

DATASET description Metadata for GDAC

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Cruise Name and Platform name: <i>[any identifier (acronyms)]</i>	KN204-1
Dataset Name/ Description <i>[Describe these data, include how you refer to the data, units]</i> This dataset includes the dissolved neodymium (Nd) concentration and isotopic composition along the second leg of the US-GEOTRACES North Atlantic Zonal Transect (GA03). Contributors in alphabetic order: <ul style="list-style-type: none">• Duggan, Brian (University of South Carolina, USA): data analysis, publication• Goldstein Steven L. (Lamont-Doherty Earth Observatory, USA): Project PI• Hartman, Alison E. (Lamont-Doherty Earth Observatory, USA, now at Hebrew University, Israel): data analysis and publication• Pahnke, Katharina (University of Oldenburg, Germany): Project PI• Scher, Howie D. (University of South Carolina, USA): Project PI• Stichel, Torben (University of Hawaii at Manoa, USA; now at University of Southampton, UK): data analysis and publication	
Originating PI name and contact information <i>(Best person to contact with any questions about these data)</i>	
Name: Torben Stichel	Email: t.stichel@soton.ac.uk Phone: 023 80593049
Mailing Address: Ocean and Earth Science National Oceanography Centre Southampton University of Southampton Southampton SO14 3ZH, UK	
Project: <i>[Name of projects and programs associated with this data]</i> Collaborative Research: US GEOTRACES North Atlantic Section – Nd isotope distribution: sources, sinks, and internal cycling (NSF funded)	
Location: <i>Where data was collected, lat, lon, depth, time (UTC)</i> Sample location, depth and time are indicated in the attached data spreadsheet.	

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Data should be reported in a tabular form with the following columns (if appropriate)

Please see attached data spreadsheet (Excel).

Event number	Time of event (UTC)	Station	Lat (units)	Lon (units)	Cast	Rosette Position	Water sampling Bottle Number	Sequence replicate	Volume (L)	Depth (m)	Data (units)	Flags

Flags=L for bad data

a description of the applied quality flag scheme is found in the data spread sheet attached and in the Figures of Merit.

Methodology (provide a detailed method including references)

A detailed description can be found in Stichel et al. (2015). The text below summarizes the described methodology from the paper.

Onboard procedure

The samples were collected along the cruise transect of KN199-4 on 8 different stations. For every sample ~12L of seawater were collected in Niskin bottles mounted on a CTD-rosette. A ~4L aliquot of each sample was used for Nd analysis. After collecting, the samples were filtered through an AcroPak500 (0.8/0.45 µm) filter cartridge and subsequently acidified to pH <2. On each station a dummy sample of 18.2 MΩcm (MilliPore) water was filtered and acidified to estimate procedural blanks. The resulting blanks were lower than 60 pg, which is lower than 1.5% of the smallest sample size of 8 ng. No blank correction was applied.

Laboratory procedures:

The samples were processed in 4 different laboratories: University of Hawaii (UH), Lamont-Doherty Earth Observatory (LDEO), and University of South Carolina (USC), and University of Oldenburg (UO) each applying a slightly different methodology. The first three institutions successfully participated in the GEOTRACES inter-calibration effort (van de Flierdt et al., 2012), whereas UO's isotope lab was established after this effort but has shown to fulfill the GEOTRACES intercalibration requirements (Basak et al., 2015). It can therefore be assumed that data produced at each laboratory is comparable to one another.

At UH and LDEO, ~20 mg cleaned iron (Fe) in form of FeCl₃-solution and a previously weighed ¹⁴⁶Nd (UH) or ¹⁵⁰Nd (LDEO) spike were added to each sample and allowed 2–5 days for equilibration. Neodymium was co-precipitated with FeOOH after raising the pH to ~8.5 and the supernatant was discarded. The FeOOH precipitate was washed and centrifuged twice with MilliPore water that was adjusted to pH =8 with purified NH₄OH solution, to remove remaining water-soluble salts.

Samples were dried and 400 µl aqua regia (UH) or 1 ml 8N HNO₃ (LDEO) were added and left capped for 24h at ~110°C. Samples were converted to Cl-form by evaporating twice in 1ml 6N HCl (UH only). At UH, Fe and other major cations were removed using 1.5ml AG50W-X8 Biorad resin (200–400 dry mesh). At LDEO, the Fe(III) in the samples was reduced to Fe(II) with L-ascorbic acid (Arcos Organics) and Nd was separated using 250 µl RE-Spec®resin (100–150µm).

At USC, an aliquot of ~500 ml was kept separately for later concentration analysis. From the

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remaining unspiked sample, Nd was extracted using C-18 cartridges (Waters Inc.) loaded with ~300mg bis(2-ethylexyl) hydrogen phosphate (HDEHP) as a REE complexant following a procedure modified after Shabani et al. (1992). Seawater was pumped through the cartridge at 20ml/min, removing major ions. The cartridges were subsequently washed with 5ml 0.01N HCl to remove barium, and 35ml 6N HCl to elute Nd.

At UH and LDEO, Nd was further purified with 0.2M alpha-hydroxyisobutyric acid (Alpha-HIBA) adjusted to a pH of 4.5 on ~700µl of AG50W-X8 (200–400) resin. At USC, 2 ml Eichrom LN-Spec® resin bed (50–100µm) was used to isolate Nd from other mass interfering REEs (Pin and Zalduegui, 1997).

Mass Spectrometry:

At UH and LDEO Nd was analyzed using a VG-Sector and VG-Sector54 TIMS, respectively. The samples were loaded with 1µl 2N HCl on 1µl silica gel as an activator on a rhenium filament and measured as NdO⁺. At UH, the samples were run at 400 to 600mV on ¹⁴²Nd¹⁶O⁺ for 18 blocks with 21 ratios each in dynamic mode (3 cycles per ratio). Repeated measurements of both spiked and unspiked Nd standard JNdi-1 yielded ¹⁴³Nd/¹⁴⁴Nd = 0.512095 ± 0.000012 (±0.23 εNd, 2σ, n = 29). The isotope composition was corrected offline for oxygen isotopes and spike contribution. Spiking and analyzing 5 aliquots from one seawater sample (surface water near Oahu, HI) yielded a variation of < 2% (2σ) in the amount of Nd with this method. At LDEO, the samples were measured for 12 blocks (20 ratios each) with a controlled oxygen bleed into the source and a target intensity of ~300 mV on ¹⁴⁴Nd¹⁶O⁺. The measurements were made during three intervals during which repeat measurements of the Nd standard JNdi-1 were ¹⁴³Nd/¹⁴⁴Nd = 0.512083 ± 0.000015 (2σ, n = 31), ¹⁴³Nd/¹⁴⁴Nd = 0.512096 ± 0.000015 (2σ, n = 29) and ¹⁴³Nd/¹⁴⁴Nd = 0.512083 ± 0.000016 (2σ, n = 30). Uncertainties in [Nd] at LDEO for sea-water measurements are less than 3% (Pahnke et al., 2012). At USC and UO, Nd IC was measured on a Thermo Neptune Multi-collector ICPMS. A JNdi – 1 standard was analyzed periodically during analytical sessions. Samples and standards were run at 20 ppb. Overall replicate analyses of JNdi yielded 0.512119 ± 0.000030 (2σ, n = 59) and 0.511985 ± 0.000037 (2σ, n = 33) for USC and UO, respectively. However, the measurements were carried out over several weeks and the 2σ range for each analysis batch was much lower on average ±0.000012 for UO. A correction was made at each lab for internal mass fractionation with ¹⁴⁶Nd/¹⁴⁴Nd = 0.7219 in an exponential mass fractionation law and the ¹⁴³Nd/¹⁴⁴Nd ratio was normalized to JNdi – 1 = 0.512115 (Tanaka et al., 2000).

At USC, Nd concentration measurements were done using a novel technique developed as a method to extract REE from marsh water (Antle, 2013). A precisely known amount ¹⁴⁵Nd spike was added to the previously separated 500ml aliquot. Neodymium was pre-concentrated with 100µl of cleaned Toyopearl AF Chelate 650 resin. After 24h the resin was washed with 1–2ml of Millipore water, followed by 1ml of single distilled 1M HNO₃ to elute and collect Nd. Once removed from the resin, this aliquot was directly analyzed using the Element-2 ICP-MS. These samples were corrected for instrumental blanks, which accounted for up 0.8% of the overall intensities. Accuracy of the analysis was checked with a seawater sample from the North Pacific (SAFe, 3000 m), which yielded an average [Nd] of 47.55 pmol/kg ± 3% (n = 6). This is within error equal to the published average value of two laboratories of 44.37 pmol/kg (Pahnke et al., 2012). No Nd concentrations were measured at UO.

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Collection details: *Sampling methods (including type of bottle used), CTD Station identifier, sample identifier (i.e. sub sample bottle number)*

Sampling methods are found in the method description above; Metadata such as CTD number, GEOTRACES number are found in the data spreadsheet.

Equipment and Techniques: *Instrument used, Sample preparation (reference), relevant calibration information for individual sensors*

Information about the sample preparation can be found in the methodology section above and in Stichel et al. (2015).

All participating labs are successfully intercalibrated and LDEO, UH and USC participated in the GEOTRACES intercalibration effort published in van de Flierdt et al. (2012). Station USGT10-07 at 24°N/24°W yielded a very good agreement with a crossover station occupied at the same location during the 2010 German GA11 GEOTRACES cruise M81/1 (Stichel et al., 2015). Station USGT11-10 (BATS) yielded very good agreement with GA02 (64PE319) crossover at the same location (Lambelet et al. 2016).

Method / analytical procedure / sub sampling: *Filter types, pore size. Wash protocols. Storage of sample before determination (time, conditions) Specific changes from published methodology.*

Samples were stored at ambient temperature for an unspecified amount of time between sample collection and sample preparation for analysis, with no indication of sample quality influence. All samples were acidified to pH<2 within a few hours using distilled HCl after filtering through 0.45µm filter membranes.

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Data acquisition and data reduction/processing methodology:

Measured ratios were corrected for mass fractionation bias using a fixed $146/144 = 0.7219$. UH used $142/144 = 1.141826$ to circumvent $146/144$ because of major spike contributions on mass 146Nd .

All final $143\text{Nd}/144\text{Nd}$ ratios were corrected for instrumental off-set using a recommended $143\text{Nd}/144\text{Nd}$ of 0.512115 (Tanaka et al., 2000)

Figures of merit: *Reporting units, missing data identifier, limit of detection, precision, number of samples analysed, any intercalibration, use of international standards e.g. SAFE, IRONAGES.*

CRUISE: text - Cruise identifier

SECTION_ID: text - agreed nomenclature on cruise section during ODU-GEOTRACES workshop in March 2013

STNNBR: Station number

CASTNO: Cast number

GEOTRC_EVENTNO: Geotraces event number

GEOTRC_SAMPNO: (US)GEOTRACES sample number

DATE: yyyyymmdd - date of sampling

TIME: UTC - time when station was logged

SAMPNO: position of sample on CTD rosette

BTLNBR: bottle identifier

LATITUDE: degrees North - latitudinal position as station was logged

LONGITUDE: degrees East - longitudinal position as station was logged

CTDDEPTHMETRES: metres - sampling depth

ND_143_ND_144_RATIO: dimensionless - final ratio of $143\text{Nd}/144\text{Nd}$ after correcting mass bias and instrumental offset

ND_143_ND_144_FLAG_W: flag value for $143\text{Nd}/144\text{Nd}$, see flag assignments below

int_ND_143_ND_144RATIO: dimensionless - Standard error of them mean using standard deviation divided by the square root of ratios in one measurement (e.g. UH used normally 378 ratios for one measurement)

EPSILON_Nd: epsilon Nd in parts per 10,000 - final $143\text{Nd}/144\text{Nd}$ normalized to 0.512638 ($143\text{Nd}/144\text{Nd}$ of the Chondritic Uniform Reservoir in Jacobsen and Wasserburg, 1980) in parts per 10,000.

EPSILON_ND_FLAG_W: flag value for epsilon Nd, see flag assignments below

EPSILON_ND_2SD: dimensionless - 2 standard deviations of the repeatedly measured standards during the analysis.

diss_Nd_pmol_kg: picomol per kg - pico-moles (10^{-12} moles) of dissolved Nd per kg sample, dissolved Nd concentration.

REE_ND_UH_FLAG_W: flag value for dissolved Nd concentration, see flag assignments below

LAB: Lab responsible for analysis; UH: University of Hawaii at Manoa, LDEO: Lamont-Doherty Earth Observatory, USC: University of South Carolina, UO: University of Oldenburg

Instrument: instrument used for analysis; TIMS: Thermal ionization mass spectrometer (VG-Sector (UH) or VG-Sector54 (LDEO)), ICPMS: Multi-Collector Inductively Coupled Mass Spectrometer (NeptunePlus)

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Reference: Publication reference

Flags:

0: good value

1: no value or unknown value

2: replacement considered good value

4: not trusted

Other:

-999: no value

Problem report: *List of problems associated with data set*

References

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