Hawaiian imprint on dissolved Nd and Ra isotopes and rare earth elements in the central North Pacific: local survey and seasonal variability

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Abstract

Dissolved neodymium isotopes ($^{143}\text{Nd}/^{144}\text{Nd}$, expressed as ϵ_{Nd}) and rare earth elements (REE) have the potential to trace the provenance of lithogenic material as well as water masses. The central North Pacific is poorly investigated with respect to its Nd isotope signature and REE cycling, and little is known about the contributions of volcanic islands, such as Hawaii, relative to dust input from Asian deserts to the surface water REE budgets. Here we present dissolved Nd isotope and REE data

along with long-lived radium isotope activities from Hawaii Ocean Time-Series Station ALOHA and coastal waters from Oahu, sampled for a GEOTRACES process study in February 2011. The data are supplemented with seasonal samples from ALOHA. Our results show a clear influence of the Hawaiian Islands on the coastal ocean and surface waters at ALOHA during February, expressed by higher surface water Ra activities, radiogenic surface ϵ_{Nd} ($\epsilon_{\text{Nd}} = +1.4$ to -1.0), and elevated Eu anomalies ($\text{Eu}/\text{Eu}^* \geq 1.3$). Seasonal cycles of Asian dust deposition most likely contribute to the seasonal ϵ_{Nd} variability of surface waters at ALOHA, as suggested by more negative ϵ_{Nd} and the lack of Eu anomalies in summer. Neodymium isotopes in the intermediate and deep water column at ALOHA trace typical North Pacific water masses, such as North Pacific Intermediate Water and North Pacific Deep Water. We suggest that a radiogenic ϵ_{Nd} excursion in 1000-2000 m water depth, observed in various North Pacific profiles, is controlled by advection of a modified Upper Circumpolar Deep Water or North Equatorial Pacific Intermediate Water. We further present an updated average ϵ_{Nd} signature of -3.5 ± 0.5 for North Pacific Deep Water and show that REE patterns of deep waters at ALOHA are dominantly controlled by vertical processes.

1. Introduction

Rare earth element (REE) patterns and neodymium isotopes in seawater, authigenic Fe-Mn oxides, and lithogenic particles are widely used to study modern and past ocean circulation, lithogenic particle provenance, and aeolian input. Nonetheless many open questions remain, including the budget of Nd and REE with potential contributions of submarine groundwater discharge (SGD) and margin sediments (Tachikawa et al., 2003; Johannesson and Burdige, 2007), benthic flux from sediment pore fluids (Abbott et al., 2015a,b), and a missing flux of radiogenic Nd to the North Pacific (e.g., Jones et al., 2008). Moreover, the importance of dust to the Nd and REE budget is still under debate. While some studies suggest little or no influence of dust particles on the Nd isotope and REE signal in the North Pacific (Nakai et al., 1993; Jones et al., 1994; van de Flierdt et al., 2004; Hongo et al., 2006), others show clear evidence that dust deposition modifies at least the surface water signal of ϵ_{Nd} and REEs in this area and in the North Atlantic under the Saharan dust

plume (e.g., Shimizu et al., 1994; Greaves et al., 1999; Tachikawa et al., 1999; Stichel et al., 2015).

Neodymium isotope ratios ($^{143}\text{Nd}/^{144}\text{Nd}$) are typically expressed in ϵ_{Nd} notation, where $\epsilon_{\text{Nd}} = [(^{143}\text{Nd}/^{144}\text{Nd})_{\text{sample}} / (^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} - 1] * 10^4$, with $(^{143}\text{Nd}/^{144}\text{Nd})_{\text{CHUR}} = 0.512638$ representing the Chondritic Uniform Reservoir (Jacobsen and Wasserburg, 1980). The ϵ_{Nd} of seawater varies locally as a result of the heterogeneity of weathered material that is delivered to the ocean in particulate, colloidal, and/or dissolved form through fluvial and aeolian input (e.g., Frank, 2002), SGD (e.g., Tachikawa et al., 2003; Johannesson and Burdige, 2007), and boundary exchange processes (Lacan and Jeandel, 2001; 2005). Apart from lithogenic input, the quasi-conservative behaviour of ϵ_{Nd} in the ocean and the short residence time of 300-1000 years (Tachikawa et al., 2003; Arsouze et al., 2009; Rempfer et al., 2011) lead to characteristic ϵ_{Nd} signatures in different parts of the ocean, with the Pacific being generally more radiogenic ($\epsilon_{\text{Nd}} \approx -4$; Piepgras and Jacobsen, 1988; Amakawa et al., 2009; Pahnke et al., 2012) than Atlantic, Indian, and Southern Ocean waters (cf. Lacan et al., 2012). Neodymium isotopes are therefore widely used as a tracer of modern and past ocean circulation (e.g., von Blanckenburg, 1999; Frank, 2002; Piotrowski et al., 2004; Lacan and Jeandel, 2005; Pahnke et al., 2008).

Neodymium concentrations, on the other hand, are mainly controlled by vertical processes of surface input, particle scavenging, and release at depth, as typical for the coherent group of REEs (e.g., Elderfield and Greaves, 1982; Elderfield, 1988; Bertram and Elderfield, 1993; Tachikawa et al., 1999), but can also be influenced by lateral transport in some areas of the ocean (e.g., Basak et al., 2015; Stichel et al., 2015). Preferential adsorption of light REEs (LREE) onto particles and stronger complexation of heavy REEs (HREE) lead to fractionation that results in a heavy over light REE enrichment in seawater (Cantrell and Byrne, 1987; Elderfield, 1988; Byrne and Kim, 1990; Sholkovitz et al., 1994; Tachikawa et al., 1999), which is typically visualised by normalisation to a reference water mass or lithogenic background. Dissolved REE patterns of seawater are further characterised by a negative Ce anomaly that results from microbially controlled Ce oxidation (Elderfield and Greaves, 1982; Moffett, 1990). Normalised REE patterns and resulting anomalies, such as of Eu and Gd, as well as individual elemental ratios can be used to identify lithogenic input to the ocean, processes associated with particle scavenging and release in the water column, and redox conditions (e.g., Bertram and Elderfield, 1993;

Greaves et al., 1994; Sholkovitz et al., 1999; Zhang et al., 2008; Grenier et al., 2013; Jeandel et al., 2013).

Here we present Nd and Ra isotope and REE concentration data of coastal waters of the Hawaiian Island of Oahu and from Hawaii Ocean Time-series Station ALOHA (HOT-ALOHA; ALOHA = A Long-term Oligotrophic Habitat Assessment) from the GEOTRACES process study cruise KM1107 (Process Study GPpr05) together with additional data from seasonal cruises conducted by the Center for Microbial Oceanography: Research and Education (C-MORE).

We evaluate the influence of the Hawaiian Islands on the coastal surface and subsurface waters and on the open ocean of the central North Pacific at Station ALOHA. Seasonal sampling of surface waters at ALOHA further allows for an assessment of local Hawaiian *versus* distal Asian dust influence on the dissolved REE and ϵ_{Nd} at this open ocean station. Boyle et al. (2005) and Fitzsimmons et al. (2015) previously argued for a prominent Asian dust impact on dissolved iron concentrations at ALOHA. Given the distinct ϵ_{Nd} and REE signatures of Asian dust ($\epsilon_{Nd} = -10.3$; Taylor et al., 1983; Goldstein et al., 1984; Nakai et al., 1993; Liu et al., 1994) and Hawaiian basalts (average $\epsilon_{Nd} = +6.2$, Tanaka et al., 2008; positive Eu anomaly, e.g., Ren et al., 2009), combined Nd isotope and REE analyses of waters from coastal sites around Oahu and Station ALOHA allow for a detailed characterisation of the Hawaiian and Asian dust impact on coastal and open ocean waters.

At selected stations and depths, long-lived radium isotope signatures were used to complement the REE information to further support the terrestrial overprinting on water masses around the island of Oahu and at Station ALOHA. Sources of long-lived radium isotopes in the ocean are bottom sediments and coastal sources that include diffusion from shelf sediments, rivers, and SGD. Radium-226 (half-life = 1600 y) occurs at relatively high activities offshore in the Pacific Ocean due to release from bottom sediments and continental sources that mix up into the open ocean where it persists due to its relatively long half-life (Broecker et al., 1967; 1970; Huh and Ku, 1998). Radium-228 (half-life = 5.8 y) decays much faster, and can only be observed near margins and bottom waters, where it provides evidence for recent terrestrial input from streams, SGD, or sediment/rocks (e.g., Moore et al., 2008; Kwon et al., 2014).

Additionally, sampling of the full water column at Station ALOHA adds significantly to the rather sparse spatial resolution of water column sites with available Nd isotope data in the central North Pacific Ocean (cf. Lacan et al., 2012)

and allows investigation of the potential contribution of volcanic islands to the intermediate and deep water ϵ_{Nd} composition in the North Pacific.

1.1 Study area

The North Pacific study area comprises the coastal waters of the Hawaiian Island of Oahu and Station ALOHA (Fig. 1). In coastal waters, the sampling sites are located a few km off the coast with a maximum sampling depth of 350 m. A station between the northern tip of Oahu and ALOHA is located approximately 15 km off Oahu with a maximum sampling depth of ~1350 m. Station ALOHA, established in 1988 as an oligotrophic ocean time-series station, is located 100 km north (i.e., upstream) of Oahu within the North Pacific Subtropical Gyre at a location where biogeochemical influence of the Hawaiian Islands is assumed to be negligible, and has a water depth of ~4800 m (Karl and Lukas, 1996).

The Hawaiian climate is characterised by higher rainfall in winter than in summer and by spatial differences in precipitation and discharge due to high mountain ranges and the predominant easterly trade winds (Oki, 2003; Giambelluca et al., 2013). On Oahu, the eastern part of the island therefore receives higher rainfall than the western part (Giambelluca et al., 2013). Submarine groundwater discharge has been shown to be an important contributor of freshwater and nutrients to the coastal ocean of the Hawaiian Islands (see review of Moosdorf et al., 2015 and references therein). In addition, the North Pacific Ocean is subject to seasonally varying dust input from the Asian continent with peak fluxes during spring (Duce et al., 1980; Uematsu et al., 1985; Prospero et al., 1989). This seasonal cycle of dust transport also affects the deposition on the Hawaiian Islands (Parrington et al., 1983) and has been proposed to influence Fe and Th concentrations in surface waters at ALOHA (Boyle et al., 2005; Fitzsimmons et al., 2015; Hayes et al., 2015). Isotope investigations have shown that dust deposited in the central North Pacific Ocean mainly consists of Chinese Loess (Nakai et al., 1993; Jones et al., 1994; 2000; Asahara et al., 1995).

2. Materials and Methods

2.1 Sampling and REE pre-concentration

Seawater samples for Nd isotope and REE concentration analyses were taken during the GEOTRACES process study cruise KM1107 (GPpr05) on *R/V Kilo Moana*

around the island of Oahu and at Station ALOHA in February 2011 (Fig. 1b; Tab. 1). Additional samples were collected during several C-MORE cruises to Station ALOHA from water depths of 0-750 m: KM1215, July 2012, C-MORE HOE-DYLAN V (Wilson and Fitzsimmons, 2012); KM1219, August 2012, C-MORE HOE-DYLAN IX (Wilson and Tozzi, 2012); KM1309, June 2013, C-MORE HOE-PhoR I (Björkman and Fontanez, 2013) (Tab. 1). Furthermore, we received samples for REE concentration measurements from three water depths (15 m, 130 m, 1000 m) from cruise KM1316 conducted in September 2013 (C-MORE HOE-PhoR II, Clemente and Samo, 2013; Tab. 1). All seawater samples were collected in 12 L Niskin/Bullister bottles with nylon-coated stainless steel springs attached to a rosette frame equipped with a Sea-Bird CTD.

Groundwater was sampled from Wailupe Spring on Wailupe Beach at the south coast of Oahu, where groundwater is discharged in discrete springs (21°16.54 N, 157°45.73 W, May 2010). The samples were taken from 0.8 m and 1.4 m sediment depth using a push-point sampler. The samples were filtered through AcroPak500 cartridges (0.8/0.45 μm) and acidified to pH = 2.

For Nd isotope analyses, five litres of seawater were filtered on board of the research vessel through AcroPak500/200 cartridges (pore size of 0.8/0.45 μm and 0.8/0.2 μm , respectively) into pre-cleaned LDPE containers (cf. Pahnke et al., 2012) and acidified to a pH of ~2 with ultra-clean 6 N HCl (self-distilled or Fisher Scientific optima grade). For analyses of dissolved REE concentrations, a volume of 50-250 mL of filtered seawater was either collected directly from Niskin/Bullister bottles (cruises KM1107, KM1316) into pre-cleaned LDPE bottles and acidified to a pH of ~2 with ultra-pure 6 N HCl, or subsamples were taken from the 5 L Nd containers in the land-based laboratory (cruises KM1215, KM1219, and KM1309). On cruise KM1316, the sample from 15 m water depth was collected with a Teflon pump directly into a pre-cleaned LDPE bottle through an AcroPak1500 filter (0.2 μm).

All samples from cruise KM1316 were additionally size fractionated by cross flow filtration to provide one dissolved sample (<0.2 μm (15m) or <0.45 μm (130 m, 1000 m)), one permeate sample (soluble Nd, <10 kDa, ~0.003 μm), and one retentate sample (10 kDa to 0.2 μm or 10 kDa to 0.45 μm , plus the soluble REEs in each case). It is important to note that during cross flow filtration, the soluble-sized REEs (like the water carrier phase) both pass through the filter into the permeate and across the filter into the retentate fractions, with a balance established based on the relative

permeate and retentate flow rates that is quantified as the concentration factor. Thus, the retentate fraction contains both the colloidal REE fraction retained by the filter as well as a portion of the soluble fraction (see below and Fitzsimmons and Boyle, 2014), such that the true colloidal REE concentration must be calculated from the permeate and retentate measurements and the concentration factor. Cross flow filtration was completed on board the ship using pre-filtered seawater following the method described for Fe in Fitzsimmons and Boyle (2014). Briefly, a pre-cleaned Millipore *Pellicon XL* filter was rinsed with 500 mL of 1.5 N HCl and conditioned with 350-400 mL of the pre-filtered (<0.2 or <0.45 μm) seawater. Cross flow filtration was executed at a total flow rate of ~25 mL/min to a final retentate and permeate volume of ~500 mL each. The colloidal REE fraction (c_{REE}) of the samples was calculated as $(\text{REE}_{\text{retentate}} - \text{REE}_{\text{permeate}}) / \text{CF}$ (Buesseler et al., 1996), with CF = 2 being the concentration factor that results from the equal permeate and retentate flows of ~12.5 mL/min. The concentration factor is calculated by $(\text{Vol}_{\text{retentate}} + \text{Vol}_{\text{permeate}}) / \text{Vol}_{\text{retentate}}$ (Buesseler et al., 1996) and the recovery of each REE can be calculated by $(s_{\text{REE}} + c_{\text{REE}}) / d_{\text{REE}} * 100\%$, where s_{REE} corresponds to the concentration of the REE in the permeate fraction and d_{REE} to the REE concentration in the dissolved (<0.2 or <0.45 μm) fraction.

2.2 Neodymium isotope analyses

For Nd isotope analyses in seawater, REEs were pre-concentrated from the samples using C_{18} SepPak[®] cartridges (Waters Inc.) following a method modified after Shabani et al. (1992) and Jeandel et al. (1998). The C_{18} cartridges were cleaned using 5-10 mL 0.5 N HCl and rinsed with MilliQ to bring the pH back to neutral. They were filled with 300 mg of a REE complexing agent (HDEHP, 2-ethylhexyl phosphate for synthesis, Merck), followed by another cleaning step with 2 mL 6 N HCl and rinsing with MilliQ prior to further use. After adjusting to a pH of 3.5 using distilled ammonia hydroxide solution (self-distilled from reagent grade ammonia hydroxide, 35%, Fisher Scientific), the samples were pumped through the pre-cleaned C_{18} cartridges at a pump rate of 20 mL/min. The cartridges were then rinsed with 0.01 N HCl to remove Ba and the REEs were eluted with 35 mL of 6 N HCl. Neodymium was then isolated by a two-step column procedure (Pin and Zalduegui, 1997). The first set of columns was filled with Eichrom TRU-Spec resin (100 μL , particle size

100-150 μm) and used for separation of REEs from any HDEHP that may have leaked out of the C_{18} cartridges. In the second step, columns filled with TrisKem LN-Spec resin (250 μL , particle size 50-100 μm) were used to isolate Nd from the other REEs with 0.23-0.25 N HCl as eluent. The Nd aliquot was treated with a 1:1 mixture of H_2O_2 (30%) and concentrated HNO_3 , dried, and re-dissolved in 2% HNO_3 for isotope measurements. All used acids were of ultra-clean quality (self-distilled or Fisher Scientific optima grade).

Neodymium isotopes were measured on a ThermoScientific *Neptune Plus* multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS) at the University of Oldenburg. A Cetac *Aridus II* desolvating nebuliser system was used for sample introduction. We varied the sample volume and measurement time depending on the Nd concentration of the samples. Samples with ≥ 5 ng Nd were analysed for 4x12 cycles at a concentration of 5-10 ppb (1 mL sample solution) with previous peak centring, whereas samples with < 5 ng Nd were measured for 1x36 cycles at a concentration of 4-5 ppb (500-600 μL sample solution). For these low concentration samples, peak centring was only done prior to the analysis of the Nd standard JNdi-1, which was measured generally every 2nd-3rd sample at the same concentration as the samples. All samples were corrected for mass bias with $^{146}\text{Nd}/^{144}\text{Nd} = 0.7219$ using an exponential law (O'Nions et al., 1977). We applied a secondary mass bias correction using linear correlation of $^{143}\text{Nd}/^{144}\text{Nd}$ to $^{142}\text{Nd}/^{144}\text{Nd}$ (Vance and Thirlwall, 2002). All data were normalised to the accepted JNdi-1 value of $^{143}\text{Nd}/^{144}\text{Nd} = 0.512115$ (Tanaka et al., 2000). External reproducibility, checked with multiple runs of 5-10 ppb JNdi-1 during each session, was generally better than 40 ppm ($\pm 0.4 \epsilon_{\text{Nd}}$ units, 2σ , $n=8-24$ per session). An independent secondary in-house standard (5-10 ppb, $n=16$) was measured one to two times per session and had a reproducibility of 30 ppm ($\pm 0.3 \epsilon_{\text{Nd}}$ units, 2σ) over the entire measurement period. Two of the secondary standards were measured in REE-free seawater matrix, produced from co-precipitation of trace metals with Fe hydroxide according to the method described in detail in Stichel et al. (2012a). The Nd isotope measurements of these standards with seawater matrix did not differ from the matrix-free standards. Three independently processed duplicate samples had the same ϵ_{Nd} within analytical uncertainty (Fig. 2; Tabs. 1, A.1). The lab is intercalibrated for Nd isotope measurements through analysis of GEOTRACES intercalibration samples BATS and SAFe. The procedural laboratory Nd blank ($n=12$; comprising column chemistry (all) and elution from C_{18} cartridges ($n=4$)) was ≤ 10 pg,

representing <1% of the Nd concentration of the samples. Therefore, no blank correction was applied. Groundwater samples were analysed at the University of Hawaii at Manoa using Fe co-precipitation for pre-concentration, two-step column chemistry for Nd isolation, and thermal ionisation mass spectrometry (TIMS) as described in Basak et al. (2015).

2.3 Rare earth element analysis

We used isotope dilution (ID) analysis for the determination of REE concentrations in the seawater samples. For this purpose, 10-80 mL aliquots of the samples, depending on REE concentrations, were mixed with a multi-element REE spike (enriched in the isotopes ^{139}La , ^{142}Ce , ^{145}Nd , ^{149}Sm , ^{153}Eu , ^{155}Gd , ^{161}Dy , ^{167}Er , ^{171}Yb , ^{175}Lu). The sample-spike mix was equilibrated for at least 24 h and pre-concentrated and purified with the commercially available *seaFAST* system (Elemental Scientific Inc.) according to a method modified from Hathorne et al. (2012). The system was operated in offline mode. Briefly, the samples were loaded together with a buffer-solution (pH = 6.2) made of ammonia hydroxide solution (ultra-quality, Carl Roth) and glacial acetic acid (supra-quality, Carl Roth) onto a column containing a REE-complexing resin (EDTriA/IDA). The column was washed with the buffer solution and MilliQ to remove the seawater matrix and REEs were eluted from the column with 500-2000 μL of 1.5 N ultra-pure HNO_3 (Fisher Scientific optima grade) depending on the used sample volume, resulting in concentration factors of 20-40.

The pre-concentrated samples were diluted with MilliQ to volumes of 0.8-1 mL for ICP-MS analysis. Rare earth element concentrations were measured on a Thermo Finnigan *Element II* sector field inductively coupled plasma mass spectrometer (ICP-MS) at the University of Oldenburg in low-resolution mode. The ICP-MS was coupled to a Cetac *Aridus II* desolvating nebuliser system that ran with argon and nitrogen gas in order to decrease oxide formation rates. Sample introduction was achieved with a 100 μL nebuliser and a Cetac *ASX-100* autosampler. Oxide formation rates were monitored for Ba and Ce before each measurement session and were lower than 0.03%. The blank of the ICP-MS measurements was checked by analysis of 2% HNO_3 every five samples and the daily-averaged blank counts were subtracted from each sample. Total procedural blanks (n=9; made from 10-80 ml 2% HNO_3) were spiked and prepared analogous to the samples.

Procedural blanks averaged <3% of the average sample concentration (except for Tb = 3.4% and Ce = 14%) and <5% of the minimum concentration of the samples (except for La = 8.2%, Ce = 31% and Tb = 7%). The average procedural blank results are given in Table A.2. The internal error was typically <5% for all elements. The reproducibility (2σ) of the measurements between sessions was checked with multiple runs (1-2 per session) of a standard solution that contains REEs at seawater-like relative concentrations (coral standard from the Coral Sea, provided by Gideon Henderson, University of Oxford, UK) and was <7% for all elements except for Gd (7.3%) (n=6). The external reproducibility (2σ) was checked by multiple processing and analyses of the international GEOTRACES reference standards BATS (15 m, n=4; van de Flierdt et al., 2012) and SAFe (3000 m, n=9; Pahnke et al., 2012 (Nd concentration only)) and was <9% for all elements except for Ce (66 %) and Gd (10.8%). Detailed results are given in Table A.2. The average measured REE concentrations are in good agreement with published values (deviation of <5% for all elements for BATS, van de Flierdt et al., 2012; 5.4% for SAFe (Nd), Pahnke et al., 2012). Analyses of three independently processed duplicate samples agreed within analytical uncertainty (Fig. 2; Tab. A.2).

2.4 Radium sampling and analysis

Seawater samples for radium isotope activity analyses were taken concurrently with REE samples during the GEOTRACES process study cruise KM1107 on *R/V Kilo Moana* around the island of Oahu and at ALOHA in February 2011 (Fig. 1b; Tab. A.1). Furthermore, radium isotopes were also analysed in Wailupe Springs in samples collected concurrently with the Nd isotope samples as described above.

The ocean sample volumes were ~100 L and the spring samples were 5 and 13 L. All samples were filtered through a MnO₂-coated acrylic fibre at flow rates below 1 L/min. The fibres were then ashed and packed into tin containers for analysis on an Ortec GEM40 coaxial gamma-spectrometer at the University of Hawaii. Radium-226 was analysed via its decay product Bi-214 at 609 keV and ²²⁸Ra via ²²⁸Ac at 911 keV (Dulaiova and Burnett, 2004).

3. Results

Detailed results are listed in Tables A.1-A.3 in Appendix A and on Pangaea
(www.pangaea.de) under doi: 10.1594/PANGAEA.855127.

3.1 Hydrography

Surface and subsurface waters within the upper ~200 m at the coastal stations and at ALOHA have salinity and density properties characteristic of North Pacific Tropical Water (NPTW; salinity >34.9; $\sigma_\theta = 23\text{-}25 \text{ kg/m}^3$; Cannon, 1966; Suga et al., 2000) (Fig. 1c; Tab. 1). North Pacific Intermediate Water (NPIW) at ALOHA is present between ~500 m and 1200 m water depth ($\sigma_\theta = 26.6\text{-}27.4$; e.g., Yasuda, 2004), while its characteristic salinity minimum (34.0-34.3; e.g., Talley, 1993; You et al., 2000; You, 2003; Yasuda, 2004) is centred at ~570 m (Fig. 2a). At station Transect #1, NPIW is found at ~400-1200 m water depth, with the salinity minimum centred at ~350 m, above the oxygen minimum at 750 m (Fig. 2b). The circulation of NPIW follows the gyre circulation and extends to about 20° N in the central North Pacific (e.g., Talley, 1993; You et al., 2000) (Fig. 1a). The water column between NPTW and NPIW may be either a mixture of both or is influenced by North Pacific Subtropical Mode Water (NPSTMW; $\sigma_\theta = 25.2 \text{ kg/m}^3$, salinity = 34.7-34.9; e.g., Suga et al., 1989; Talley et al., 2011) and/or Eastern North Pacific Central Water (ENPCW; $\sigma_\theta = 26.0 \text{ kg/m}^3$; Talley et al., 2011). The $\sigma_\theta = 27.0 \text{ kg/m}^3$ density surface that separates old (lower) and new (upper) NPIW (Yasuda, 2004), is located at ~660 m depth, thus separating samples taken at 500 m and 750 m at ALOHA. The oxygen minimum is centred at ~750 m depth ($\sigma_\theta = 27.2 \text{ kg/m}^3$) within the lower NPIW layer (Fig. 2a). Influence of North Equatorial Pacific Intermediate Water (NEqPIW) at ALOHA, characterised by an oxygen minimum north of the equator and a higher salinity (34.5-34.6) than NPIW (Bostock et al., 2010) may also contribute to the oxygen minimum in the lower NPIW layer. Bostock et al. (2010) show that the Hawaiian Islands lie within the mixing zone of NPIW and NEqPIW.

North Pacific Deep Water (NPDW; salinity >34.6, $\sigma_\theta > 27.6 \text{ kg/m}^3$; e.g., Talley, 2008; Talley et al., 2011) can only be identified at Station ALOHA, where its characteristic properties cover water depths below ~1900 m (Fig. 1c, Tab. 1), comprising the four deepest samples of cruise KM1107 (1979-4644 m water depth). The hydrography at ALOHA does not allow for a clear identification of Upper

Circumpolar Deep Water (UCDW) that is centred at ~1000 m water depth in the North Pacific, sandwiched between NPIW and NPDW (Talley et al., 2011) and mixes with NPDW close to Hawaii, forming modified NPDW (Kawabe and Fujio, 2010). The typical salinity and temperature values and high oxygen concentrations of Lower CDW (LCDW) (e.g. Wijffels et al., 1996; Orsi, 1999; Talley et al., 2011) are not reached in the lowermost samples at ALOHA, suggesting the absence of LCDW and the extension of NPDW to the bottom at this location.

3.2 Dissolved neodymium isotope composition

The dissolved neodymium isotope composition at the stations around Oahu and at ALOHA ranges from -4.2 to +1.4 (Figs. 2,3,4, Tab. 1). Three significantly less radiogenic values ($\epsilon_{Nd} \leq -5.2$) are considered to be subject to contamination (Tab. A.1). The negative ϵ_{Nd} at 51 m water depth at Kahuku Point is not paralleled by anomalous REE concentrations or REE pattern, which indicates a contamination of the ϵ_{Nd} sample (Fig. 5d). Since REE and ϵ_{Nd} samples were taken separately during cruise KM1107 (see Section 2), it is likely that the ϵ_{Nd} sample was contaminated during sampling or processing, while the REE sample was not. For the other two samples (25 m from July 2012 and 5 m from June 2013) the REE sample is a subsample from the Nd isotope sample and thus potentially both ϵ_{Nd} and REE aliquots are contaminated (Fig. 4).

The coastal sites have the most radiogenic ϵ_{Nd} of -1 to +1.4 within the upper 50 m of the water column, with the highest surface values found at stations Waimea ($\epsilon_{Nd} = +1.4$) and Kahuku Point ($\epsilon_{Nd} = +1.3$). All surface values decrease by 1-1.5 ϵ_{Nd} units towards ~30 m water depth (Fig. 3). At stations Makaha, Pearl Harbor, and Waimea, this is followed by a shift towards more positive values at ~50 m depth. Below 50 m, we find gradually decreasing ϵ_{Nd} signatures that reach -0.5 to -2.8 at 100-150 m depth and least radiogenic values of ≤ -3 below 150 m depth at stations Makaha and Pearl Harbor.

Groundwater samples from Wailupe Spring (southeast coast of Oahu) have ϵ_{Nd} values of +0.6 at 0.8 m sediment depth and +1.3 at 1.4 m sediment depth, similar to the coastal surface waters.

Similar to the coastal sites, ϵ_{Nd} at station Transect #1, some 15 km off the coast of Oahu, is most radiogenic ($\epsilon_{Nd} = -0.7$ to -0.9) within the upper 50 m, although these

values are slightly less radiogenic than those at more coastal sites at corresponding depths (Fig. 2b, 3). At 250-350 m, ϵ_{Nd} decreases to ~ -3.3 at Transect #1 followed by an increase to constant ϵ_{Nd} of about -2.2 from 500 m depth to the bottom (1345 m).

At Station ALOHA, we observe a seasonal variability of the isotope composition within the upper 250 m of the water column (Fig. 4, Tab. 1). The largest differences are found within the upper 100 m, where ϵ_{Nd} ranges from +0.8 in February 2011 to -2.0 in June 2013. We observe a general trend of decreasing ϵ_{Nd} values with depth between the surface and 250 m. Below, the signatures show increasing conformity, being indistinguishable at 500 m and 750 m depth, the depth range of NPIW. The only full water column profile from February 2011 shows a gradual ϵ_{Nd} decrease in deep waters starting from -2.3 at ~ 1000 m towards -3.8 ± 0.2 (mean and standard deviation of the replicate samples) close to the bottom (Fig. 2a).

3.3 Rare earth element concentrations and patterns

In the following description of the REE concentrations, we will use Nd as a representative for LREE concentrations and Er for the HREEs. Middle REEs (MREE) have an intermediate behaviour and are not described in detail. Three samples are excluded from the discussion due to potential contamination (Tab. A.2; crosses in the figures). Contamination in two of these samples, expressed by anomalously high Nd, Pr, and Dy values (25 m from July 2012 and 5 m from June 2013), is also observed in ϵ_{Nd} (see section 3.2). In the sample from 100 m at Transect #1, the LREE subsurface maximum is only supported by one data point without corresponding ϵ_{Nd} change (Fig. 3e) and is therefore not thought to be a natural feature but the result of contamination of the REE aliquot during sampling or processing.

Coastal waters are characterised by elevated REE concentrations (~ 5 -8 pmol Nd/kg; ~ 1.6 -2.1 pmol Er/kg) in the upper 50 m compared to 100-200 m water depth, with highest surface concentrations at Waimea and Kahuku Point (>6 pmol Nd/kg; >1.8 pmol Er/kg) (Figs. 3, 6, Tab. A.2). Subsurface (50 m) maxima are present at Pearl Harbor and Makaha (~ 5.7 pmol Nd/kg; ~ 1.6 -1.8 pmol Er/kg). Coastal waters below 200 m, only sampled at station Makaha, show a rapid REE increase towards the bottom. At stations Transect #1 and ALOHA, surface REE concentrations are similar to the coastal waters at Makaha and Pearl Harbor, but clearly depleted compared to Waimea and Kahuku Point. They are rather constant within the upper 250 m of the

water column and increase below that depth. At ALOHA, subsurface maxima in REE concentrations are found at 25 m in August 2012 (potential contamination in July 2012), while they are absent in June (25 m was not sampled in February) (Fig. 6). Surface LREE and MREE maxima are found in February (5.6 pmol Nd/kg in February vs. 4.6-4.9 pmol Nd/kg in July and August). Below 250 m, we observe a typical nutrient-type profile with increasing concentrations towards the bottom for all REEs except for Ce, which also increases with depth below 500 m but varies within the analytical uncertainty (Tab. A.2).

Rare earth elements normalised to Post-Archean Australian Sedimentary rock (PAAS) concentrations (Taylor and McLennan, 1985) of stations ALOHA (cruise KM1107, February 2011), Transect #1, and coastal sites are shown in Fig. 5. REE patterns ≥ 500 m water depth (ALOHA and Transect #1) show a pronounced HREE over LREE enrichment typical for seawater, which is also visualised by PAAS-normalised Nd/Er ratios $((\text{Nd/Er})_N$, in the following referred to as Nd/Er) in Fig. 7a. Samples from the upper 250 m of the coastal sites and the open ocean station, show a flatter PAAS-normalised pattern (higher Nd/Er) and a slight depletion of the heaviest REEs (Tm, Yb, Lu) compared to their precursor Er (Fig. 5). REE patterns at 250 to 350 m water depth mark a transition between surface and deep waters. The HREE over LREE enrichment is lower in surface waters above ~ 200 m (high Nd/Er), and also decreases (increasing Nd/Er) in the deep samples at ≥ 3000 m (Fig. 7a). The surface depletion of the heaviest REEs Tm, Yb, and Lu, visualised by PAAS-normalised Er/Lu ratios $((\text{Er/Lu})_N$, in the following referred to as Er/Lu) and also clearly seen in the REE patterns in Fig. 5, is a feature of surface samples and vanishes with increasing depth (Fig. 7b). Similarly, MREE anomalies $([\text{MREE/MREE}^*]_N = [2 \cdot (\text{Gd} + \text{Tb} + \text{Dy})_N / (\text{La} + \text{Pr} + \text{Nd} + \text{Tm} + \text{Yb} + \text{Lu})_N]$; Martin et al., 2010) are elevated in surface waters and rapidly decrease within the upper 500 m (Fig. 7d; Tab. A.2).

We observe a consistent increase of Ce anomalies with increasing depth (Tab. A.2). However, measurements of Ce are subject to high errors, which are potentially caused by high and variable blank contributions and low initial Ce concentrations (Tab. A.2 and section 2), precluding the detailed discussion of Ce data. Europium anomalies (calculated using Tb instead of Gd as $[\text{Eu/Eu}^*]_N = [3 \cdot \text{Eu}_N / (2 \cdot \text{Sm}_N + \text{Tb}_N)]$, to account for potential anomalies of Gd in seawater; e.g., Zhang et al., 2008) are higher in some surface and subsurface samples than at depth and show an overall range of 1.0 to 1.48, with highest anomalies at stations Waimea and Kahuku Point

(>1.4) (Fig. 7c; Tab. A.2). Gadolinium anomalies ($[\text{Gd}/\text{Gd}^*]_{\text{N}} = [\text{Gd}_{\text{N}}/(\text{Sm}_{\text{N}}*0.33+\text{Tb}_{\text{N}}*0.67)]$, Bau and Dulski, 1996) in coastal waters and at ALOHA range from 1.2 to 1.4 and are only slightly increased to >1.4 at 10-50 m depth at station Pearl Harbor (Tab. A.2).

3.4 Colloidal REEs

We use the dissolved and ultra-filtrated permeate and retentate samples of cruise KM1316 (0 m, 130 m, 1000 m water depth at ALOHA) to distinguish between truly dissolved (i.e., soluble, s_{REE}) and colloidal REE fractions (c_{REE}), the sum of which make up the dissolved REE (d_{REE}) pool (e.g., Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz, 1992; Rousseau et al., 2015). Given the analytical uncertainty of 4-9% (except for Gd: 10.8% and Ce: 66%, 2σ SD), derived from the routine analysis of standards of the same concentration as the samples (section 2.3 and Tab. A.2), the three fractions, $\text{REE}_{\text{dissolved}}$, $\text{REE}_{\text{retentate}}$ and $\text{REE}_{\text{permeate}}$, are identical (Tab. A.3). Using a concentration factor of 2 and a calculation of c_{REE} concentrations as described above in section 2, then, there is no significantly measurable colloidal fraction for any of the REEs in Station ALOHA seawater, and the similar concentrations in each fraction are explained by the presence of soluble-sized REEs in each fraction. The REE recovery through the cross flow filtration system is >95% for the 0 m and 130 m samples and >88% for the 1000 m sample.

3.5 Radium isotopes

Due to terrestrial influences (streams, SGD, and diffusion from sediments), all samples collected had detectable ^{228}Ra (8-22 dpm/m³). Except for stations Pearl Harbor and Makaha, all stations also had elevated ^{226}Ra (87-98 dpm/m³) over the established 80 dpm/m³ for offshore northwest Pacific Ocean seawater (e.g., Broecker et al., 1967). The nearshore springs were slightly depleted in ^{226}Ra (40 and 47 dpm/m³) and enriched in ^{228}Ra (19 and 53 dpm/m³) compared to expected offshore activities (Tab. A.1).

Radium patterns agree very well with the REE signature in that all stations were enriched and Waimea and Kahuku Point samples had the highest surface water ^{226}Ra and ^{228}Ra . At Station ALOHA and Transect #1, the radium depth profile reached down to 500 m, and ^{226}Ra activities increased at 500 m depth at both stations as

expected for a Pacific Ocean profile. ^{228}Ra was present at both stations and persisted down to 500 m, although at Station ALOHA its activity significantly decreased at depth (Fig. 2).

4. Discussion

4.1 Hawaiian imprint on surface and subsurface waters at the coastal sites and at ALOHA in February 2011 (KM1107)

Surface waters at the coastal sites, Transect #1, and ALOHA show REE patterns that are different from typical seawater patterns (e.g., ALOHA deep water; Fig. 5). All surface samples show elevated PAAS-normalised Nd/Er and Er/Lu ratios that are indicative of lithogenic input (e.g., Bertram and Elderfield, 1993; Hongo et al., 2006; Zhang et al., 2008; Jeandel et al., 2013; Pearce et al., 2013) (Fig. 7). Radiogenic ϵ_{Nd} signatures and the occurrence of positive Eu anomalies (Eu/Eu^*) and MREE enrichment ($\text{MREE}/\text{MREE}^*$) are characteristic of Hawaiian basaltic material (e.g., Tanaka et al., 2008; Ren et al., 2009) (Fig. 5f), suggesting that the lithogenic signature in coastal waters as well as at Transect #1 and ALOHA is derived from the Hawaiian Islands. High surface Er/Lu ratios and similar Er/Lu profiles as Nd/Er, Eu/Eu^* , and $\text{MREE}/\text{MREE}^*$ (Fig. 7), suggest that Er/Lu also reflects lithogenic input. This confirms the assumption of Hongo et al. (2006), who suggested that high Er/Lu ratios may develop during weathering of source material similar to what has been observed for MREE enrichment in an experimental study by Hannigan and Sholkovitz (2001).

The upper 100 m of the water column at ALOHA have much more positive ϵ_{Nd} ($\epsilon_{\text{Nd}} = -1.4$ to 0.8) than surface waters at other open ocean stations in the central North Pacific ($\epsilon_{\text{Nd}} = -5.4$ to -1.8 , Piepgras and Jacobsen, 1988; Amakawa et al., 2009; Zimmermann et al., 2009, Pahnke et al., 2012) and are similar to those at our coastal sites (Figs. 3, 8a). Similar surface ϵ_{Nd} was also observed by Vance et al. (2004) near the Hawaiian Islands and at ALOHA. Surface [Nd] (4.6 – 5.6 pmol/kg) is similar to published Nd concentrations from the region (Fig. 8b; Greaves et al., 1999; compilation in Hongo et al., 2006) and to the surface [Nd] at Pearl Harbor, Makaha, and Transect #1 (Fig. 3). The most radiogenic surface ϵ_{Nd} values at Waimea and Kahuku Point ($1.3 < \epsilon_{\text{Nd}} < 1.4$) are accompanied by highest REE and ^{228}Ra concentrations and most positive Eu ($\text{Eu}/\text{Eu}^* > 1.4$) and MREE anomalies, providing evidence for increased input from Oahu through rivers near these sites (Figs. 3, 6, 7).

It is consistent with the spatial heterogeneity of precipitation and surface runoff on Oahu (Oki, 2003; Giambelluca et al., 2013), as rivers originating from the Ko'olau Range drain into the coastal ocean near these sites. SGD is another important source for REEs to the coastal ocean (e.g., Johannesson and Burdige 2007; Johannesson et al., 2011; Kim and Kim, 2011; 2014) and has been shown to equal or exceed river volumetric discharge and river nutrient input on both the windward and leeward sides of Oahu (Moosdorf et al., 2015; Garrison et al., 2003; Kelly et al., 2013), suggesting that SGD is an important contributor of REE along the shoreline of Oahu.

Positive Eu anomalies of the same magnitude as observed here were reported in seawater near Papua New Guinea and the Kerguelen Plateau and attributed to a basaltic (submarine) source (Zhang et al., 2008; Grenier et al., 2013). The linear correlation of our ϵ_{Nd} and Eu/Eu* ($R^2 = 0.65$, excluding three outliers) supports a similar source of these signals. Samples from Wailupe Spring (southeast coast of Oahu; Fig. 1b) have an isotope composition of +0.6 to +1.3, similar to the coastal waters, confirming the Hawaiian source of the radiogenic signal in coastal waters and at ALOHA. Groundwater and coastal surface water ϵ_{Nd} signatures are less positive than the Hawaiian basaltic bedrock (average ϵ_{Nd} of +6.2; Tanaka et al., 2008), because of the influence of Asian dust ($\epsilon_{Nd} = -10.3$; Taylor et al., 1983; Goldstein et al., 1984; Nakai et al., 1993; Liu et al., 1994) that modifies the soil ϵ_{Nd} signature (Kurtz et al., 2001), and the mixture with open ocean water near the coast (Fig. 1c). Groundwater ϵ_{Nd} may also be subject to seawater admixture (salinity of 1-6 in the spring samples) and modified towards less radiogenic ϵ_{Nd} values by the presence of calcareous reef rocks at the southeast coast of Oahu.

Normalisation of our surface water REE data to those from an open ocean North Pacific station that is thought to be unaffected by lithogenic input (177° E, 24° N, see Fig. 1a; Greaves et al., 1999) further visualises the clear Hawaiian imprint on coastal waters and ALOHA during February by showing a pronounced Eu anomaly and MREE enrichment (Fig. 9), with most pronounced signals at Waimea and Kahuku Point. These anomalies, however, are absent or attenuated at ALOHA in July and August. Middle REE enrichments have been proposed to result from input of REEs from weathered phosphate minerals through river water (Sholkovitz et al., 1999; Hannigan and Sholkovitz, 2001), dissolution of oxy-hydroxides in pore waters (Haley et al., 2004), discharge of MREE-enriched groundwater (Kim and Kim, 2011; 2014)

or submarine weathering of basaltic particles (Grenier et al., 2013). The latter is consistent with the influence of Hawaiian basalts on surface waters around Oahu and at ALOHA, suggested based on positive ϵ_{Nd} and Eu/Eu^* (Figs. 3, 7c, d). A small positive Gd anomaly ($Gd/Gd^* > 1.4$) at Pearl Harbor (Figs. 5a, 9) may be a hint for a contribution of anthropogenic Gd (Bau and Dulski, 1996) from the urban area around Honolulu, thus providing additional evidence for Hawaiian input.

Elevated surface ^{228}Ra activities at ALOHA, indicating recent terrestrial freshwater and sediment input, further support local Hawaiian influence as far offshore as station ALOHA (Fig. 2a, Tab. A.1). Radium-226 activity at ALOHA is uniform between 0-250 m and increases at 500 m at the depth of NPIW. The $^{228}Ra/^{226}Ra$ activity ratios therefore decrease from 0.25 at the surface to 0.09 at depth at ALOHA, indicating decreasing local Hawaiian influence and increasing contribution of NPIW with depth. At Transect #1, the ^{228}Ra profile is uniform down to 500 m, except for a small excursion to higher activity at 100 m, which coincides with a similar excursion in the [Nd] signature (Fig. 2b). The ^{228}Ra 0-500 m inventory at Transect #1 was 9450 dpm/m² and at ALOHA 7590 dpm/m², reflecting the proximity of Transect #1 to Oahu and dilution of water masses by mixing and decay at Station ALOHA. Nevertheless, the elevated ^{228}Ra inventory at Station ALOHA is a clear indicator of a strong terrestrial contribution. Due to the fact that Oahu is probably not the only island contributing the terrestrial signature, it is difficult to quantify the terrestrial radium contribution to Station ALOHA.

At subsurface depths (>180 m – 350 m), similar ϵ_{Nd} of -3.8 to -3.0 at ALOHA, Transect #1, Makaha, and Pearl Harbor (only sites covering these depths) suggests the presence of a uniform water mass (Fig. 3). This unradiogenic signature is identical to that at North Pacific open ocean stations from intermediate depth (Vance et al., 2004; Amakawa et al., 2009; Zimmermann et al., 2009; Pahnke et al., 2012) (Figs. 3, 8), suggesting a North Pacific-wide extent of this subsurface water mass rather than a local Nd imprint. Hydrographic properties do not allow for a characterisation of this water (NPSTMW, ENPCW, or NPIW), but the salinity decreases rapidly towards the characteristic salinity minimum of NPIW (Fig. 2) and the ϵ_{Nd} signatures are identical to those of NPIW elsewhere (e.g., Amakawa et al., 2009), suggesting that the unradiogenic ϵ_{Nd} at this depth represents NPIW. Rare earth element patterns rapidly lose the characteristic surface features (high Nd/Er and Er/Lu ratios, positive Eu and MREE anomalies) and evolve towards the typical seawater pattern (Figs. 5b, 7). This

suggests that Hawaiian input controls both REE concentrations and ϵ_{Nd} of the surface waters, but that subsurface waters are unaffected by local overprints. The isotope results further show that there is no radiogenic ϵ_{Nd} imprint from bottom sediments on the deepest waters at each station (20-40 m above the seafloor) (Tab. 1). Abbott et al. (2015a,b) showed significant influence of benthic REE flux from sediment pore fluids on the bottom water ϵ_{Nd} signature several hundreds of metres above the seafloor and suggested that the diffusive flux of pore water REE are a major REE source to the ocean. We do not find any evidence for this flux at our study sites based on the Nd isotope signature (Fig. 3) and REE patterns (Fig. 5) at stations above the Hawaiian shelf. This suggests that pore water REE contributions to bottom waters need to be investigated on a regional basis. For the Hawaiian region it is obvious that surface processes are more important for controlling the REE budget and Nd isotope signature than sedimentary pore water fluxes.

4.2 The intermediate and deep water column at Station ALOHA

4.2.1 Intermediate waters

The most negative ϵ_{Nd} values ($\epsilon_{Nd} = -3.3$ to -3.8) at intermediate depth at ALOHA are found at or just above the salinity minimum, which corresponds to the upper NPIW layer and is similar to the ϵ_{Nd} signature of NPIW in the central North Pacific and close to its formation region (Piepgras and Jacobsen, 1988; Vance et al., 2004; Amakawa et al., 2004; 2009; Pahnke et al., 2012). The waters below the salinity minimum, through the oxygen minimum of lower NPIW at ~800 m water depth, are marked by an ϵ_{Nd} increase towards maximum values of -2.3 to -2.8 at ~750-1500 m water depth and rather constant Nd concentrations of 17.7-22 pmol/kg (Figs. 2a, 8). Even at a depth of ~2000 m, the isotope signatures at ALOHA are still more radiogenic ($\epsilon_{Nd} = -2.7$) than expected from typical NPDW ($\epsilon_{Nd} = -3.9 \pm 0.7$, Amakawa et al., 2009, calculated from 26 data points from 1500-4000 m depth from Amakawa et al., 2009, Piepgras and Jacobsen, 1988, and Amakawa et al., 2004). Based on the presence of a similar feature at other sites in the North Pacific (Piepgras and Jacobsen, 1988; Zimmermann et al., 2009; Pahnke et al., 2012; Figs. 1a, 8a), we suggest that it may represent the presence of modified NEqPIW or UCDW. However, previous studies suggested input from the nearby Loihi seamount (18.55° N, 156.15° W) to explain high Fe concentrations at 1000-15000 m water depth at ALOHA (Boyle et al.,

2005; Fitzsimmons et al., 2015) and we will therefore discuss this and the possibility of margin and hydrothermal exchange first.

Loihi basalts have a very radiogenic isotope signature of $\epsilon_{\text{Nd}} = +6.0$ (cf. compilation in Tanaka et al., 2008) and may therefore influence the isotope signature as suggested for seawater from above the East Pacific Rise which was suggested to be subject to ridge exchange processes (Jeandel et al., 2013). However, Stichel et al. (2012b) showed the very limited (if any) influence of hydrothermal fluids on dissolved ϵ_{Nd} within the hydrothermal plume at the Mid Atlantic Ridge (TAG hydrothermal vent). This is in line with other studies that do not consider hydrothermal activity to change seawater ϵ_{Nd} (e.g., German et al., 1990; Halliday et al., 1992). Additionally, Basak et al. (2015) observed influence of the East Pacific Rise on seawater ϵ_{Nd} only at one station directly above the ridge and suggested boundary exchange processes for this, while the remaining sites showed pure seawater signatures, pointing towards very limited spatial extent of hydrothermal or ridge exchange processes. We would further expect increased Eu/Eu* if hydrothermal fluids determine the seawater ϵ_{Nd} composition in intermediate waters, which is not observed (Fig. 7c). Thus, the hydrothermal influence from Loihi seamount is an unlikely candidate to explain the positive ϵ_{Nd} .

We further exclude the possibility of boundary exchange at the Hawaiian margin (bulk sediment $\epsilon_{\text{Nd}} = +5.6$; Vance et al., 2004) due to the lack of basaltic REE signals, especially positive Eu anomalies, seen in surface waters at our sites and in subsurface waters influenced by basaltic margins elsewhere (Zhang et al., 2008; Grenier et al., 2013). Moreover, the lack of a radiogenic ϵ_{Nd} signal in the deepest coastal samples (Figs. 3a-d, section 4.1) also argues against boundary exchange to explain the positive ϵ_{Nd} at mid-depth.

The presence of a water mass with positive ϵ_{Nd} is supported by a slower [Nd] increase at these depths compared to waters above and below (Fig. 8b), as previously observed in the North Atlantic at the depth of strong lateral advection (Stichel et al., 2015). The positive ϵ_{Nd} excursion is centred at a potential density of 27.4 to 27.5 at all sites, hence below NPIW and in the density range of UCDW (~27.7 in the tropical West Pacific; Grenier et al., 2013) and NEqPIW (~27.3; Bostock et al., 2010). Since the hydrography at ALOHA does not allow for a clear classification of the mid-depth water, both NEqPIW and UCDW could influence these depths. For NEqPIW, present at 700-1000 m in the equatorial Pacific (Bostock et al., 2010), there is no information

on its Nd isotope signature from the open ocean Pacific north of the equator (cf. compilation of Lacan et al., 2012). Yet, modified Antarctic Intermediate Water (AAIW), one of the precursors of NEqPIW (Bostock et al., 2010), carries an ϵ_{Nd} signature of -2.1 to -3.4 in the central Pacific at 140° W close to the equator (Lacan and Jeandel, 2001). Potential further modification of AAIW/NEqPIW in the equatorial East Pacific by radiogenic Nd from the shelf (Grasse et al., 2012) may contribute to a positive ϵ_{Nd} signature of NEqPIW that reaches the Hawaiian Islands and mixes there with NPIW (Bostock et al., 2010). Upper CDW, centred at ~1000 m in the North Pacific (e.g., Talley et al., 2011), is modified in its ϵ_{Nd} in the tropical West Pacific through exchange with margin sediments from an original $\epsilon_{\text{Nd}} = \sim -8$ near its source (e.g., Basak et al., 2015) to values as radiogenic as -0.7 (Grenier et al., 2013). Modified UCDW is transported towards the central North Pacific, where it mixes with NPDW (Kawabe and Fujio, 2010) (Fig. 1a) and is therefore another possible candidate for the positive mid-depth ϵ_{Nd} in the North Pacific.

4.2.2 Deep waters

At Station ALOHA, the average ϵ_{Nd} of NPDW (1979-4644 m) of -3.3 ± 0.5 is similar to the typical average NPDW value of $\epsilon_{\text{Nd}} = -3.9 \pm 0.7$ (-3 to -5) suggested by Amakawa et al. (2009). Using available data from central and northeast Pacific stations between 20° and 30° N (BO-3, Amakawa et al., 2009; TPS24-76-1, Piepgras and Jacobsen, 1988; SAFe, Pahnke et al., 2012; ALOHA, this study: see Fig. 1a for locations) from water depths below 1900 m, we calculate a new average ϵ_{Nd} for NPDW of -3.5 ± 0.5 (n=15) and an average Nd concentration of 44.4 ± 10 pmol/kg (n=16) in this region (we excluded the lowermost sample of BO-3, due to influence from bottom sediments as stated by Amakawa et al., 2009). This new value excludes stations from the Northwest Pacific that lack the contribution of upwelled UCDW/LCDW and therefore do not represent the deep water that ultimately travels to the Southern Ocean to mix with other water masses. Since the central North Pacific is the region from where modified NPDW starts its way to the Southern Ocean (Kawabe and Fujio, 2010), the new ϵ_{Nd} and [Nd] values seem to be a good approximation of the endmember composition of NPDW in mixing calculations of modern and past Circumpolar Deep Water.

Lower CDW cannot be identified at Station ALOHA based on hydrographic properties (section 3.1). Similarly, the ϵ_{Nd} of the deep water does not indicate the presence of LCDW with a typical signature of $\epsilon_{Nd} = -8$ near its source (e.g., Basak et al., 2015), as this should shift the isotope signature towards less radiogenic values at ALOHA, as observed at station BO-5 west of Hawaii (Amakawa et al., 2009). The absence of LCDW influence in the bottom samples confirms previous conclusions that LCDW (or Antarctic Bottom Water) is less present in the eastern and central North Pacific (Piepgras and Jacobsen, 1988; Amakawa et al., 2009), in line with the main travel path of LCDW in the West Pacific (Kawabe and Fujio, 2010).

4.2.3 Vertical vs. lateral control on deep water REE concentrations

The REE pattern of ALOHA bottom water (4644 m) normalised to the widely used reference NPDW (~2500 m water depth; Alibo and Nozaki, 1999; Ref. NPDW in Figs. 1 and 10) is highly enriched in LREEs (Fig. 10a), representing the typically observed higher proportional increase of LREEs compared to HREEs with increasing depth through preferential LREE regeneration from particles or bottom sediments (e.g., Elderfield and Greaves, 1982; Sholkovitz et al., 1994). The same is illustrated in the increase of Nd/Er ratios towards the bottom at Station ALOHA (Fig. 7a). The ϵ_{Nd} and [REE] of our deepest samples do not point towards REE release from bottom sediments at ALOHA, as we do not observe a significant increase in concentrations in the lowermost samples and only a small decrease in ϵ_{Nd} , which matches typical NPDW values (Fig. 8; section 4.2.2). We point out, however, that our deepest sample was taken 105 m above the seafloor, where any potential bottom influence may have been mixed away already. The results show that porewater fluxes as observed on the Oregon margin, which influence the [REE] and ϵ_{Nd} of the water column several hundreds of metres above the seafloor (Abbott et al., 2015a,b), do not contribute to the signals at ALOHA and the Oahu coastal sites of this study (see section 4.1).

Based on REE concentrations in the South Pacific, Molina-Kescher et al. (2014) recently proposed that a pattern of LREE enrichment in deep waters when normalised to the reference NPDW of Alibo and Nozaki (1999) is a characteristic feature of LCDW. However, the deep water at ALOHA (this study) as well as deep water in the North Pacific as far north as 44.67° N (Station DE-4, 177° W, 4500 m, Shimizu et al., 1994) and in the eastern North Pacific (Station TPS24-76-1, 24.3° N, 142° W, 4621

m, Piepgras and Jacobsen, 1992), which are not or only very slightly influenced by LCDW, show a similar LREE enrichment as the stations of Molina-Kescher et al. (2014) in the South Pacific when normalised to the reference NPDW (Fig. 10a). Furthermore, the REE patterns from the deep North Pacific show no attenuation of the LREE enrichment relative to the site in the South Pacific (Fig. 10b), which would be expected as a result of increasing mixing with NPDW towards the north. The similarity of REE patterns from the North Pacific to those of LCDW in the South Pacific is further visualised by normalisation of the North Pacific deep water REE to LCDW (Station 66, 5155 m depth of Molina-Kescher et al., 2014) (Fig. 10b). The patterns of all deep stations are flat, except for a positive Eu anomaly. We thus suggest that the LREE enrichment in our bottom sample is a typical feature of deep waters from the North and South Pacific and is a function of depth and water mass age (overall REE concentrations are highest in the North Pacific, Fig. 10b) rather than related to the presence of LCDW. This observation indicates that deep water REE patterns are largely controlled by vertical processes and thus are a function of water depth and water mass age rather than of specific water masses (see also Osborne et al., 2015), suggesting they cannot be used to trace water masses in the deep North Pacific. This is in contrast to the suggestion of Alibo and Nozaki (2004) that characteristic LREE- and Gd-depleted NPDW-normalised REE patterns in the deep eastern Indian Ocean can be used to trace the southward flow of deep waters. In the North Pacific, a vertical control is further supported by distinct positive Eu anomalies in the LCDW-normalised patterns and reflect REE release from particles at depth.

4.3 Seasonal variability at Station ALOHA

As discussed in section 4.1, contributions from the Hawaiian Islands clearly determine the surface ϵ_{Nd} and REE signatures at ALOHA during February 2011. Comparison of ϵ_{Nd} and Nd concentrations from water column profiles sampled at ALOHA during June, July, and August suggest seasonal changes within the upper 400 m (Fig. 4). There are two possible explanations for the observed seasonality of ϵ_{Nd} in surface waters at ALOHA: 1) variable dust input from Asia to the central North Pacific ($\epsilon_{Nd} = -10.3$; Taylor et al., 1983; Goldstein et al., 1984; Nakai et al., 1993; Liu et al., 1994) with highest deposition during dust outbreak events in spring-early summer (e.g., Duce et al., 1980; Parrington et al., 1983; Uematsu et al., 1985;

Prospero et al., 1989) and 2) variable contributions from Hawaii that are subject to seasonal variations in precipitation and runoff (higher in winter, Oki, 2003; Giambelluca et al., 2013).

Variable Fe and Th isotope concentrations measured at ALOHA are highest during spring and have been attributed to the seasonal deposition of Asian dust (Johnson et al., 2003; Boyle et al., 2005; Fitzsimmons et al., 2015; Hayes et al., 2015). The less radiogenic ϵ_{Nd} signature and absent Eu anomaly in surface waters at ALOHA during summer (July and August, $\epsilon_{Nd} = -1.4$ to -0.6) compared to February ($\epsilon_{Nd} = +0.8$, $Eu/Eu^* = 1.3$), may suggest increased dust influence in summer or reduced Hawaiian influence due to reduced freshwater discharge (Figs. 4a, 7c, 9). Rare earth element concentrations are relatively constant in the upper 200 m with a slight LREE minimum observed during all months within and below the deep chlorophyll maximum (DCM, at ~130 m), potentially due to enhanced scavenging of REEs by organic particles there (Fig. 6; see also Stichel et al., 2015). During the summer months, we observe a maximum at subsurface depth (25 - 75 m), which is also seen in Th concentrations and has been attributed to particle cycling (Hayes et al., 2015). Below ~200 m, the REE concentrations increase gradually and are similar throughout the investigated months.

With a simple calculation we can test if dust dissolution could influence [Nd] and ϵ_{Nd} at ALOHA. We assume an average Nd concentration of approximately 30 ppm for Chinese loess (Taylor et al., 1983; Goldstein et al., 1984; Liu et al., 1993; Nakai et al., 1993) and a measured annual dust deposition rate of $0.43 \text{ g/m}^2\text{yr}^1$ at Oahu (Uematsu et al., 1985) of which 80% is deposited during the dust season between February and June (Parrington et al., 1983). Given the wide range of the estimated REE dissolution fraction from dust of 1-20% (Greaves et al., 1994; Tachikawa et al., 1999) we use a fraction of 10% Nd dissolved from dust. This implies a release of $7155 \text{ pmol Nd/m}^2\text{yr}^1$ during the dust season to the sea surface. We apply this rate to the upper 5 m of the water column (i.e., the depth of our surface water sample) instead of the mixed layer depth (~30 m; Tab. 1), since our data and those of Stichel et al. (2015) show that ϵ_{Nd} and [Nd] strongly vary within the mixed layer, suggesting a dust influence mainly on the surface layer. This leads to an estimated addition of 1.43 pmol Nd/kg to seawater, which is ~35% of the [Nd] signal at the DCM concentration minimum (~4 pmol/kg; used as background concentration). A mass balance calculation for this dust addition results in a surface water value of $\epsilon_{Nd} = -2.7$

(endmembers: ALOHA surface water: $\epsilon_{Nd} = 0$ and $[Nd] = 4$ pmol/kg; Asian dust: $\epsilon_{Nd} = -10.3$ and $[Nd] = 1.43$). For this approach, we assume that the surface water ϵ_{Nd} signature accumulates in the water column, which is supported by our data, while Nd is rapidly removed through scavenging. These calculations do not allow for a quantification of the dust impact at ALOHA due to uncertainties in the parameters, but they clearly show that dust has the potential to lower the isotope composition of surface waters at ALOHA during times of high input towards values that we observe during summer. The highest uncertainties in our calculation include the dissolution fraction of 1-20%, the uncertainty in the depth used for the inventory calculation, and the unknown background surface water ϵ_{Nd} and $[Nd]$ at ALOHA, which may be subject to variable contributions from Hawaii.

If dust has an effect on the ϵ_{Nd} signature in the upper water column, why do we not see increased concentrations? From previous studies, it is known that Nd is released from dust particles, which significantly enhances the surface water concentration (e.g., Greaves et al., 1999; Stichel et al., 2015). Given the proposed impact of dust on surface iron and thorium concentrations at ALOHA (Johnson et al., 2003; Boyle et al., 2005; Fitzsimmons et al., 2015; Hayes et al., 2015), and the above shown influence on the isotope composition, the lack of any changes in REE concentrations suggests that REEs are most likely too rapidly scavenged to be visible in our data. Since none of our samples were taken during a dust event, we are not able to quantify the effect of dust dissolution on REE concentrations. However, the results demonstrate that while the REEs are scavenged from the surface waters, the modified ϵ_{Nd} signal is still visible in summer i.e., a few months after the highest dust deposition rates.

The second hypothesis for variable surface ϵ_{Nd} values at ALOHA is that Hawaiian input more significantly overprints the surface water ϵ_{Nd} and REE signatures during times of higher rainfall (winter). In this case, the ϵ_{Nd} signatures would be more open ocean-like during the summer months with only little influence from Hawaii ($\epsilon_{Nd} = -2.0$ to -0.6 compared to $\epsilon_{Nd} = -4.5$ at the nearest open ocean station BO-3; Amakawa et al., 2009). We observe that the most radiogenic surface ϵ_{Nd} values in February are accompanied by slightly higher Nd concentrations than in June-August (Fig. 4), indicating increased input from Hawaii. The coastal waters were only sampled during cruise KM1107 in February 2011, precluding the direct monitoring of seasonal variability in Hawaiian input.

Our data clearly show that Station ALOHA has a more radiogenic ϵ_{Nd} signature throughout the year than open ocean stations remote from any Hawaiian influence (e.g., station BO-3 of Amakawa et al., 2009; station SAFe of Pahnke et al., 2012). This clearly demonstrates the dominance of Hawaiian influence on surface waters around Oahu and at station ALOHA. Given the clear impact of Asian dust on surface water Fe concentrations and thorium isotopes, a seasonal modification of the ϵ_{Nd} and REE by Asian dust is very likely. More detailed time-series of dissolved and, ideally, particulate ϵ_{Nd} and [REE] at ALOHA and in coastal waters would be required to better characterise these sources and their seasonal variability. Our data demonstrate that the seasonality observed in the upper water column is limited to the surface and subsurface waters. At 750 m depth, the nearly identical ϵ_{Nd} values of -2.4 to -2.8 throughout the year demonstrate the rapid loss of the seasonal differences with depth.

4.4 Colloidal vs. truly dissolved REE concentrations

Colloids are a dominant fraction of REE physicochemical speciation in river water (e.g., Goldstein and Jacobsen, 1988; Elderfield et al., 1990; Sholkovitz, 1992; 1995; Andersson et al., 2001; Rousseau et al., 2015). It has been shown that the colloidal REE fraction is largely removed from water during estuarine mixing and that the resulting colloidal-poor water shows a REE distribution similar to seawater (Sholkovitz and Elderfield, 1988; Elderfield et al., 1990; Sholkovitz, 1992; 1995; Rousseau et al., 2015). Bertine and VernonClark (1996) reported colloidal REE concentrations that make up 0.6-2% of coastal waters in Buzzards Bay, Massachusetts, and up to 6-22% if they consider the loss of 10% through retention by the membrane during filtration. Further, Rousseau et al. (2015) showed that colloidal REE make up less than 10% of the REE at seawater salinity in the Amazon estuary. To our knowledge, there are no studies available in the literature that address the presence or absence of colloidal REEs in open ocean seawater.

Neglecting our measurement uncertainty (see section 3.4), REE colloidal fractions of 0-4% ($\text{La} = 0\text{-}8\%$) are on the same order of magnitude as those reported by Bertine and VernonClark (1996). However, the fact that our measurements of the $\text{REE}_{\text{dissolved}}$, $\text{REE}_{\text{retentate}}$ and $\text{REE}_{\text{permeate}}$ fractions are identical within error is a first indication for the absence of colloidal REEs in these waters. This is in contrast to Fe and Th, which have more significant (>40% and 8-25%, respectively) colloidal fractions within the

same samples from Station ALOHA (Fitzsimmons et al., 2015; Hayes et al., 2015). The potential absence of colloidal REEs in September 2013, however, does not exclude the presence of colloidal REEs during the other seasons sampled for this study or during times of maximum dust input.

From the results obtained here, we have to assume that we are monitoring only the truly soluble fraction of REEs in our samples. If this is true during the other seasons, this implies that the dissolved REE concentrations in open ocean surface waters can be attributed entirely to REE cycling in the water column and the interaction between the truly dissolved and particulate phases.

5. Conclusions

We showed that Hawaiian coastal waters carry distinct Nd and Ra isotope and REE signals that clearly indicate a prominent lithogenic influence from the Hawaiian Islands. Increased REE surface concentrations in combinations with elevated LREE/HREE ratios and MREE anomalies reflect lithogenic input. This lithogenic influence is clearly sourced by the Hawaiian Islands as shown by radiogenic ϵ_{Nd} signatures of -1.7 to +1.4 and positive Eu anomalies in surface and subsurface waters, as well as by the presence of relatively short-lived ^{228}Ra in all surface water samples.

Dissolved Nd isotope ratios of $\epsilon_{Nd} = -2$ to $+0.8$ in surface waters at ALOHA, significantly more radiogenic than other open ocean surface waters in the central North Pacific, demonstrate that the Hawaiian Islands not only influence the surrounding coastal waters, but also Station ALOHA, located 100 km north of Oahu. The most prominent Hawaiian influence is observed in February, when Eu and MREE anomalies are similar to those in coastal waters and $\epsilon_{Nd} = +0.8$. In June, July, and August, on the other hand, Eu and MREE anomalies at ALOHA are absent, and ϵ_{Nd} is more negative ($\epsilon_{Nd} = -2, -0.6, -1.4$, respectively). Mixing calculations support the assumption that this is either due to reduced Hawaiian influence as a result of lower precipitation and runoff in summer and/or to an overprint from dust (loess) transported to ALOHA from Asia, which is marked by negative ϵ_{Nd} and no Eu and MREE anomalies. The fact that seasonally variable ϵ_{Nd} and Eu/Eu* signatures are accompanied by low absolute REE concentrations without pronounced surface maxima suggests a very rapid cycling of REEs in the upper water column.

Our deep water column ϵ_{Nd} and [REE] profiles at Station ALOHA (0-4644 m) contribute to the sparse coverage of complete water column profiles in the North Pacific. The ϵ_{Nd} of the upper intermediate (~180-500 m) and deepest layer (> 2000 m) resemble published ϵ_{Nd} signatures and Nd concentrations of NPIW and NPDW. Radiogenic ϵ_{Nd} signatures in waters at 1000-2000 m ($\epsilon_{Nd} = -2.3$ to -2.8) most likely result from influence of a radiogenic water mass, the most probable candidates being modified UCDW or NEqPIW. Using new and existing data for NPDW, we further narrow the ϵ_{Nd} and [Nd] of NPDW to $\epsilon_{Nd} = -3.5 \pm 0.5$ and $[Nd] = 44.4 \pm 10$ pmol/kg.

Results of the analysis of the colloidal and truly dissolved fractions at ALOHA indicate that there was no significant amount of colloidal REEs at 15 m (in the mixed layer), 130 m (at the DCM), and 1000 m water depth in September 2013. This does not exclude the presence of colloidal REEs during dust input events and needs further investigation. Potential future investigations should include higher-resolution time-series measurements of surface waters at ALOHA, a transect from Oahu to ALOHA, and ground- and river water analyses to better characterise the dust and Hawaiian influence on the isotope and REE compositions at ALOHA.

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- 1246

1247 Table 1: Site information, hydrographic data, and dissolved Nd isotope ratios for all
 1248 seawater samples of this study. For more detailed information refer to Table A.1.
 1249

Site information	Water depth ^a [db]	θ ^a [°C]	S ^a	σ_{θ} ^a [kg/m ³]	ϵ_{Nd}	Error ^b ±	Water mass
Pearl Harbor (KM1107-2)							
21°17.087' N; 157°57.596' W	10	24.49	35.19	23.64	0.5	0.6	NPTW
02/25/2011	29	24.28	35.21	23.72	-1.0	0.6	NPTW
Bottom Depth: 226 m	50	24.18	35.22	23.75	0.0	0.5	NPTW
MLD: 17 m	99	22.41	35.23	24.28	-1.5	0.6	NPTW
	179	18.49	34.94	25.10	-3.0	0.5	NPTW
Makaha (KM1107-4)							
21°27.93' N; 158°14.466' W	10	24.53	35.23	23.66	0.5	0.5	NPTW
02/23/2011	31	24.48	35.24	23.68	-0.6	0.5	NPTW
Bottom Depth: 367 m	49	24.30	35.27	23.75	0.5	0.5	NPTW
MLD: 62 m	100	23.56	35.24	23.96	-2.8	0.5	NPTW
	150	20.88	35.17	24.66	-1.9	0.5	NPTW
	249	15.32	34.58	25.58	-3.3	0.5	
	344	10.08	34.15	26.28	-3.1	0.4	
Waimea (KM1107-6)							
21°39.453' N; 158°5.508' W	10	24.55	35.18	23.61	1.4	0.5	NPTW
02/23/2011	29	24.10	35.20	23.77	0.1	0.5	NPTW
Bottom Depth: 72 m	50	23.91	35.21	23.82	0.9	0.5	NPTW
MLD: 21 m							
Kahuku Point (KM1107-7)							
21°45.042' N; 157°59.123' W	11	24.33	35.20	23.70	1.3	0.5	NPTW
02/23/2011	30	24.32	35.21	23.70	0.4	0.5	NPTW
Bottom Depth: 124 m	51	24.25	35.21	23.73	-5.4	0.4	NPTW
MLD: 55 m	100	23.38	35.23	24.00	-0.6	0.5	NPTW
	108	23.25	35.23	24.04	-0.5	1.5	NPTW
Transect #1 (KM1107-8)							
21°50.679' N; 157°58.973' W	11	24.41	35.18	23.66	-0.7	0.6	NPTW
02/23/2011	49	24.06	35.22	23.79	-0.9	0.6	NPTW
Bottom Depth: 1389 m	100	23.17	35.26	24.08	-1.7	0.5	NPTW
MLD: 41 m	251	15.31	34.49	25.51	-3.2	0.5	
	347	9.90	34.10	26.27	-3.3	0.6	
	496	6.94	34.14	26.75	-2.4	0.3	NPIW
	743	4.88	34.35	27.18	-2.1	0.3	NPIW
	993	4.00	34.46	27.36	-2.1	0.3	NPIW
	1188	3.54	34.50	27.43	-2.2	0.2	NPIW
	1189	3.54	34.50	27.43	-2.3	0.3	NPIW
	1345	3.13	34.53	27.50	-2.1	0.3	
ALOHA (KM1107-11)							
22°45.022' N; 157°59.995' W	9	24.20	35.21	23.74	0.8	0.4	NPTW
02/24/2011	49	24.05	35.21	23.78	0.3	0.5	NPTW
Bottom Depth: 4749 m	102	23.35	35.35	24.10	-1.4	0.5	NPTW
MLD: 66 m	248	17.03	34.76	25.32	-3.8	0.5	
	351	11.88	34.23	26.02	-3.3	0.4	
	496	7.44	34.03	26.59	-3.5	0.3	NPIW
	745	4.62	34.27	27.14	-2.6	0.3	NPIW
	746	4.62	34.27	27.14	-2.8	0.5	NPIW
	991	3.90	34.45	27.36	-2.3	0.3	NPIW

1489	2.66	34.56	27.56	-2.4	0.3	
1979	1.98	34.61	27.66	-2.7	0.2	NPDW
2960	1.36	34.65	27.74	-3.0	0.4	NPDW
3938	1.14	34.67	27.77	-3.5	0.3	NPDW
4644	1.10	34.67	27.78	-3.9	0.3	NPDW
4644	1.10	34.67	27.78	-3.6	0.3	NPDW

ALOHA (KM1215/Hoe-Dylan V)

22°48.45' N; 158°1.92' W	4	25.10	35.29	23.53	-0.6	0.5	NPTW
07/21/2012	24	24.74	35.30	23.65	-5.8	0.4	NPTW
Bottom Depth: 4742 m	75	23.95	35.31	23.90	-0.8	0.4	NPTW
MLD/DCM ^a : 37 m / 137 m	136	22.02	35.36	24.49	-2.3	0.4	NPTW
	175	20.37	35.22	24.83	-3.7	0.5	NPTW
	250	14.77	34.41	25.57	-3.0	0.5	
	500	6.94	34.07	26.70	-3.0	1.7	NPIW
	749	4.80	34.30	27.14	-2.4	0.3	NPIW

ALOHA (KM1219/Hoe-Dylan IX)

22°48.48' N; 158°3' W	5	25.68	35.24	23.32	-1.4	0.2	NPTW
08/27/2012 and 08/28/2012	25	25.66	35.25	23.33	-0.4	0.3	NPTW
Bottom Depth: 4739 m	75	23.65	35.27	23.95	-0.9	0.6	NPTW
MLD/DCM ^a : 33 m / 132 m	126	22.23	35.35	24.42	-1.2	0.5	NPTW
	174	19.77	35.07	24.88	-2.5	0.3	NPTW
	248	15.28	34.46	25.50	-3.0	0.3	
	496	7.66	34.08	26.60	-3.3	0.3	NPIW
	744	4.79	34.26	27.12	-2.7	0.3	NPIW

ALOHA (KM1309/Hoe-Phor I)

22°44.986' N; 157°59.994' W	5	25.53	34.93	23.13	-5.2	0.6	NPTW
06/01/2013 and 06/02/2013	25	25.43	34.94	23.17	-2.0	0.5	NPTW
Bottom Depth: ~4800 m	75	23.62	35.24	23.94	-1.8	0.6	NPTW
MLD/DCM ^a : 34 m / 147 m	120	22.42	35.42	24.42	-3.0	0.4	NPTW
	175	21.02	35.29	24.71	-3.9	0.5	NPTW
	250	17.51	34.76	25.21	-4.2	0.7	
	500	7.82	34.22	26.69	-2.8	0.3	NPIW
	750	4.81	34.29	27.14	-2.5	0.3	NPIW

ALOHA (KM1316/Hoe-Phor II)

~22°45' N; 158° W	15	26.89	35.52	23.15			NPTW
09/18-19-20/2013	130	21.33	35.29	24.62			NPTW
Bottom Depth: ~4800 m	1000	3.88	34.46	27.37			NPIW
MLD/DCM ^a : 57 m / 130 m							

Wailupe Spring

21°16.54' N; 157°45.73' W	0.8 ^c	24.49	5.68	23.64	0.6	0.2
05/30/2010	1.4 ^c	24.28	1.81	23.72	1.3	0.2
		24.18		23.75		
		22.41		24.28		

MLD: Mixed layer depth; DCM: Deep chlorophyll maximum; S: Salinity. Mixed layer depth corresponds to 0.125 kg/m³ density offset from surface value (Miller, 1976). DCM not determinable during cruise KM1107.

^a The hydrographic data (potential temperature, potential density, salinity, MLD, DCM) of cruises KM1215, KM1219, KM1309 and KM1316 used in this publication came from the Center for Microbial Oceanography: Research and Education (C-MORE), an NSF Science and Technology Center (EF-0424599); <http://hahana.soest.hawaii.edu/cmoreds/interface.html>.

^b Calculated propagated error combined from internal and external error (both 2σ), with external errors representing session-based repeated analysis of JNdi-1.

^c Sediment depth

Figure Captions

Figure 1: Maps showing locations of the Hawaiian Islands in the central North Pacific and sampling sites around Oahu, Hawaii. a) North Pacific general circulation scheme (after Kawabe and Fujio, 2010) with sampling sites from other studies discussed in the text. TPS24 271-1 and TPS24 76-1 (Piepgras and Jacobsen, 1988; 1992); DE-4 (Shimizu et al., 1994); 180-PSSW (Greaves et al., 1999); BO-3 and BO-5 (Amakawa et al., 2009); St. 7 (Zimmermann et al., 2009); SAFe (Pahnke et al., 2012); and a site near Japan (Alibo and Nozaki, 1999), here named Ref. NPDW. b) Map of Oahu, Hawaii with sampling stations of cruise KM1107 and at time series Station ALOHA (different cruises), and groundwater sampling site at Wailupe Spring (black square). Maps created with GeoMapApp. c) Potential temperature vs. salinity plot of KM1107 samples. Water masses that could be identified based on their hydrographic properties were NPTW, NPIW and NPDW. The presence of the remaining water masses was not explicitly established. Figure c) was created with Ocean Data View (Schlitzer, 2014).

Figure 2: Full water column profiles of dissolved ϵ_{Nd} , Nd concentrations, and ^{228}Ra activity from cruise KM1107 (February 2011) at a) Station ALOHA and b) Station Transect #1. Error bars represent propagated errors (ϵ_{Nd} , Ra) or external reproducibility (Nd). Salinity profiles from the same casts. Grey shaded bar marks the approximate depth of the oxygen minimum. Duplicate samples at 745 m and 4644 m water depth in a) and at 1188 m water depth in b) agree within error for both ϵ_{Nd} and Nd concentrations. Note different scales of the Nd concentration axes. The depth ranges of NPTW, NPIW and NPDW, which could be clearly identified based on their hydrographic properties, are illustrated by vertical arrows.

Figure 3: ϵ_{Nd} and Nd concentrations of all stations of cruise KM1107 for the upper 500 m of the water column. For full water column profiles of stations Transect #1 and ALOHA see Fig. 2. One data point in d) and e) is excluded from profiles due to potential contamination (blue and red crosses; for details see section 3.2 and 3.3). Errors bars for Nd concentration are generally smaller than size of the symbols.

Figure 4: Dissolved seawater ϵ_{Nd} and Nd concentration profiles at Station ALOHA of four cruises during different months. a) Dissolved ϵ_{Nd} , b) dissolved Nd concentrations. Samples at 5 m depth of cruise KM1309 (black crosses) and 25 m depth of KM1215 (red crosses) are excluded from the profiles due to potential contamination (see section 3 for details).

Figure 5: PAAS-normalised REE patterns of a)-d) coastal waters, e) selected depths of Transect #1 (blue) and ALOHA (red) from cruise KM1107, and f) typical patterns of Hawaiian Basalts (based on average REE concentrations from Ren et al., 2009) and Chinese loess (based on average REE concentrations from Taylor et al., 1983; Liu et al., 1993; Nakai et al., 1993) on a logarithmic scale. PAAS data from Taylor and McLennan (1985). Note different scale in f).

Figure 6: a) Nd (LREE), and b) Er (HREE) concentration profiles for the upper 400 m of the coastal stations (coloured circles) and ALOHA (open symbols). Arrow marks approximate position of the DCM obtained from summer cruises (Tab. 1). The crosses indicate samples that are subject to contamination (see section 3 and Figs. 3,4).

Figure 7: PAAS-normalised REE ratios and anomalies for all coastal sites and ALOHA profiles of this study: a) Nd/Er, b) Er/Lu, c) Eu/Eu*, and d) MREE/MREE*. Coastal sites of Pearl Harbor (blue circles), Makaha (green circles), Waimea (pink circles), Kahuku Point (red circles) and Transect #1 (yellow squares). ALOHA profiles of KM1107 (February 2011, open squares), KM1215 (July 2012, open inverted triangles), KM1219 (August 2012, open triangles), KM1309 (June 2013, open diamonds), and KM1316 (September 2013, open asterisks). Bracketed data points in a) potentially influenced by contamination (see section 3). Note break in y-axis at 1000 m water depth.

Figure 8: Comparison of ALOHA full water column profiles of a) ϵ_{Nd} and b) Nd concentrations to other North Pacific stations (for locations see Fig. 1a). Bottom samples of BO-3 out of depicted range. BO-3 and BO-5 from Amakawa et al. (2009), St. 7 from Zimmermann et al. (2009), Hawaii composite from Vance et al. (2004), SAFe (two profiles) from Pahnke et al. (2012), TPS24 271-1 and TPS24 76-1 from Piepgras and Jacobsen (1988). For errors bars of Station ALOHA see Fig. 2a. Grey shaded area marks the depth of the radiogenic ϵ_{Nd} excursion at ALOHA.

Figure 9: Surface waters of coastal sites and ALOHA normalised to surface seawater from the North Pacific believed to lack lithogenic influence (station 180-PSSW, $\sim 24^\circ N$, $\sim 176^\circ E$; Greaves et al., 1999). Surface sample of June 2013 excluded due to potential contamination (for details see section 3).

Figure 10: REE patterns of North Pacific stations normalised to a) NPDW from site Ref. NPDW ($34.4^\circ N$, 2500 m, Alibo and Nozaki, 1999) and b) LCDW (Station 66, $45^\circ S$, 5155 m, Molina-Kescher et al., 2014). Ce data excluded for better visualisation. North Pacific sites: ALOHA (this study), DE-4 ($44.4^\circ N$, 4500 m, Shimizu et al., 1994), TPS24 271-1 ($24.2^\circ N$, 5073 m, Piepgras and Jacobsen, 1992) TPS24 76-1 ($24.2^\circ N$, 4621 m, Piepgras and Jacobsen, 1992) (for locations see Fig. 1a).

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