Concentrations of the rare earth elements (REE) and Thorium-232 (232Th) in glacial dust from the northern Gulf of Alaska region

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Project
» Inferring trace element inputs to North Pacific surface waters from Alaskan and Asian dust (Dust Flux to North Pacific)

Contributors	Affiliation	Role
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Abstract
Concentrations of the rare earth elements (REE) and Thorium-232 (232Th) are presented for filtered air (dust) samples collected from the northern Gulf of Alaska region, including from Middleton Island (AK)(59.4214 N, 146.3493 W) and the Copper River delta (60.4324 N, 145.0954 W). Size-fractionated samples were collected in November 2019, using a Tisch Volumetric Flow Controlled (VFC) high volume sampler (Tisch Environmental, TE-5170V- BL) outfitted with a Cascade impactor. The six size fractions collected ranged from <0.49 micrometers (um) to >7.2 um in diameter. This sampler technology is discussed in greater detail in Morton et al, 2013. Samples were filtered with acid-washed Whatman 41 (W41) cellulose fiber filters. Additional bulk dust samples were collected in October 2012, using a Thermo Partisol Plus 2025 using Teflon filters. Samples were fully digested using concentrated nitric and hydrofluoric acids, following the approach of Morton et al, 2013. Samples were analyzed using a Thermofisher iCAP inductively coupled plasma mass spectrometer (ICP-MS) in KED mode, with He as a collision cell gas, adapted from the approach of Trommetter et al (2020). Concentrations were determined from standard curves using a REE ICP-MS standard from High-Purity Standards (that also contained 232Th). Three internal standards (Ge, In, and Bi) were added to both samples and standards, to correct for short-term variability in the instrument response and to evaluate stability of mass response during the ICP-MS run. Concentration estimates for the REE and 232Th were blank-corrected using full-process blanks that included filters deployed during times when there was no known dust deposition. Most of the full-process blank concentrations were 100 times or more smaller than the concentrations of our lowest standard (with the exception of Ce, the concentration of which was ~seven times smaller than our lowest standard. This means that our blank concentrations were very low but also not quantified extremely accurately. Our best estimates are that the full-process blanks, including filters, ranged from 0.02 picograms per square centimeter (pg cm-2) for Eu, Tb, and Ho, to 2 pg cm-2 for Ce. These blank concentrations were in all cases 40 times or more smaller than our lowest REE sample concentration for the <0.49 um size fraction with the smallest amount of dust, and ~3 orders of magnitude smaller than the signal of the largest samples. The REE data are also presented in a double-normalized format that first normalizes to concentrations of Post Archean Australian Shale and then normalizes to the mean REE concentration. The normalization approach is slightly modified from that of Serno et al, 2014.

Table of Contents

Coverage

Location: Northern Gulf of Alaska
Spatial Extent: **N**:60.4324 **E**:-145.0954 **S**:59.42144 **W**:-146.3493
Temporal Extent: 2011-07-29 - 2019-11-12

Methods & Sampling

Sampling approaches:
Alaskan glacial dust samples were collected in a variety of ways from two different locations, during multiple years. Bulk dust was collected using a Thermo Partisol Plus 2025 on Middleton Island, Alaska (59.42144 °N, 146.3493 °W) continuously during two years from 2011-2012, as described in Schroth et al, 2017. The sampling location, at a high point in the southwestern third of the ~50-meter (m) high island, was selected to be close to a source of needed electricity but far from frequently traveled roads and other local sources of aerosol (e.g. diesel generators at the northeastern end). Size-fractionated samples were also collected on Middleton Island (same location) during a large glacial dust event from 10-12 November 2019 using a Tisch Volumetric Flow Controlled (VFC) high volume sampler (Tisch Environmental, TE-5170V- BL) outfitted with a Cascade impactor. The six size fractions collected ranged from <0.49 micrometers (um) to >7.2 um in diameter. This sampler technology is discussed in greater detail in Morton et al, 2013. Samples were filtered with Whatman 41 (W41) cellulose fiber filters. Filters were acid-washed using environmental grade 0.5 M HCl and very thoroughly rinsed with milli-Q water, then dried, in a HEPA filtered laminar flow hood.

Finally, one large-volume sample was generated by collecting dust on July 29, 2011, from the shelves of a shed in the Copper River delta (close to Million Dollar Bridge, at 60.67454 °N, 144.74811 °W) that was in the path of the Copper River-derived dust plume and had a hole in its roof, which served as the sample collection device. This large dust sample probably integrated over a few years prior to collection. The validity of this sample, despite a very unconventional sampling approach, is confirmed by the striking similarity of its rare earth element (REE) signature to the REE signature of the other samples collected from Middleton Island (especially to the >7.2 um diameter sample)).

Digestion methods:
Samples of a few milligrams (mg) of dust (typical for the largest size fractions; sometimes less) were weighed after equilibration in lab air overnight in a laminar flow hood to minimize moisture content fluctuations. Moisture content of the dust has the potential to alter mass estimates substantially, hence this step was essential. Total particle digestions were carried out in Savillex 15-milliliter (mL) Teflon vials on a hotplate using a three-step digestion, at 140-150 degrees Celsius (°C), patterned after Morton et al (2013) using: 1) Optima concentrated HNO3; 2) a 4:1 mixture of Optima concentrated HNO3 and Optima concentrated HF; 3) Optima concentrated HNO3, followed in each case by evaporation to dryness. Samples were then redissolved in 4 M HNO3 at 90°C for two hours. Digestions and evaporation steps were carried out within a polycarbonate enclosure, with HEPA-filtered air intake, on top of clean polyethylene sheet, within an exhausting fume hood.

Analyses:
Concentrations of the REE and 232Th were determined on a Thermofisher iCAP inductively coupled plasma mass spectrometer (ICP-MS) in KED mode, with He as a collision cell gas, adapted from the approach of Trommetter et al (2020). Concentrations were determined from standard curves using a REE ICP-MS standard from High-Purity Standards (that also contained 232Th). Three internal standards (Ge, In, and Bi) were added to both samples and standards, to correct for short-term variability in the instrument response and to evaluate stability of mass response during the ICP-MS run. Concentration estimates for the REE and 232Th were blank-corrected using full-process blanks that included filters deployed during times when there was no known dust deposition. Most of the full-process blank concentrations were 100 times or more smaller than the concentrations of our lowest standard (with the exception of Ce, the concentration of which was ~7 times

smaller than our lowest standard. This means that our blank concentrations were very low but also not quantified extremely accurately. Our best estimates are that the full-process blanks, including filters, ranged from 0.02 picograms per square centimeter (pg cm-2) for Eu, Tb, and Ho, to 2 pg cm-2 for Ce. These blank concentrations were in all cases 40 times or more smaller than our lowest REE sample concentration for the <0.49 um size fraction with the smallest amount of dust, and ~3 orders of magnitude smaller than the signal of the largest samples. Hence, the blanks did not impact our REE concentration estimates significantly.

Solid reference materials were analyzed to evaluate the completeness of the particle digestion process and the accuracy of the standard solution calibrations. These included PACS-3 and a large sample of Columbia River Basalt (BCR-UW) collected, ground, and homogenized by Prof. Bruce Nelson of UW Earth and Space Sciences, from the same location as BCR-1 and BCR-2. In addition, Arizona test dust and a large-volume dust sample from the Copper River delta (see sampling methods discussion) were analyzed multiple times as additional constraints on reproducibility. Our REE concentration estimates agree within roughly four percent of the published concentrations for the reference materials PACS-3 and BCR-UW, while 232Th concentrations agree within ~5%. We used BCR-UW as a reference material because the USGS Geochemical Reference Materials lab was not able to provide us with any BCR-2 upon request, and we assume that this sample is of the same composition as BCR-2, as is suggested by the REE concentrations.

Double normalized REE data processing:
REE concentrations were double normalized as follows. They were normalized to the average Post-Archean Australian Shale (PAAS) REE concentration (McLennan, 1989), following recent practice (Grenier et al, 2018; Zhang et al, 2008; Friend et al, 2008). Such normalization generates smooth plots of the REE because it helps to reduce the effect whereby even atomic-numbered REE are more abundant than odd atomic-numbered REE (see Grenier et al, 2018). Concentrations were then normalized again to the mean PAAS-normalized REE concentration of each sample, similar to the approach Serno et al (2014) used normalizing to average Upper Continental Crust. See Serno et al (2014) for more detail on double normalization. This normalization approach differs slightly from the Upper Continental Crust normalization used by Serno et al (2014), although there is a very minor impact on the REE patterns (Garcia-Solsona et al, 2014, Appx. A.). Another reason we used this PAAS normalization approach is that it has been used in recent publications where the europium anomaly, Eu/Eu*, is estimated (e.g. Friend et al, 2008; Zhang et al, 2008; Grenier et al, 2018) and is thus consistent with recent practice in the oceanographic community.

The double normalized data are in the attached Supplemental File, "925359_v1_ree_th232_normalized_copperriverdust.csv".

Data Processing Description

The raw REE concentrations were double normalized, and REE data were saved in this format, as well, as follows. Concentrations were normalized to the average Post-Archean Australian Shale (PAAS) REE concentration (McLennan, 1989), following recent practice (Grenier et al, 2018; Zhang et al, 2008; Friend et al, 2008). Such normalization generates smooth plots of the REE because it helps to reduce the effect whereby even atomic-numbered REE are more abundant than odd atomic-numbered REE (see Grenier et al, 2018). Concentrations were then normalized again to the mean PAAS-normalized REE concentration of each sample, similar to the approach Serno et al (2014) used normalizing to average Upper Continental Crust. This normalization approach differs slightly from the Upper Continental Crust normalization used by Serno et al (2014), although there is a very minor impact on the REE patterns (Garcia-Solsona et al, 2014, Appx. A.). Another reason we used this PAAS normalization approach is that it has been used in recent publications where the europium anomaly, Eu/Eu*, is estimated (e.g. Friend et al, 2008; Zhang et al, 2008; Grenier et al, 2018) and is thus consistent with recent practice in the oceanographic community.

BCO-DMO Processing Description

- Imported original file "REE_Th232_raw_data_CopperRiverDustBCO-DMO.csv" into the BCO-DMO system.
- Made longitude values negative to indicate West direction.
- Renamed fields to comply with BCO-DMO naming conventions.
- Converted date field to YYYY-MM-DD format.
- Saved the final file as "925359_v1_ree_th232_raw_data_copperriverdust.csv".

- Imported original file "REE_Th232_PAAS_MeanNorm_CopperRiverDustBCO-DMO.csv" into the BCO-DMO

system.
- Made longitude values negative to indicate West direction.
- Renamed fields to comply with BCO-DMO naming conventions.
- Converted date field to YYYY-MM-DD format.
- Saved the final supplemental file as "925359_v1_ree_th232_normalized_copperriverdust.csv".

[table of contents | back to top]

Data Files

File
925359_v1_ree_th232_raw_data_copperriverdust.csv (Comma Separated Values (.csv), 1.24 KB) MD5:ee15fb5c63682f7a353662743e8cd660 Primary data file for dataset ID 925359, version 1. REE and Th-232 data (raw data, in concentrations of ppm (ug/g)).

[table of contents | back to top]

Supplemental Files

File
925359_v1_ree_th232_normalized_copperriverdust.csv (Comma Separated Values (.csv), 3.46 KB) MD5:490464996fd291edf1459a0b2ca3f324

Supplemental file for dataset ID 925359, version 1. REE data normalized by Post-Archean Australian Shale (PAAS) and then by the mean REE concentration.

Colum descriptions (name,description,units):
sample_description,Simple description of the sample,unitless

location_description,Description of the sample location,unitless

latitude,"Station latitude, north is positive",decimal degrees

longitude,"Station longitude, west is negative",decimal degrees

ISO_Date_UTC,Station timestamp (UTC) in ISO 8601 format yyyy-mm-dd,unitless

La,dust/sediment lanthanum ,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Ce,dust/sediment cerium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Pr,dust/sediment praseodymium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Nd,dust/sediment neodynium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Sm,dust/sediment samarium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Eu,dust/sediment europium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Gd,dust/sediment gadolinium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Tb,dust/sediment terbium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Dy,dust/sediment dysprosium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Ho,dust/sediment holmium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Er,dust/sediment erbium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Tm,dust/sediment thulium ,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Yb,dust/sediment ytterbium,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

Lu,dust/sediment lutetium ,"unitless, normalized to PAAS, then to mean, following Crusius et al, GRL, 2024."

NOTES,Relevant notes about a sample or analysis.,unitless

[table of contents | back to top]

Related Publications

Crusius, J. (2021). Dissolved Fe Supply to the Central Gulf of Alaska Is Inferred to Be Derived From Alaskan Glacial Dust That Is Not Resolved by Dust Transport Models. Journal of Geophysical Research: Biogeosciences, 126(6). Portico. https://doi.org/10.1029/2021jg006323
General

Crusius, J., Lao, C.A., Holmes, T.M., & Murray, J.W. (2024, submitted). Alaskan glacial dust is an important iron source to surface waters of the Gulf of Alaska.
Results

Crusius, J., Schroth, A. W., Gassó, S., Moy, C. M., Levy, R. C., & Gatica, M. (2011). Glacial flour dust storms in the Gulf of Alaska: Hydrologic and meteorological controls and their importance as a source of bioavailable iron. Geophysical Research Letters, 38(6), n/a-n/a. https://doi.org/10.1029/2010gl046573
General

Friend, C. R. L., Nutman, A. P., Bennett, V. C., & Norman, M. D. (2007). Seawater-like trace element signatures

(REE + Y) of Eoarchaean chemical sedimentary rocks from southern West Greenland, and their corruption during high-grade metamorphism. Contributions to Mineralogy and Petrology, 155(2), 229–246. https://doi.org/10.1007/s00410-007-0239-z
Methods

Garcia-Solsona, E., Jeandel, C., Labatut, M., Lacan, F., Vance, D., Chavagnac, V., & Pradoux, C. (2014). Rare earth elements and Nd isotopes tracing water mass mixing and particle-seawater interactions in the SE Atlantic. Geochimica et Cosmochimica Acta, 125, 351–372. https://doi.org/10.1016/j.gca.2013.10.009
Methods

Grenier, M., Garcia-Solsona, E., Lemaitre, N., Trull, T. W., Bouvier, V., Nonnotte, P., van Beek, P., Souhaut, M., Lacan, F., & Jeandel, C. (2018). Differentiating Lithogenic Supplies, Water Mass Transport, and Biological Processes On and Off the Kerguelen Plateau Using Rare Earth Element Concentrations and Neodymium Isotopic Compositions. Frontiers in Marine Science, 5. https://doi.org/10.3389/fmars.2018.00426
Methods

McLennan, S. M. (1989). Chapter 7. RARE EARTH ELEMENTS IN SEDIMENTARY ROCKS: INFLUENCE OF PROVENANCE AND SEDIMENTARY PROCESSES. Geochemistry and Mineralogy of Rare Earth Elements, 169–200. https://doi.org/10.1515/9781501509032-010
Methods

Morton, P. L., Landing, W. M., Hsu, S.-C., Milne, A., Aguilar-Islas, A. M., Baker, A. R., … Zamora, L. M. (2013). Methods for the sampling and analysis of marine aerosols: results from the 2008 GEOTRACES aerosol intercalibration experiment. Limnology and Oceanography: Methods, 11(2), 62–78. doi:10.4319/lom.2013.11.62
Methods

Schroth, A. W., Crusius, J., Gassó, S., Moy, C. M., Buck, N. J., Resing, J. A., & Campbell, R. W. (2017). Atmospheric deposition of glacial iron in the Gulf of Alaska impacted by the position of the Aleutian Low. Geophysical Research Letters, 44(10), 5053–5061. Portico. https://doi.org/10.1002/2017gl073565
Methods

Serno, S., Winckler, G., Anderson, R. F., Hayes, C. T., McGee, D., Machalett, B., Ren, H., Straub, S. M., Gersonde, R., & Haug, G. H. (2014). Eolian dust input to the Subarctic North Pacific. Earth and Planetary Science Letters, 387, 252–263. https://doi.org/10.1016/j.epsl.2013.11.008
Methods

Trommetter, G., Dumoulin, D., & Billon, G. (2020). Direct determination of rare earth elements in natural water and digested sediment samples by inductively coupled plasma quadrupole mass spectrometry using collision cell. Spectrochimica Acta Part B: Atomic Spectroscopy, 171, 105922. https://doi.org/10.1016/j.sab.2020.105922
Methods

Zhang, Y., Lacan, F., & Jeandel, C. (2008). Dissolved rare earth elements tracing lithogenic inputs over the Kerguelen Plateau (Southern Ocean). Deep Sea Research Part II: Topical Studies in Oceanography, 55(5–7), 638–652. https://doi.org/10.1016/j.dsr2.2007.12.029
Methods

[table of contents | back to top]

Parameters

Parameter	Description	Units
sample_description	Simple description of the sample	unitless
location_description	Description of the sample location	unitless
latitude	Station latitude, north is positive	decimal degrees
longitude	Station longitude, west is negative	decimal degrees
ISO_Date_UTC	Station timestamp (UTC) in ISO 8601 format yyyy-mm-dd	unitless
La	dust/sediment lanthanum	ppm (ug/g)
Ce	dust/sediment cerium	ppm (ug/g)
Pr	dust/sediment praseodymium	ppm (ug/g)
Nd	dust/sediment neodynium	ppm (ug/g)
Sm	dust/sediment samarium	ppm (ug/g)
Eu	dust/sediment europium	ppm (ug/g)
Gd	dust/sediment gadolinium	ppm (ug/g)
Tb	dust/sediment terbium	ppm (ug/g)
Dy	dust/sediment dysprosium	ppm (ug/g)
Ho	dust/sediment holmium	ppm (ug/g)
Er	dust/sediment erbium	ppm (ug/g)
Tm	dust/sediment thulium	ppm (ug/g)
Yb	dust/sediment ytterbium	ppm (ug/g)
Lu	dust/sediment lutetium	ppm (ug/g)
Th232	dust/sediment thorium-232	ppm (ug/g)
NOTES	Relevant notes about a sample or analysis.	unitless

[table of contents | back to top]

Instruments

Dataset-specific Instrument Name	Tisch Environmental, TE-5170V- BL
Generic Instrument Name	Aerosol Sampler
Dataset-specific Description	Size-fractionated samples were collected using a Tisch Volumetric Flow Controlled (VFC) high-volume sampler (Tisch Environmental, TE-5170V- BL) outfitted with a Cascade impactor.
Generic Instrument Description	A device that collects a sample of aerosol (dry particles or liquid droplets) from the atmosphere.

Dataset-specific Instrument Name	Thermofisher iCAP ICP-MS
Generic Instrument Name	Inductively Coupled Plasma Mass Spectrometer
Dataset-specific Description	Concentrations of the REE and 232Th were determined on a Thermofisher iCAP inductively coupled plasma mass spectrometer (ICP-MS) in KED mode.
Generic Instrument Description	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

Dataset-specific Instrument Name	Thermo Scientific Partisol 2025i Sequential Air Sampler
Generic Instrument Name	Thermo Scientific Partisol 2025i Sequential Air Sampler
Dataset-specific Description	Bulk dust was collected using a Thermo Partisol Plus 2025
Generic Instrument Description	The Thermo Scientific Partisol 2025i Sequential Air Sampler stores 16 filter cassettes, allowing for two weeks of unattended daily-sampling of particulate matter. Developed on the iSeries software platform design, this sampler features USB ports for improved data downloads, and exchanged 47mm diameter sample filters automatically, which can be preset to a user-defined time interval.

[table of contents | back to top]

Project Information

Inferring trace element inputs to North Pacific surface waters from Alaskan and Asian dust (Dust Flux to North Pacific)

Coverage: subarctic North Pacific

NSF Award Abstract:
An important part of understanding chemical cycling in the ocean is understanding the processes that deliver elements and nutrients to or remove them from the oceans. The atmosphere can be an important source of material from rain and from dust. In some parts of the oceans, input of elements such as iron from dust (and possibly rain) can play an important role in stimulating the growth of phytoplankton, the base of the marine food chain. This study will involve collection and analysis of a two-year time-series of filtered air samples from two locations in the subarctic North Pacific, aimed at understanding the inputs of metals to the ocean surface from Alaskan and Asian dust and from fossil fuel combustion. The dust time series observations and analyses proposed will provide insight that will aid the interpretation of observations from the 2018 U.S. GEOTRACES Pacific Meridional Transect expedition. This project will support a graduate student for two years and will be the basis of his or her Ph.D. research.

The investigators will collect atmospheric dust samples from two land-based locations well suited to capture the flux to surface waters of the subarctic North Pacific. One is on the northern side of the Aleutian chain, and the second is an island to the northeast (Middleton Island), at the shelf break, in the northern Gulf of Alaska. Sampling will be carried out year round at Middleton Island using an automated sampling system, while high-volume sampling will be carried out for one month at each of the two locations during targeted known seasonal

events. These will help infer and characterize inputs from Asian dust, known to occur primarily in the spring, and from Alaskan dust, known to occur primarily in the autumn. Samples from large events will be made available to the GEOTRACES research community for analyses. The HYSPLIT model will be used to simulate dust transport and deposition, for comparison to observations. Previous work documents substantial interannual variability in dust fluxes from Alaska and from Asia, and volcanic ash input is even more variable. Given the seasonality and interannual and spatial variability of the dust sources, and the short residence time of Fe and other trace elements and isotopes in surface waters, this history of deposition from dust and fossil fuel combustion, and its geochemical characterization, will help to distinguish the various inputs more comprehensively than is possible with a single research cruise. A variety of size fractions will be collected and analyzed to infer the particle size range that contains each of the metals. Analyses will be carried out on over twenty elements, including Fe, Al, the REE, the isotopes of Pb, Sr and Nd (the tracers that best distinguish the dust source end members), and metals including V and Ag to infer contributions from fossil fuel combustion. Activities in air of the natural radionuclides lead-210 and beryllium-7, and their depositional fluxes, will be determined to convert elemental concentrations in dust into flux estimates to surface waters. Experiments will evaluate the control of different organic ligands on the solubility of iron and other metals in surface seawater, the relative solubility of different size fractions, and the relative solubility of dust- versus fossil fuel-derived metals.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

[table of contents | back to top]

Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1756126

[table of contents | back to top]