zhang and Nozaki (1996); Equatorial Pacific St. SA5 in 1240–5149 m depth range (filled purple triangles) after Zhang and Nozaki (1996). Open symbols are for upper water column data of only Vertex IV, St. SA12 and St. SA5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

trations of both Nd, Er and silicate at our Vertex IV station in the central North Pacific (Fig. 18A, B). Finally for the sake of completeness and comparison with the deep Atlantic datasets, the Nd and Er versus silicate in upper waters of the Pacific Ocean are plotted as open symbols (Fig. 18A, B).

In summary the world ocean trends of LREE Nd and HREE Er versus silicate are by no means uniform.

5.2.5. Conceivable mechanisms underlying the relations of REE with nutrients

This section is going from very simple minimal approach to eventually including a quantitative description of all underlying mechanisms. First and foremost the world ocean distribution of any ocean tracer is always dominated by the hydrographic circulation and mixing of water masses. Notably in the Atlantic Ocean that has much stronger circulation than the Pacific Ocean, the distributions of the REE and the major nutrients are mostly conservative, i.e. dominated by hydrography. Superimposed on this hydrography, the most simple description of REE distributions in the world oceans is by adsorptive scavenging of dissolved REE on newly formed biogenic particles in the surface oceans. Latter biogenic particles always comprise the biological elements C, N, P and, here or there, may also comprise Si, notably in opaline frustules of diatoms algae, and/or Ca in CaCO_3 , for example the coccolith platelets of coccolithophore algae. Latter opal and CaCO_3 have much higher density than seawater, and enhance the settling of biogenic debris particles into the subsurface waters. Most respiration and mineralization of this biogenic debris takes place in the 100–1000 m depth range and this leads to strong increases of dissolved nutrients as well as the REE as shown in above Section 5.2.3. Below ~1000 m the nitrate and phosphate do not further increase with depth (Fig. 6A, B) but the silicate (Fig. 6C) and the dissolved REE (Fig. 8, except Ce) increase to 3000 m depth and beyond. This steady increase in the ~1000 to ~3000 m depth range is seen as the result of the ballast effect of opal causing a general deeper dissolution of Si, in combination with an apparent relationship of the adsorbed REE with the settling opal, that upon dissolution of the opal carrier yields inevitable desorption of the REE that therefore dissolve again.

Given these trends of REE with both phosphate (or nitrate) and silicate, the overall vertical distribution of the REE in the central North Pacific (Vertex IV) may also be described by multivariate regressions for Nd representing the LREE and Er representing the HREE:

$$Nd = -10.84 Si + 0.384 P + 8.45 \quad (6)$$

with $R^2 = 0.84$ ($R = 0.92$ $n = 19$ and $p < 0.001$)

$$Er = -1.14Si + 0.067P + 2.22 \quad (7)$$

with $R^2 = 0.93$ ($R = 0.96$ $n = 19$ and $p < 0.001$)

The ensuing R^2 values for $n = 19$ samples yield a very low probability p of exceeding R in a non-related population. In other words, there exists a statistical significant relationship of these REE, Nd and Er respectively, with both nutrient elements Si and P. This being stated, the R values still are less than the above (Section 5.2.1) mentioned $r = 0.995$ (i.e. $R^2 = 0.99$) for the multivariate relationship of Ni with both Si and P in the North Pacific Ocean, as reported by Bruland (1980). This is more obvious for Nd ($R = 0.92$) than for Er ($R = 0.97$), both compared to Ni ($r = 0.995$). This would leave some room for the hypothesis of an extra mechanism of net deep water scavenging to explain the REE distributions. Indeed the LREE Nd has far more free ion in seawater than the HREE Er (Fig. 1)

and therefore dissolved Nd is deemed to be more prone to removal by net deep water scavenging than dissolved Er. In other words by introducing an extra deep water scavenging term, one may compensate for the more (Nd) or less (Er) deviation from the multivariate relation of Ni versus Si and P that does not indicate such additional deep water scavenging. One caveat is that the particle reactivity of the free REE³⁺ ion (i.e. here either Nd³⁺ or Er³⁺) also is different, the net effect being determined by the type and abundance of scavenging particles. The suggested net deep water scavenging of Nd and Er is akin to such term required to understand dissolved Cu (Bruland, 1980; de Baar et al., 1985a). For dissolved Ni such extra deep scavenging term is not required. Similar multivariate equations may be expected for the REE versus both phosphate and Alkalinity_{adjusted}, with similar hypothetical room for additional more (Nd) or less (Er) deep water scavenging. Finally one must realize that such apparent relations of REE with nutrients and Alkalinity_{adjusted}, such as Eqs. (6) and (7), do not necessarily inform about the biogeochemical causality and mechanisms of these relations. For example, in the Atlantic Ocean such relations are also strongly controlled by hydrography (de Baar et al., 1983; Zheng et al., 2016; Behrens et al., 2018).

Thus far are discussed the conceivable interactions of (i) REE adsorptive scavenging in surface waters, (ii) net REE adsorptive scavenging from deep waters, with (iii) formation of biogenic particles in surface waters, and (iv) respiration/reminerzalization in deep waters, all superimposed on (v) the hydrography. For the scavenging agent on the outside of the biogenic particles one may envision organic functional groups and/or external Fe-Mn-oxides-hydroxides coatings.

In addition one may envision one or two extra mechanisms. These are the more intrinsic incorporations of the REE into either (v) the opal amorphous structure and/or (vi) the CaCO₃ crystalline structure (either calcite or aragonite) of biogenic hard parts. Akagi et al. (2011) and Akagi (2013) have suggested significant incorporation of REE, notably the HREE, into diatom opal, where silicic acid complexes of the rare earths in seawater would play a role (Akagi, 2013). Latter work has recently been criticized by Patten and Byrne (2017), the latter arguing that the preceding literature values of silicate formation constants, as chosen by Akagi (2013), were not suitable. Similarly incorporation of REE into CaCO₃ hard parts can be envisioned, but natural marine carbonates precipitating in the water column generally tend to show low REE contents (Tanaka et al., 2009). The evidence pro and con significant incorporation of REE into hard parts has recently been discussed by Garcia-Solsona et al. (2014), Hathorne et al. (2015), Zheng et al. (2016) and Patten and Byrne (2017). This incorporation into hard parts (either opal or CaCO₃) may perhaps occur, here or there, in the surface oceans, and upon deep remineralization, would then contribute, to some extent, to the observed relationships of REE with silicate and Alkalinity_{adjusted}. However for the sake of brevity, these incorporation mechanisms will not be further discussed in the sections on 5.3. Gd anomaly, 5.4. HREE enrichment, and 5.5. Pacific/Atlantic intercomparison.

5.3. Gadolinium and Gd anomaly

5.3.1. Gadolinium anomaly normalized versus shales

Gadolinium is midway in the REE series and its 4f shell is exactly half filled with 7 electrons. This has been suggested to cause a Gd anomaly in seawater (e.g. Masuda and Ikeuchi, 1979). Indeed the predicted inorganic speciation in seawater (Fig. 1) does show anomalies of Gd, both positive and negative. Not knowing whether or not Gd anomalies also exist in adsorptive bonding to the suspended particles, we cannot with certainty predict what would happen. Nevertheless the dissolved anomalies of inorganic complexation of Gd lead to justified expectations of Gd anomalies of the overall dissolved concentration in seawater. In order to resolve such relatively subtle anomaly from the overruling even/odd predominance (the Oddo-Harkins rule, see above 1. Introduction), the seawater data are commonly normalized to the average REE composition of Post Archean Australian Shale (P). Ideally, then, one would define an anomaly of Gd relative to its direct neighbours Eu and Tb in the REE series:

$$\text{Gd/Gd}_{\text{Eu,Tb}}^* = 2(\text{Gd/Gd}_P)/(\text{Eu/Eu}_P + \text{Tb/Tb}_P) \quad (8)$$

However at Vertex IV there is no data of (mono-isotopic) Tb, while the Eu may be subject to its own anomaly due to the Eu-enriched REE patterns in hydrothermal vents (see Section 5.5.4). The Gd anomaly can alternatively be defined relative to Sm and Dy, as follows:

$$\text{Gd/Gd}_{\text{Sm,Dy}}^* = 2(\text{Gd/Gd}_P)/(\text{Sm/Sm}_P + \text{Dy/Dy}_P) \quad (9)$$

For Vertex IV one may also define the Gd anomaly versus Eu and Dy as follows:

$$\text{Gd/Gd}_{\text{Eu,Dy}}^* = 3(\text{Gd/Gd}_P)/(2\text{Eu/Eu}_P + \text{Dy/Dy}_P) \quad (10)$$

For Vertex IV, the Gd anomaly relative to Sm and Dy varies in between 1.1 and 1.2 when ignoring four outliers of which three outliers with Gd/Gd* > 1.2 and one outlier with Gd/Gd* < 1 (Fig. 19A). When defined relative to Eu and Dy, the Gd/Gd* values show more variability at Vertex IV (Fig. 19B). There is no Gd value at 3000 m depth, hence no Gd anomaly could be calculated. However the data at other depths are consistent with the Gd/Gd* value of the SAFe sample at 3000 m. Its values defined relative to either Sm, Dy or Eu, Tb are virtually identical. These Gd/Gd* values at Vertex IV plus SAFe sites, can now be compared with other sites.

Station S3 of Bonus Good Hope in the Southern Ocean (Garcia-Solsona et al., 2014) is shown here for comparison (Fig. 19A). The Gd/Gd* was calculated relative to Sm and Dy which were taken to yield more robust results than versus Eu and Tb. For this S3 station and 4 other stations (not shown) of Bonus Good Hope, the vertical profiles of Gd/Gd* are very uniform (Garcia-Solsona, 2014; Gd/Gd* listed in their Table 1). This convincing dataset in itself would be in support of the existence of a real Gd anomaly in the oceans. Garcia-Solsona et al. (2014) reported careful calculations of propagation of the 5–7% reproducibility error on the REE concentrations in their dataset, yielding an anomaly uncertainty of +0.07 to −0.10 for Gd/Gd* such that 60–81% of all their Gd anomalies in 50 samples were

Fig. 19. Various ways of defining an anomaly of Gd in the REE series. (A) The Gd anomaly Gd/Gd^* calculated versus Sm and Dy at Vertex IV site shown as filled black dots. There is no Gd data for the 3000 m sample at Vertex IV, but the Gd/Gd^* at SAFe site (red cross) versus Sm and Dy fills the gap, here calculated after Behrens et al. (2016). Also shown Gd/Gd^* at BATS site (blue filled squares) versus Sm and Dy, here calculated after Pahnke et al. (2012); Gd^* versus Sm and Dy at Bonus Good Hope station S3 (filled green diamonds) after Garcia-Solsona et al. (2014), values taken from their Table 1. (B) Gd/Gd^* at Vertex IV versus Eu and Dy shown as open dots. Also shown are Gd/Gd^* versus directly adjacent elements Eu and Tb at 3000 m depth at SAFe (black open star), BATS (blue open squares) and at Vertex II (red open triangles). (C) The Gd-anomaly_{intrinsic} of even atomic numbered ^{64}Gd versus ^{62}Sm and ^{66}Dy that does not require an arbitrary choice of normalization reference. Vertex IV shown as black filled dots. Also shown are SAFe sample at 3000 m (red cross), BATS (filled blue squares) and Bonus Good Hope S3 (filled green diamonds). Red filled square is average of 3 Amazon river end-member samples after Elderfield et al. (1990) and Sholkovitz (1993). Red filled circle is average of 18 Amazon river samples after Barroux et al. (2006). Red filled diamond is average of 18 samples of 12 different rivers (including the Amazon end-member sample) after Elderfield et al. (1990, their Table 1). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

reportedly statistically significant. Interpretation of such anomaly was said to be done with caution until better precision in the measurements is achieved.

For the northwest Atlantic BATS site, the vertical profile of Gd/Gd^* also is quite uniform with depth with values in the 1.1–1.13 range, thus an about 10% enrichment of Gd relative to Sm and Dy (Fig. 19A). When defined relative to Eu and Tb the values of Gd/Gd^* are systematically higher in the 1.15–1.21 range (Fig. 19B).

Finally for the Vertex II site (de Baar et al., 1985a, 1985b) the Gd anomaly is re-calculated here relative to the PAAS reference (McLennan, 1989), instead of at the time versus the ‘global’ average shale reference (a mixture of North Atlantic Shale Composite NASC, and European shales and Russian platform shales; Haskin and Haskin, 1966). This normalization versus PAAS, now shows a Gd/Gd^* vertical profile defined relative to Eu and Tb with values mostly in the 1.07–1.20 range, with four outliers in the 1.25–1.29 range (Fig. 19B). Apart from one outlier (1.29) in surface water (15 m depth), the three other outliers (1.25, 1.27, 1.29) are in the 300–500 m depth range where dissolved O_2 is very low (Fig. 5B).

In summary, the Gd/Gd^* datasets of Vertex IV and several other stations, when normalized versus PAAS,

tend to show a positive Gd anomaly (Fig. 19A, B). Garcia-Solsona et al. (2014) did mention that interpretation of the, in itself quite subtle, Gd anomaly would be enhanced with better precision of the measurements. Also one realizes that the choice of normalization reference, i.e. nowadays PAAS, is in itself in principle an arbitrary choice. Moreover, the inherent accuracy of the REE database underlying the PAAS reference, also affects the definition and accuracy of the calculated Gd/Gd^* in seawater. The overall stability pattern for REE complexation with carbonate actually has a negative Gd anomaly (see Luo and Byrne, 2004). Distribution coefficients for REE sorption on most particles also have a negative Gd anomaly (Schijf et al., 2015). These two effects partially cancels when the two terms are combined (see Schijf et al., 2015). The net effect is usually a slightly positive Gd anomaly in seawater and variations throughout the ocean are thought to be due to very subtle interactions of (i) seawater inorganic complexation, with (ii) different types and concentrations of particles.

5.3.2. Gadolinium anomaly without shale normalization

The choice of normalization reference does make a difference. In the original article (de Baar et al., 1985b), there

was found both a positive enrichment of Gd and a negative depletion of Tb, when defined relative to the then available shale reference of Haskin and Haskin (1966). Thus at the time it was concluded that there was either a positive Gd anomaly, or a negative Tb anomaly, or both (de Baar et al., 1985b). Alternatively, when defined versus the PAAS reference, there remains a distinct positive Gd anomaly at the Vertex II site (Fig. 19B). The difference of Vertex II in the current Fig. 19B with the original report (de Baar et al., 1985b) is due to the different shale references, as shown by the elemental ratios (Fig. 20) of the original Haskin and Haskin (1966) shale reference relative to the since then published PAAS reference (McLennan, 1989). Briefly the element ratio is 1.36 for Gd and 1.57 for Tb, in other words in the Haskin and Haskin (1966) shales dataset the Gd is 37% and the Tb is 57% higher than in the PAAS shales dataset (Fig. 20). This strong offset for Tb, relative to the offset for Gd, explains why originally a negative Tb anomaly was considered a possibility at Vertex II.

The shale normalization is commonly used to remove the overruling even/odd predominance (Oddo-Harkins) along the REE series. However it is realized that the elements ^{62}Sm , ^{64}Gd and ^{66}Dy all three are even-numbered elements. Therefore shale normalization can be avoided by using only these even-numbered elements. This also avoids the arbitrary choice of most suitable shales composite, as well as the error propagation due to the intrinsic limits of accuracy of the shale concentration values. Thus by simply defining the intrinsic Gd anomaly within any geochemical reservoir, in this case the oceans:

$$\text{Gd-anomaly}_{\text{intrinsic}} = 2\text{Gd}/(\text{Sm} + \text{Dy}) \quad (11)$$

the right hand term comprises merely 3 variables, instead of 6 variables in above Eq. (9) for the shale-normalized version. All resulting values (Fig. 19C) are higher than the 0.9 values for PAAS and therefore evidence in support of a positive Gd-anomaly_{intrinsic} in seawater of the Pacific, Atlantic and Indian Oceans, relative to shales.

Fig. 20. The REE elemental ratio values of average shales of Haskin and Haskin (1966) divided by PAAS (McLennan, 1989). The factor 1.57 for Tb relative to the factor 1.39 for Gd does affect the definition of the Gd anomaly Gd/Gd^* in seawater.

However this does not necessarily imply that the positive Gd-anomaly_{intrinsic} of seawater versus PAAS has developed within the oceans. Notably, the Amazon represents ~20% of all river water supply into the oceans and its REE signature is relevant. The Amazon River end-member shows a positive Gd anomaly of 1.22 (S.D. = 0.13, n = 3) for 3 river end-member samples (Fig. 19C, red square symbol) after Elderfield et al. (1990) and Sholkovitz (1993). Similarly, a positive anomaly of 1.1 (S.D. = 0.1, n = 18) is calculated for 18 samples collected at the Obidos Station upstream of any marine influence (red dot in Fig. 19C; after Barroux et al., 2006, their Table 2). For 12 different rivers (including the Amazon), an average Gd anomaly of 1.16 (S.D. = 0.28, n = 19) is calculated (red diamond in Fig. 19C, after Elderfield et al. (1990); their Table 1). Thus rivers tend to have a more positive Gd-anomaly_{intrinsic} than most ocean waters, although not statistically significant due to the wide variability (i.e. S.D.) of the river values. Despite latter variability in rivers, this would suggest that the Gd-anomaly_{intrinsic} of seawater may, at least partly be ascribed to freshwater weathering of continental rocks and soils, rather than being only the result of processes within the oceans.

Also please notice the Gd-anomaly_{intrinsic} = 0.90 of PAAS (Fig. 19C). The preceding shale reference after Haskin and Haskin (1966) has a higher Gd-anomaly_{intrinsic} = 0.97.

Summarizing, there exists a positive Gd-anomaly_{intrinsic} in the oceans relative to the value 0.9 of PAAS. This more positive Gd anomaly in the oceans may well be partly due to freshwater weathering on the continents, and partly due to processes within the oceans.

5.3.3. Absence of anthropogenic gadolinium

Nowadays there exists an anthropogenic source of Gd due to its use in medical diagnostics. The first gadolinium-based contrast agent (GBCA), gadopentetate dimeglumine (Magnevist), became available globally in 1988 for clinical use in magnetic resonance imaging (MRI) and, since then, eight further gadolinium chelates have been developed and approved in many regions worldwide (Lohrke et al., 2016). Most of this injected Gd is released again from the human body and enters into waste water streams. Recently this has led to anthropogenic-enhanced positive Gd anomalies in river water and also in coastal waters such as San Francisco Bay (Bau and Dulska, 1996; Hatje et al., 2016, and many references therein). Because our samples at Vertex IV site were collected in year 1983, there cannot have been an effect of this anthropogenic source (introduced after 1988) on the Gd concentrations here reported.

5.4. Gradual trend of HREE enrichment

The gradual trend of HREE enrichment in shale-normalized patterns (Fig. 11) is deemed to be due to the gradual trends in inorganic complexation in seawater, in combination with gradual trends in particle sorption and perhaps also gradual trends in organic complexation in seawater. The overall resulting REE pattern (Fig. 11) thus

depends on the relative affinities of the REE along the series, in combination with the abundance and REE-affinities of both the dissolved complexing substances and the suspended particles.

5.4.1. Stronger inorganic complexation in seawater with increasing atomic number

The REE series normalized relative to shales (PAAS) shows a steady enrichment with increasing atomic number (Figs. 11 and 12). As mentioned, this is partly due to (i) the stronger inorganic complexation (Fig. 1) of the HREE with the carbonate ion (CO_3^{2-}) in seawater (Goldberg et al., 1963; de Baar et al., 1991; Schijf et al., 2015; their Table 3). The total dissolved La exists for 52% as LaCO_3^+ ion and 36% as $\text{La}(\text{CO}_3)_2^{2-}$ ion, the total dissolved Lu exists for 88% as $\text{Lu}(\text{CO}_3)_2^{2-}$ ion and 11% as LuCO_3^+ ion (Schijf et al., 2015, their Table 3). Other inorganic complexes with Cl^- , SO_4^{2-} , OH^- and HCO_3^- ions do play a minor role. Due to the overall inorganic complexation, the percentage free ion steadily decreases from 4.8% for La to merely 0.1% for Lu (Fig. 1, after Schijf et al., 2015; their Table 3). Accordingly La is more prone to removal by adsorption on suspended particles, and therefore is indeed removed more from seawater than the REE with higher atomic number up to Lu.

5.4.2. Fractionations by different affinities of particles and/or dissolved organics

Fractionations within the REE series may also occur due to different affinities of the REE versus (ii) the functional groups on the suspended particles, and (iii) any dissolved organic ligands in seawater. These two effects (ii) and (iii) have been studied by Schijf and co-workers in many published articles, and the current state of knowledge is represented in the recent article of Schijf et al. (2015). Briefly both the effects of (ii) a suite of adsorbing agents (*Ulva lactuca*, hydrous ferric oxide, hydrous manganese oxide, synthetic and planktic foraminiferal calcite), and (iii) model dissolved organic complexing compounds (represented by the siderophore DFOB) have been presented and discussed. Similar fractionation effects are likely to occur in the oceans, where the concentrations of the particles and the dissolved organic ligands also play a role. Overall the net resulting concentrations of the dissolved REE series in a seawater sample thus depend on a balancing act between both the concentrations and the affinities of the 3 pools: (i) dissolved inorganic ligands, (ii) suspended particulate functional groups, and (iii) dissolved organic ligands. While there exists literature data on the REE contents of natural marine particles (e.g. de Baar et al., 1988; Sholkovitz et al., 1994; Garcia-Solsona et al., 2014), to the best of our knowledge there exists no data on (iii) natural dissolved organic-REE interactions. Hence we will further refrain from discussing dissolved REE-organics interactions. Moreover our current dataset at Vertex IV is only for (i) dissolved REE, and does not comprise any parallel data on (ii) REE content of particles, let alone the nature and affinity for REE of the adsorbing agent on particles. Thus for the time being we must refrain from further interpretation about such fractionation effects of particles at Vertex

IV site. Similarly for the Gd anomaly (see Section 5.3) these effects cannot yet be addressed.

5.5. Pacific/Atlantic enrichment of REE, PO_4 and NO_3 in deep waters

Processes that affect the REE distributions within the ocean basins can also be approached by intercomparison of such ocean basins, thus also avoiding the in itself arbitrary choice of a reference deemed to represent external sources to the oceans, i.e. REE composition of shales. The dataset at Vertex IV and the recent datasets of the SAFe 3000 m sample (Behrens et al., 2016) now can be compared with the recent REE dataset at the BATS site in the Northeast Atlantic Ocean (Pahnke et al., 2012). Briefly the deep waters in the northeast Atlantic at the BATS site have a circulation age of ~ 200 years and a ^{14}C -based age in the order of ~ 800 years (Matsumoto, 2007). The deep waters in the North Pacific Ocean near the Vertex IV site have a circulation age of ~ 1100 years and a ^{14}C -based age of ~ 2100 years. Either way (circulation age or ^{14}C based age), the age difference between deep Northeast Atlantic and deep North Pacific is on the order of ~ 1000 years. During those ~ 1000 years the deep Pacific waters have accumulated more nutrients PO_4 , NO_3 and SiO_4 , as well as also more Dissolved Inorganic Carbon (DIC) and more Alkalinity. All this accumulation is due to the ocean biological cycle of uptake of C, N, P, Si, and Ca in surface waters and remineralization in the deep waters, where Alkalinity_{adjusted} serves as a tracer for Ca uptake and mineralization. Similarly all REE, except Ce, have accumulated more in the deep Pacific waters.

5.5.1. Interoceanic comparison of dissolved REE concentrations

The REE series and PO_4 , NO_3 are compared in the Pacific/Atlantic element ratio graphs shown in Fig. 21, for 4 depth regimes 1000 m, 4000 m/3750 m, 3000 m, and 4500 m. First and foremost the dissolved Ce is lower in the deep Pacific Ocean (by a factor ranging from 0.34 to 0.9), as discussed in Section 5.1. Secondly the other, strictly trivalent REE, all are enriched some 1.5-fold to ~ 2.5 -fold in the deep Pacific versus the deep Atlantic. This is similar to the relative $\sim$ twofold enrichments of nutrients PO_4 and NO_3 . In contrast the relative enrichment of nutrient SiO_4 is much higher at each depth as follows: 4-fold at 4500 m, 4.8-fold at 4000 m, 7.8-fold at 3000 m and 10-fold at 1000 m. (off-scale and therefore not shown in Fig. 21). This major difference of the trivalent REE and PO_4 , NO_3 , versus SiO_4 , in combination with the very good correlations of REE with PO_4 and NO_3 in the thermocline region at Vertex IV (Section 5.2.3), does support the notion that the ocean cycling of REE is more closely linked with the cycle of organic matter than the cycling of hard parts, i.e. diatom opal frustules and their dissolution.

5.5.2. Dissolved inorganic speciation along the REE series for individual samples

Looking more in detail along the REE series there is an interesting trend (Fig. 21). The relative enrichment with

Fig. 21. The REE concentration ratio of the deep North Pacific Ocean versus the deep Northwest Atlantic Ocean. Also shown (at right hand side) the similar ratio for major nutrients phosphate (PO_4) and nitrate (NO_3). Horizontal black dotted line at value 1.0 is benchmark where Pacific and Atlantic concentrations would be the same. BATS is Bermuda Atlantic Time Series station (Pahnke et al., 2012) with PO_4 and NO_3 at same depths after the BATS station of the GEOTRACES GA02 section. There is a comparison (purple filled triangles) at 900 m for 10 REE at Vertex IV site with REE at 1000 m depth at BATS site. Also (green filled diamonds) for all 14 REE at 3000 m depth of SAFe (Behrens et al., 2016; nutrients of nearby GEOSECS station 202) and BATS (Pahnke et al., 2012). Also at Vertex IV site for 8 REE at 3000 m versus BATS at 3000 m (filled red squares), 10 REE comparisons of Vertex IV at 4000 m versus BATS at 3750 m (filled black dots), and 10 REE of Vertex IV at 4500 m versus BATS also at 4500 m (filled blue dots; for Er barely visible because overlapping with purple triangle of 900 m/1000 m comparison). For Ce the Pacific/Atlantic ratio is lower than 1, i.e. at 0.34, 0.5, 0.53, 0.66 and 0.9 for Vertex IV (4500 m), Vertex IV (4000 m), Vertex IV (3000 m), Vertex IV (900 m) and SAFe (3000 m), respectively. For all other REE the deep Pacific is higher than 1, at about 1.5–2.5-fold enrichment versus the deep Northwest Atlantic. This is similar to the about twofold enrichment of the Pacific versus the Atlantic for nutrients PO_4 and NO_3 . In contrast the relative enrichment of nutrient SiO_4 is much higher at each depth as follows: 4-fold at 4500 m, 4.8-fold at 4000 m, 7.8-fold at 3000 m and 10-fold at 1000 m (off-scale and therefore not shown). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

increasing atomic number is less apparent in the Pacific/Atlantic deep concentration ratio graphs than in the Pacific samples alone normalized versus PAAS (Fig. 11, left hand graphs).

As discussed (see Section 5.4) the net resulting concentrations of the dissolved REE series in a seawater sample depend on a balancing act between the concentrations and the REE-affinities of 2 pools: (i) dissolved inorganic ligands, and (ii) suspended particulate functional groups. Lacking data on latter (ii) suspended particles at our Vertex IV site, we cannot fully unravel this balancing act. Nevertheless below we will shed some light on one part of the puzzle, (i) the dissolved inorganic complexation of individual water samples.

Along the REE series, the generally quite constant Pacific/Atlantic concentration ratio for each given depth

(Fig. 21) may, at least partly, be attributed to the inorganic speciation of the REE series in seawater of each ocean. Briefly, due to the generally higher DIC in deep Pacific waters, the concentration of carbonate ion (CO_3^{2-}) in fact is less in these older waters (Fig. 6D). Such lower $[\text{CO}_3^{2-}]$ at higher overall DIC may seem counterintuitive, but is a well known fact in the chemistry of the dissolved CO_2 system in seawater. Moreover the Alkalinity also plays a role and tends to be higher in the older deep Pacific waters due to higher concentrations of both Ca^{2+} and nitrate (NO_3^-) as the result of overall more net remineralization of both CaCO_3 and organic matter, respectively. For example, at 1001.2 m depth in the northeast Atlantic (BATS site; Geotraces GA02 section, Pelagia cruise 64PE319, station 21) our data are $\text{DIC} = 2180.8 \mu\text{mol}\cdot\text{kg}^{-1}$, $\text{Alkalinity} = 2318.5 \mu\text{mol}\cdot\text{kg}^{-1}$ and $[\text{CO}_3^{2-}] = 103.4 \mu\text{mol}\cdot\text{kg}^{-1}$. In the deep North Pacific (28°N , 152°W) at 1090 m depth, the corresponding concentrations are $\text{DIC} = 2366.3 \mu\text{mol}\cdot\text{kg}^{-1}$, $\text{Alkalinity} = 2377.5 \mu\text{mol}\cdot\text{kg}^{-1}$ and $[\text{CO}_3^{2-}] = 44.3 \mu\text{mol}\cdot\text{kg}^{-1}$. (WOCE P16N, station 050; RV T.G. Thompson, R.A. Feely and C.L. Sabine; <https://cchdo.ucsd.edu/cruise/325020060213>). Similarly at 3000 m depth the $[\text{CO}_3^{2-}] = 112 \mu\text{mol}\cdot\text{kg}^{-1}$ in the deep Atlantic as compared to $[\text{CO}_3^{2-}] = 67.7 \mu\text{mol}\cdot\text{kg}^{-1}$ at the Pacific site. In other words, the $[\text{CO}_3^{2-}]$ ion concentration in the 1000–3000 m depth range in the deep Pacific is merely ~40% to ~60% of that at similar depths at the deep Atlantic site (Fig. 6D).

The parallel dataset of the dissolved CO_2 system now permits to go beyond the general world ocean description of REE speciation in standard seawater (Fig. 1), in order to calculate the inorganic REE speciation in seawater for the exact sample collected at given location and depth in either the Pacific or the Atlantic Ocean. The underlying rationale is that the dissolved free REE^{3+} ion is deemed to be prone to removal from seawater by adsorptive scavenging, whereas the dissolved inorganic REE-complexes are stable in the seawater solution. Fig. 22A shows that at 1090 m depth at the Pacific site the free REE^{3+} ion decreases from 17.1% for La to merely 0.97% for Lu. The complementary inorganic REE-complexes (not shown) thus range from 82.9% for La to 99.3% for Lu. Similarly at the Atlantic site at 1001 m depth, the free REE^{3+} ranges from 9.12% for La to merely 0.28% for Lu. Please notice these Atlantic free REE^{3+} percentages are about half those for the Pacific site. The complementary Atlantic inorganic REE-complexes (not shown) thus range from 90.9% for La to 99.72% for Lu.

The chance or risk for a dissolved REE to become removed by adsorptive scavenging is proportional to the percentage free REE^{3+} divided by the 100% total dissolved REE. Similarly the chance for NOT being removed is proportional to the percentage dissolved inorganic complexes divided by the 100% total dissolved REE. Next by defining the Seawater Inorganic Complexation Factor (SICF) as follows:

$$\text{SICF} = (\% \text{ REE complexes}/100\%)/(\% \text{ free REE}^{3+}/100\%) \quad (12)$$

one finds for the Pacific (Fig. 22B) that the stability in seawater solution increases from $\text{SICF}_{\text{Pacific}} = 4.85$ for La to

Fig. 22. Inorganic speciation of the REE in specific seawater sample (A) and Seawater Inorganic Complexation Factor (SICF) (B) show steep trends with increasing atomic number along the REE series. However these more or less cancel out in an intercomparison of Pacific and Atlantic Oceans (C). (A) The percentage free REE³⁺ ion is about twice as high in the deep North Pacific (1090 m depth; black filled dots) than in the deep North Atlantic (1001 m, blue filled diamonds). The complementary remaining major percentage is the sum of all REE-complexes (not shown) ranging from 83% (La) to 99% (Lu) in the Pacific, and 91% (La) to 99.7% (Lu) in the Atlantic. (B) Seawater Inorganic Complexation Factor (SICF) = (% REE-complexes/100%)/(% free-REE³⁺/100%) along the REE series as in (Eq. (12)) in main text Section 5.5.2. (C) The interoceanic Pacific/Atlantic Ratio = SICF_{Pacific}/SICF_{Atlantic} along the REE series as in (Eq. (13)) in main Text Section 5.5.2 shown for ~1000 m (more exact 1090 m/1001 m) based on above (A) and (B); and also for 4500 m depth. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

SICF_{Pacific} = 102.4 for Lu, an about 21-fold increase along the REE series. Similarly for the Atlantic one derives SICF_{Atlantic} = 9.96 for La to SICF_{Atlantic} = 356 for Lu, an about 36-fold increase along the REE series. Yet finally, by defining an interoceanic Pacific/Atlantic seawater inorganic stability ratio:

$$\text{Stability Ratio} = \text{SICF}_{\text{Pacific}} / \text{SICF}_{\text{Atlantic}} \quad (13)$$

one finds (Fig. 22C) that along the REE series the interoceanic stability ratio of inorganic complexation in seawater at ~1000 m depth is quite uniform ranging from 0.49 for La to 0.39 for Lu. This fairly uniform trend with increasing atomic number from La to Lu, somewhat matches the also quite uniform trend within a factor 2 of the interoceanic concentration ratio at 900–1000 m depth (Fig. 21), ranging from 1.44 for La to 0.99 for Sm and then slowly increasing to 1.42 and 1.25 for Yb and Lu, respectively (here Ce at value 0.66 is also plotted, but excluded from consideration, this due to its unique oxidative removal).

Similarly at 4500 m depth the Pacific/Atlantic Seawater Inorganic Stability Ratio is fairly uniform, ranging from 0.71 for La to 0.55 for Lu (Fig. 22C). This also matches the fairly uniform trend of the interoceanic concentration ratio at 4500 m depth (Fig. 21) ranging from 1.51 for La to 1.81 for Eu and then decreasing again to 1.42 and 1.47 for Yb and Lu, respectively.

There are some caveats to this approach. Firstly the graphs in Fig. 22 represent a snapshot at the given time and location, whereas the concentration ratio (Fig. 21) is the result from some 1000 years preceding history of dissolved REE accumulation during deep ocean circulation. This notion may, at least partly, account for the non-perfect fit at 1000 m and 4500 m depths between the graphs (Fig. 21 versus Fig. 22C). Secondly, as mentioned beforehand, this (i) inorganic complexation in seawater is only part of the story, the other key part being (ii) the different affinities along the REE series to particles that also play a role in fractionations along the REE series, but can as yet not be addressed for the Vertex IV site due to lack of data on REE in particles. Thirdly, the classical paradigm that dissolved REE in seawater are stabilized by complexation with dissolved carbonate, i.e. somewhat countering REE adsorption on marine particles, may need to be reconsidered. Laboratory experiments have shown that under given experimental conditions, the dissolved (REECO₃)⁺ complexes and also (REEOH)₂⁺ complexes may in fact become adsorbed by model adsorbents on particles (Quinn et al., 2006; Schijf and Marshall, 2011; Zoll and Schijf, 2012). Nevertheless, the above approach on (i) inorganic complexation in seawater is one step forward towards more complete simulation by next also including (ii) adsorption on particles, with the ultimate aim of further understanding the REE behaviour in the world oceans.

5.5.3. Interoceanic disappearance of Gd anomaly

The Gd anomaly also appears to be canceled out and has disappeared (Fig. 21), this presumably for the same reasons as above (Section 5.5.2) for complexation with the [CO₃²⁻] ion. This observation that there is no apparent interoceanic Gd anomaly (Fig. 21) is independent of the arbitrary choice of an external source reference, i.e. shales, consistent also with Gd-anomaly_{intrinsic} (Fig. 19C). Nevertheless, in the Pacific/Atlantic comparison (Fig. 22C) there seems to be a predicted slightly better seawater inorganic stability of Gd in the Pacific. Subtle Gd anomalies are also seen in the underlying predicted speciation graphs (Fig. 22A, 22B; see also the general Fig. 1). Distribution coefficients for REE sorption on marine particles also play

a role, yet lacking such information on marine particles in the Pacific versus the Atlantic, we cannot draw a firm conclusion on the overall lack of an interoceanic Gd anomaly.

5.5.4. Interoceanic Eu anomaly

There appears a positive Eu anomaly in the comparison (Fig. 21) at 3000 m and at 4500 m, but less visible in the 4000 m/3750 m comparison (but still there, at interoceanic Eu ratio 2.15 relative to 2.11 and 2.13 for neighboring Sm and Gd, respectively). The Pacific Ocean is well known to have a faster spreading rate of the underlying plate tectonics than the Atlantic Ocean, i.e. also a higher rate of formation of new Mid Ocean Ridge Basalt (MORB). Therefore the emissions of hydrothermal vents also are higher in the Pacific than in the Atlantic. Hydrothermal vents have been found to show a distinct positive Eu anomaly (Michard et al., 1983; Klinkhammer et al., 1983, 1994a, 1994b; Sverjensky, 1984; Bau, 1991; Mitra et al., 1994; Mills and Elderfield, 1995; and others). Upon mixing with the ambient deep waters this positive Eu anomaly does contribute to the Eu signal of these deep waters. This now is visible in the interocean comparison of deep waters (Fig. 21). Moreover upon plotting the dissolved Eu versus dissolved Sm, the linear regression trend in the northeast Atlantic BATS site shows a lower slope value of 0.19 as compared to the slope value of 0.25 in the deep North Pacific at Vertex IV site (Fig. 23). Both illustrations (Figs. 21 and 23), albeit not independent, do support the notion of a relative Eu enrichment in the deep Pacific Ocean.

Fig. 23. Eu [$\text{pmol}\cdot\text{kg}^{-1}$] versus Sm [$\text{pmol}\cdot\text{kg}^{-1}$] in seawater along the complete water column depths at the North Pacific site (Vertex IV; black filled dots; $n = 19$; 25–5500 m depth) and the Northwest Atlantic site (BATS, blue filled squares; $n = 10$; 20–4500 m depth). The higher value 0.253 of the regression slope in the Pacific versus slope value 0.194 in the Atlantic is consistent with the faster spreading rate of the Pacific plate tectonics with more formation of mid-ocean ridges, hence more hydrothermal inflow of Eu enriched waters. BATS after Pahnke et al. (2012), their Table 5. Numerical values in the regressions are rounded to 3 decimals that is perhaps more flattering than the true significance, the R^2 also rounded to 3 decimals, because as rounded to 2 decimals $R^2 = 1.00$ is deemed to be less informative if not misleading as if perfect. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6. CONSIDERATIONS FOR FUTURE RESEARCH

An overall review of all existing datasets of the the REE in seawater, in conjunction with key ancillary tracers, notably the major nutrients, would be very useful, but also a very demanding challenge. This would not only require much effort, but also the inevitable task to select those datasets of REE, as well as ancillary tracers, with high accuracy, and to define the criteria for such selection. For example in the, relatively simple, pursuit of the world ocean relationship between Cd and phosphate (de Baar et al., 1994), at the time the Cd data was in general accurate but several phosphate datasets not (Löscher et al., 1997). For Fe in seawater, a community effort in 2001 did yield a selection of dissolved Fe data that at that time was deemed accurate (de Baar and de Jong, 2001), yet in the GEOTRACES era from 2007 onwards, several of these before 2001 datasets did after all appear to be less than accurate due to presumably inadvertent contamination. This also leads to the issue of whether or not ultraclean sampling and filtration of the REE is advisable, notably for Ce that has very low concentrations in the oceans. Integration in such efforts of the existing articles and datasets on the Nd isotope ratio in seawater would be beneficial, yet also very demanding. These overall challenges best are done as a community effort, the GEOTRACES intercalibrations of the REE and Nd isotopes are an excellent example.

Organic complexation in seawater is known to be very important for several transition metal elements, notably Fe, Cu, Zn, but not for others such as Mn. Complexation of REE by model organics has been studied in the laboratory, whether or not such dissolved organic complexation does exist in natural seawater is an outstanding question. Similarly more research on REE in the colloid size fractions in seawater may be of interest.

7. CONCLUSIONS

The very old deep waters in the central North Pacific show systematic low concentrations of dissolved Ce, as well as low values of dissolved Ce relative to the other REE as defined by either the Ce/Nd ratio or the Ce anomaly Ce/Ce^* .

The very old deep waters in the central North Pacific show the highest concentrations of dissolved strictly trivalent REE, i.e. except for Ce.

Within the thermocline region there exist very close linear relations of the REE series with the nutrients PO_4 and NO_3 , but the REE show more of a curvature with nutrient SiO_4 . This and the general about twofold enrichment of deep Pacific versus deep Atlantic of REE and PO_4 , NO_3 , would support the notion that ocean biogeochemical cycling of the REE is mostly coupled with the ocean cycling of biogenic soft tissue.

Multiple regressions of Nd, representing the LREE, and Er, representing the HREE, versus both phosphate and silicate are significant. Nevertheless there is room for the hypothesis of invoking additional net deep water scavenging of mostly the LREE (i.e. Nd) but also the HREE (i.e. Er).

There is a trend of increasing REE abundance with increasing atomic number, when the dissolved seawater data at Vertex IV site is normalized relative to PAAS reference. This trend is consistent with stabilization due to stronger inorganic complexation with carbonate ion with increasing atomic number from $_{57}\text{La}$ to $_{71}\text{Lu}$.

There are indications for a positive Gd anomaly in the North Pacific Ocean. Similar positive Gd anomaly values are also discernible in other datasets of dissolved REE in the Atlantic and Indian Oceans.

The deep North Pacific is enriched with Eu relative to the deep Northeast Atlantic, likely due to more emissions of Eu-enriched hydrothermal fluids in the Pacific basin.

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The interpretations in the current manuscript do make comparisons with the new REE dataset of the BATS vertical profile (Pahnke et al., 2012), where we are grateful to Prof. Katharina Pahnke and her co-authors for their excellent work and results.

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