c[1]

continental crust composition) normalised Ce concentrations ~10 times

Surface water samples were collected using a towed steel fish or the seawater intake system during transit time, pumping seawater from 2–5 m water depth (see Stichel et al., 2012b for details). Deeper samples were collected from Niskin bottles mounted on a CTD-rosette (see Stichel et al., 2012a for details). All samples were filtered through 0.45 μm Millipore® or Supor® fi

250 mL of a BATS 2000 m sample. Pahnke et al. (2012) used an eight-element spike (not spiking La and Lu) isotope dilution technique to measure the REEs in 50–100 mL aliquots and obtained an external reproducibility (2σ) better than 3%, except for Ce, which was 3.8%. Clearly our method that gives an estimated external precision (2σ) ranging from 4% to 18% (Table 1), consumes at least 5 times less sample, and requires no additional sample preparation, compares favourably with these methods. Additional improvements have been made to the measurement technique since most of the data presented here were measured (Table 1: station 113, 1000 m sample by Time Resolved Analysis; also Osborne et al. this volume), which now enable the seaFAST online preconcentration technique to achieve a precision similar to the other methods mentioned above while still consuming significantly less sample material.

3. Results

Yttrium and REE concentrations in the < 0.45 μm filtered seawater generally increase with water depth (Fig. 2), for example Lu increases from 0.4 pmol/kg in the surface waters to 1.4 pmol/kg Lu at 4500 m depth. Over the same depth range La and Y concentrations increase from 12 and 90 pmol/kg to 45 and 190 pmol/kg, respectively. The shape of the increase with depth varies from near linear for LREEs to more convex for HREEs with relatively constant HREE concentrations in intermediate and deep waters (Fig. 2). The vertical distribution (or profile) of the HREEs is very similar to that of the hard part (i.e., skeletal opal or $CaCO_3$) forming nutrients silicic acid (silicate) and alkalinity (Fig. 3). Similar to silicate, the depth distribution of the REEs evolves along the zero meridian section in that the difference between the surface and deep water concentrations decreases southward. The stations in the Weddell Gyre (131, 161, 193) exhibit virtually constant silicate concentrations below 1000 m and constant alkalinity below 500 m. Similarly, the REE concentrations are high and constant in intermediate and deep waters within the WG. The Drake Passage station (241) has an alkalinity profile (and silicate, not shown) intermediate between the WG stations and those from within the ACC near the Zero meridian (101, 104) and also exhibits REE concentration profiles intermediate between the WG and ACC extremes.

3.1. Comparison of crossover data

One central component of the GEOTRACES programme is to ensure that crossover stations between cruises are sampled at similar depths and the resulting data are compared as a cross calibration exercise while also providing some information on the short term variability of some parameters. The Southern Ocean cruises of the IPY achieved this and stations 101, 104 and 113 were sampled at almost identical locations as stations S2, S3, and S4 from the "Bonus Good Hope" GIPY4 cruise, for which REE concentrations were published by Garcia-Solsona et al. (2014). The GIPY4 cruise sampled these locations only 2 weeks after the Polarstern cruise and the crossover data, measured following different pre-concentration techniques, generally agree within uncertainties (Fig. 4 and Supplementary Fig. 1). In a few instances there are differences in REE concentrations at similar depths but in most cases careful comparison of the silicate data suggests that these differences are related to real short-term variations of the water masses sampled. A good example is station 113 which shows higher silicate concentrations and slightly elevated LREE concentrations compared to GIPY4 station "super 4" at intermediate depths (Figs. 3 & 4). The deepest sample of GIPY4 station "super 3" has much lower REE concentrations than all other samples at such depths. While near bottom scavenging of Nd has been reported in the Pacific sector of the Southern Ocean (Carter et al., 2012), removal of essentially half the bottom water REE inventory, including Ce (Fig. 4), within two weeks seems unlikely. Instead this most likely indicates a leaking Niskin bottle, but tparrare[htwo thi

The similarity of the HREE concentration depth profiles with those of

acquired on the shelf during the process of AABW formation. AABW was also found to have less radiogenic Nd isotopic compositions than CDW at these stations suggesting an eastern Antarctic source (Stichel et al., 2012a). Similarly unradiogenic results were obtained near station 131 at GIPY4 station super 5 (Garcia-Solsona et al., 2014). Additionally, the particulate REE pattern of the AABW sample at this location was shale like indicating a fresh continental source of these particles (Garcia-Solsona et al., 2014).

4.2. Meridional variability of REE water column profiles

Crossing the different zones and frontal systems of the ACC, Rutgers van der Loeff et al. (2011)

stratification of the water column may also play a role in controlling the shape of the REE depth profiles (see Section 4.3 below). In support of this the Nd concentration profiles from station SAVE 271 in the

the Indian Ocean (Bertram and Elderfield, 1993). Values of Δ[Nd] near 0.4 pmol/100 m and below were found in the Arabian Sea (German and Elderfield, 1990a), in the N Pacific (Shimizu et al., 1994), in the eastern equatorial Pacific (Grasse et al., 2012), in the south east Pacific (Molina-Kescher et al., 2014) and in the eastern Pacific sector of the Southern Ocean (Carter et al., 2012). This suggests that lower Δ[Nd] values are generally associated with higher productivity areas or water masses that travelled through such areas.

The assumption of a linear increase in [Nd] with depth is not always valid. A marked break in slope, similar to nutrients, occurs off Japan where Δ[Nd] is 1.33 in the upper 800 m and then 0.36 below 1000 m (Alibo and Nozaki, 1999). In contrast, near Bermuda in the Sargasso Sea the Δ[Nd] is 0.39 in the upper 1000 m, then effectively zero (0.04 pmol/100 m) from 1000 m to 3000 m, before a near linear Δ[Nd] of 0.6 prevails below (Pahnke et al., 2012). This suggests a role of advection in controlling the Δ[Nd] given that the body with the nearly constant concentrations corresponds to NADW. Invariant REE concentrations with depth, such as those from the WG, have been found below 1000 m in the Andaman Sea in the eastern Indian Ocean where the water column is homogenous for all measured properties including temperature and salinity (Nozaki and Alibo, 2003a). In this case, the well homogenised water column was attributed to efficient vertical mixing of the deep waters in this semi-enclosed basin (Nozaki and fluxes, or most likely a combination of both, is linked to the development of homogenous REE depth profiles such as in the WG. However, 1995;

(e.g. Schijf et al., 1995). Cerium oxidation kinetics are relatively slow and the Ce anomaly (Ce/Ce*) in Mn–FeOH crusts, representative of the main sink for REEs from seawater, has been shown to be related to the growth rate of crusts (e.g. Bau et al., 2014). In seawater a general relationship with water mass age has been observed with the strongest Ce anomalies being found in old deep Pacific waters (German et al., In other regions, such as the Bay of Bengal (e.g. Amakawa et al., for the different metals a correlation matrix was constructed after extracting the data from the GEOTRACES 2014 intermediate data product (http://www.bodc.ac.uk/geotraces/data/idp2014/). In some instances the ultra-clean rosette and the normal rosette (used to sample

German, C.R., Elderfield, H., 1990b.

Stramma, L., England, M., 1999.