

# Rare earth element adsorption onto Pacific marine sediments sampled by coring during Kilo Moana cruise(s) KM2012 and KMxxxx in October and November 2020.

**Website:** <https://www.bco-dmo.org/dataset/955597>

**Data Type:** Cruise Results, experimental

**Version:** 1

**Version Date:** 2025-03-10

## Project

» [Collaborative Research: How and Why eNd Tracks Ocean Circulation](#) (Pacific Porewater Nd)

Contributors	Affiliation	Role
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## Abstract

Batch adsorption experiments were conducted in the laboratory to examine the adsorption behavior of the 14 naturally occurring lanthanides plus yttrium (Y) onto deep Pacific Ocean sediments and synthetic goethite ( $\alpha$ -FeOOH). The focus was on the interactions that govern rare earth element (REE) and Y retention in natural environments. Our results demonstrate preferential adsorption of middle REEs (MREEs) and heavy REEs (HREEs) onto goethite compared to light REEs (LREEs), with yttrium showing adsorption behavior similar to holmium (Ho), which we infer to be caused by their nearly identical ionic radii and charge density. Results of the experiments show that the middle REYs (MREE) and heavy REYs (HREE) are preferentially adsorbed onto stations 3 and 4 (STD3 & STD4) compared to the light REYs (LREE). Yttrium has an ionic radius nearly identical to holmium (Ho) and consequently exhibits chemical properties and behavior like the HREEs, with positive Y anomalies reflected in STD3 and station 5 (STD5). Using the generalized double-layer model formalism, the adsorption data were employed to develop a surface complexation model (SCM) for REYs onto these marine sediments. The surface complexation species consisted of the weak and strong sites for the free metal ion ( $\equiv$  FeOREY<sub>2</sub><sup>+</sup>), and the weak site for the carbonado ( $\equiv$  REYCO<sup>+</sup>). The SCM predicts REY 3 adsorption onto Pacific sediments from pH 3-10, has been developed, and successfully simulates the sorption of REYs. The combination of experimental data coupled SCMs will be highly beneficial to further understanding REY in diagenetic environments.

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## Coverage

**Location:** Three sites in the Equatorial Pacific Basin along a north to south transect along 152W south of the Hawaiian Islands in the Pacific Ocean.

**Spatial Extent:** N:12 E:-152 S:2 W:-152

**Temporal Extent:** 2020-10-31 - 2021-11-25

## Methods & Sampling

Equatorial Pacific sediments were sampled using a \_\_\_\_\_ corer during R/V Kilo Moana cruise KM2012 (was there another cruise?). Recovered cores with negligible sedimentary and sampling disturbance (i.e., sediment-water interface visibly intact) were sub-sampled immediately in the laboratory at 4°C on the ship. Cores were sectioned every 1 cm between 0 and 10 cm, and sectioned at 2 cm between 10 and 40 cm. Sectioned mud was placed in a cold van after sectioning and later analyzed for REY, εNd, other isotopic (41K; Li et al., 2022), trace metals, porewater and bulk geochemistry, and mineralogical (XANES, XRD; Li et al., 2022) analysis at Oregon State University, Bigelow Laboratory for Ocean Sciences, University of Tokyo, and University of Massachusetts Boston. Porewaters were preserved following the methods described by (Abbott et al., 2015b; 2019). Briefly, the cores were sectioned on board the ship into hydrochloric acid (HCl) cleaned centrifuge tubes in a glove bag filled with an inert (N<sub>2</sub>) atmosphere. After centrifugation, pore water was pulled off using HCl clean syringe, filtered with a 0.45 μm syringe filter, and acidified with ultrapure distilled HCl to a pH ≤ 2. Sediments were frozen and later freeze-dried prior to analysis.

Batch adsorption experiments to investigate REE sorption were conducted at UMass Boston. We employed the pH drift technique, which involves adjusting the pH of a solution stepwise and allowing the system to reach equilibrium at each step. This technique helps to identify the pH at which maximum adsorption occurs by gradually adjusting the pH and monitoring how the adsorption behavior changes. Solutions of 0.01M sodium nitrate (NaNO<sub>3</sub>) were freshly prepared from stock solutions using ultrapure water (i.e., 18.2 MΩ·cm; MilliQ IQ 7000 with multipack 0.22 μm). Solutions were equilibrated for 24 hours before use to allow stabilization of pH, ionic strength, and dissolved species concentrations. To minimize changes in solution composition, they were used within one week of preparation, stored in airtight, acid-washed containers at room temperature, and monitored periodically for pH drift. These precautions ensured that adsorption experiments were conducted under consistent and reproducible geochemical conditions.

YREE concentrations were quantified using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Nu Instruments AttoM ES). Isotopes were monitored at various resolution modes—low (300), medium (4000), and high (10000). Precisely, <sup>139</sup>La, <sup>140</sup>Ce, <sup>141</sup>Pr, <sup>143</sup>Nd, <sup>145</sup>Nd, <sup>146</sup>Nd, <sup>147</sup>Sm, <sup>149</sup>Sm, <sup>151</sup>Eu, <sup>153</sup>Eu, <sup>155</sup>Gd, <sup>157</sup>Gd, <sup>158</sup>Gd, <sup>159</sup>Tb, <sup>161</sup>Dy, <sup>163</sup>Dy, <sup>165</sup>Ho, <sup>166</sup>Er, <sup>167</sup>Er, <sup>169</sup>Tm, <sup>172</sup>Yb, <sup>173</sup>Yb, and <sup>175</sup>Lu were measured in low, medium, and high-resolution modes. The high-resolution mode was explicitly used to monitor <sup>151</sup>Eu and <sup>153</sup>Eu to resolve interferences from BaO<sup>+</sup> species on the Eu isotopes, as well as LREEO<sup>+</sup> and MREEO<sup>+</sup> interferences on other heavy REEs. Before instrumental analysis, an internal standard (100 μL of <sup>115</sup>In at ~871 nM) was added to each filtered and acidified sample to account for potential matrix effects and signal drift. Recoveries of the internal standard ranged between 92% and 100% for all YREE. Calibration was performed using a series of NIST traceable YREE standard solutions (Inorganic Ventures; CMS-1-125 mL in 5% HNO<sub>3</sub>) with concentrations ranging from 0.01, 0.1, 1, 5, and 10 μg L<sup>-1</sup>. All reported YREE concentrations were derived from five replicate analyses for which the analytical precision consistently remained better than 5% relative standard deviation.

*Detailed operating parameters for the HR-ICP-MS, including resolution settings, plasma conditions, and calibration methods, are provided in the supplemental appendix. (Not provided to BCO-DMO. Please provide the manuscript's expected citation!)*

## **BCO-DMO Processing Description**

- loaded in the file "PacMrnSeds\_h\_ion\_conc.xlsx" which was pivoted from the original file of "REE Adsorption\_Pacific Marine Sediments.xlsx"
- added column for sediment type (goethite, carbonate-rich, radiolarian ooze)
- renamed columns/fields to comply with interoperable characters (A-Z, a-z, and underscore)

## **Problem Description**

COVID-19 created issues with timing of sampling

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## **Related Publications**

Herbelin, A.L. and Westall, J.C. (1999). FITEQL: a computer program for determination of chemical equilibrium

constants from experimental data. (Version 4). Department of Chemistry, Oregon State University.  
*Software*

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## **Parameters**

<b>Parameter</b>	<b>Description</b>	<b>Units</b>
Station	Station where sediment coring occurred	unitless
Sediment_type	Sediment type at station	unitless
Hydrogen_ion_conc	pH (hydrogen ion concentration)	unitless
La_conc	Lanthanum concentration	millimole per liter (mM)
Ce_conc	Cerium concentration	millimole per liter (mM)
Pr_conc	Praseodymium concentration	millimole per liter (mM)
Nd_conc	Neodymium concentration	millimole per liter (mM)
Sm_conc	Samarium concentration	millimole per liter (mM)
Eu_conc	Europium concentration	millimole per liter (mM)
Gd_conc	Gadolinium concentration	millimole per liter (mM)
Tb_conc	Terbium concentration	millimole per liter (mM)
Dy_conc	Dysprosium concentration	millimole per liter (mM)
Y_conc	Yttrium concentration	millimole per liter (mM)
Ho_conc	Holmium concentration	millimole per liter (mM)
Er_conc	Erbium concentration	millimole per liter (mM)
Tm_conc	Thulium concentration	millimole per liter (mM)
Yb_conc	Ytterbium concentration	millimole per liter (mM)
Lu_conc	Lutetium concentration	millimole per liter (mM)

## Instruments

<b>Dataset-specific Instrument Name</b>	Nu Instrument Atom ES high resolution (magnetic sector) inductively coupled plasma mass spectrometer
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	YREE concentrations were quantified using high-resolution inductively coupled plasma mass spectrometry (HR-ICP-MS; Nu Instruments AttoM ES).
<b>Generic Instrument Description</b>	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.

<b>Dataset-specific Instrument Name</b>	Sediment corer
<b>Generic Instrument Name</b>	Sediment Corer
<b>Dataset-specific Description</b>	During Kilo Moana cruise in the Equatorial Pacific, a sediment corer was used to sample at depths >4000 meters
<b>Generic Instrument Description</b>	A generic term for a coring device that allows for relatively undisturbed penetration of the sediment. Generally, core samplers consist of a core barrel (a hollow pipe or box) and a core cutter (or cutting head), located at the advancing end of the core barrel to facilitate the sampler's advancement into the sediment. Core catchers are commonly inserted into the cutting head to prevent sample loss during retrieval.

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## Deployments

### KM2012

<b>Website</b>	<a href="https://www.bco-dmo.org/deployment/928159">https://www.bco-dmo.org/deployment/928159</a>
<b>Platform</b>	R/V Kilo Moana
<b>Start Date</b>	2020-10-09
<b>End Date</b>	2020-11-02
<b>Description</b>	See more information at R2R: <a href="https://www.rvdata.us/search/cruise/KM2012">https://www.rvdata.us/search/cruise/KM2012</a>

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## Project Information

**Collaborative Research: How and Why eNd Tracks Ocean Circulation (Pacific Porewater Nd)**

**Coverage:** Central Pacific

### *NSF Award Abstract:*

Circulation of water is a fundamental trait of the oceans that impacts its physics, chemistry and biology; however, understanding modern and past patterns of circulation - especially in the vast bodies of deep water - is challenging because global circulation defies direct measurement. The problems with direct measurement largely stem from the vast scales of space and time that are of interest in understanding global circulation. One tool for estimating global circulation patterns that holds promise is seen in neodymium isotopes which appear to be powerful tracers of deep ocean circulation, over a variety of timescales. Unfortunately, the elemental behavior of neodymium contrasts the isotopic behavior of neodymium in the oceans, a puzzle branded the "neodymium paradox." This inconsistency of geochemical behavior opens to question the application of neodymium isotopes as a tracer of circulation. Therefore, scientists from Oregon State University, Tulane University, and Bigelow Laboratory of Ocean Sciences propose to test the hypothesis that there is a yet unconstrained (even poorly identified) source of neodymium to the oceans that can explain the discrepancies seen between the elemental and isotopic neodymium marine budgets. The scientists further seek to understand the mechanistic cause of this source and thus be able to start making global constraints on its influence. Understanding these processes will fundamentally change our interpretations of neodymium data and allow us to more accurately quantify ocean circulation with a greater degree of confidence. For outreach activities, the scientists plan to participate in open house days held at Oregon State University, da Vinci days, National Ocean Science Bowls, Salmon Bowl and Bigelow Laboratory for Ocean Sciences' Cafe Scientifique. Undergraduate students and one graduate student from Tulane University would be supported and trained as part of this project.

Scientists from Oregon State University, Tulane University, and Bigelow Laboratory for Ocean Sciences propose to test the hypothesis that there is a benthic source of neodymium (Nd) to the oceans that exerts a primary control over the distribution of this element and its isotopes (eNd) in the ocean. This benthic flux results from early diagenetic reactions that release rare earth elements (REEs) from the solid phase to pore fluid. The scientists contend this flux will explain eNd distributions throughout the modern and past global oceans. The planned research will be guided by three questions:

- (1) What are the mechanisms that control the magnitude and isotope composition of the benthic flux?
- (2) What are the relationships among bottom water, pore fluid, and the terminal solid phase compositions? Particularly, how and under what chemical conditions does an eNd signature become part of a preserved archival record of [Nd] and eNd?
- (3) Can our understanding of the deep water benthic fluxes account for the integrated bottom water eNd as a function of apparent water mass age and circulation path (e.g., how do the pore fluid and solid phase values reconcile with the existing water column signature and water mass age data)?

To test these ideas, sediments and their pore fluids will be collected from a diverse set of deep sea sites in the Pacific Ocean that reflect slow-to-fast sedimentation rates, carbonate-, terrigenous-, volcanoclastic- and siliceous-sediment, and low-to-high organic carbon. The sediments and porewater samples, as well as samples from the overlying water column will be characterized for the following parameters: major, minor, and trace metals, Nd isotopes, carbonate chemistry, oxygen, nutrients, particulate organic carbon, particulate organic nitrogen, radiocarbon, porosity, and grain size. With these observations we will build a quantitative numeric geochemical model (e.g., PHREEQC, Geochemist's Workbench, Humic Ion Binding Model) that can capture the cardinal controls over the benthic source. Our goal is to provide a new interpretive framework for Nd and eNd, such that we can offer quantitative estimates of benthic fluxes for use in models of global circulation. This work has potentially transformative implications on our understanding and application of REEs and Nd isotope data in both the modern and ancient oceans.

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.

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## **Funding**

<b>Funding Source</b>	<b>Award</b>
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-2037556</a>

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