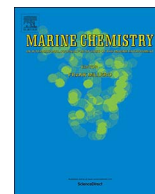




Contents lists available at ScienceDirect

## Marine Chemistry

journal homepage: [www.elsevier.com/locate/marchem](http://www.elsevier.com/locate/marchem)

## Intense hydrothermal scavenging of $^{230}\text{Th}$ and $^{231}\text{Pa}$ in the deep Southeast Pacific

Frank Pavia<sup>a,b,\*</sup>, Robert Anderson<sup>a,b</sup>, Sebastian Vivancos<sup>a,b</sup>, Martin Fleisher<sup>a</sup>, Phoebe Lam<sup>c</sup>, Yanbin Lu<sup>d</sup>, Hai Cheng<sup>d,e</sup>, Pu Zhang<sup>d</sup>, R. Lawrence Edwards<sup>d</sup>

<sup>a</sup> Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA

<sup>b</sup> Department of Earth and Environmental Sciences, Columbia University, New York, NY, USA

<sup>c</sup> Department of Ocean Sciences, University of California, Santa Cruz, CA 95064, USA

<sup>d</sup> Department of Earth Sciences, University of Minnesota, Minneapolis, MN, USA

<sup>e</sup> Institute of Global Environmental Change, Xi'an Jiaotong University, Xi'an, China

## ARTICLE INFO

## Keywords:

GEOTRACES  
Thorium  
Protactinium  
Scavenging  
Hydrothermal  
East Pacific Rise

## ABSTRACT

Hydrothermal circulation and subsequent eruption of seawater at mid-ocean ridges and back-arc basins has great potential to modulate deep ocean biogeochemistry, acting as both a source and a sink for many trace elements and their isotopes. The influence of hydrothermal vents as a source of iron and manganese has been demonstrated in all ocean basins. However, the long-range impact of scavenging by hydrothermal particles has yet to be documented in detail. We use dissolved and particulate measurements of long-lived radiogenic ( $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ ) and primordial ( $^{232}\text{Th}$ ) radionuclides to investigate the nature and geographic scale of scavenging processes occurring within a hydrothermal plume in the Southeast Pacific Ocean sampled during the GEOTRACES GP16 section. Due to their radioactive disequilibrium with respect to production by their parent uranium isotopes,  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  provide unique insights into the rates of scavenging. We find strong deficits in  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  coincident with elevated particulate Mn and  $\text{Fe}(\text{OH})_3$ , indicating that trace metal scavenging is widespread and likely the result of the strong affinity of trace metals for nanoparticulate metal surface sites. The chemical composition of the particulate material is closely linked to the scavenging intensity of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$ , expressed as distribution coefficients between solid and solution. A comparison of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  inventories with mantle-derived  $^3\text{He}$  as well as a mass balance of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  suggests continuous scavenging removal over the course of the entire 4000 km transect. Unlike the two radiogenic isotopes,  $^{232}\text{Th}$  is enriched above what would be expected from assuming identical scavenging behavior to  $^{230}\text{Th}$ , indicating a hydrothermal source of colloidal, unreactive  $^{232}\text{Th}$ .

### 1. Introduction

Throughout the global mid-ocean ridge system, hydrothermal circulation occurs when cold seawater percolates through and reacts with the upper ocean crust, heating to temperatures surpassing 400 °C. After reacting with the host rock, the hot, geochemically-altered fluids are sufficiently buoyant to rise back towards the ocean floor, where they are re-emitted into the deep ocean via submarine vents. The fluid rapidly mixes with ambient seawater and rises to form a neutrally buoyant hydrothermal plume (German and Seyfried, 2014). Due to high particle abundance (e.g. Estapa et al., 2015; Feely et al., 1987) and unique chemical and isotopic composition with respect to ambient deep ocean waters (German and Seyfried, 2014), hydrothermal activity has great potential for modulating elemental budgets and ocean chemistry.

Studies have identified hydrothermal plumes as a large source of many elements, such as iron and manganese (Klinkhammer et al., 1977; Resing et al., 2015; Saito et al., 2013), zinc (Von Damm et al., 1985; Roshan et al., 2016), and a large sink for many others, including rare earth elements (German et al., 1990), uranium (Michard and Albarède, 1985), and thorium (German et al., 2002; German et al., 1991; Kadko, 1996), via adsorption onto or co-precipitation with hydrothermal particles.

Whether hydrothermal plumes exert basin-scale influence on geochemical budgets in the ocean has been a much-debated topic. Hydrothermal inputs of iron have received significant attention (Tagliabue et al., 2014, 2010; Tagliabue and Resing, 2016) due to the biological necessity of Fe and the broad regions of the surface ocean in which primary production is limited by a lack of iron (e.g. Falkowski

\* Corresponding author at: Lamont-Doherty Earth Observatory of Columbia University, Palisades, NY, USA.  
E-mail address: [fpavia@ldeo.columbia.edu](mailto:fpavia@ldeo.columbia.edu) (F. Pavia).

<http://dx.doi.org/10.1016/j.marchem.2017.08.003>

Received 27 April 2017; Received in revised form 26 July 2017; Accepted 5 August 2017  
0304-4203/ © 2017 Elsevier B.V. All rights reserved.

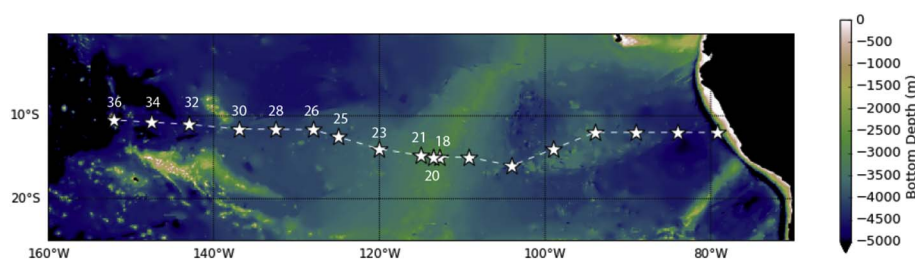


Fig. 1. Locations of the GP16 full-depth stations overlying seafloor bathymetry. Stations for which results are presented here are numbered.

et al., 1998). Early studies argued that, despite iron being heavily enriched ( $10^6$  times greater than seawater) in hydrothermal vent fluids, the long-range effect of hydrothermal activity on dissolved iron content in the deep ocean would be limited by rapid precipitation of oxides and sulfides when vent fluids initially come into contact with oxygenated seawater (Feely et al., 1996; German et al., 1991; Rudnicki and Elderfield, 1993). However, in recent years the paradigm of negligible far-field transport of hydrothermal iron has been upended by several studies finding plumes of dissolved iron and manganese thousands of kilometers away from their sources along the global mid-ocean ridge system, indicating that stabilization and/or slow oxidation rates in hydrothermal environments allow Fe to spread throughout entire ocean basins (Bennett et al., 2008; Fitzsimmons et al., 2014; Resing et al., 2015; Saito et al., 2013; Sander and Koschinsky, 2011). The long-range spread of plume particles and their influence on trace metal scavenging remain mysteries.

Two unique tracers of particulate scavenging are the long-lived radionuclides of protactinium ( $^{231}\text{Pa}$ ) and thorium ( $^{230}\text{Th}$ ), as their disequilibrium from production by parent nuclides ( $^{235}\text{U}$  and  $^{234}\text{U}$ , respectively) provides a rare ‘clock’ for calculating removal rates with respect to adsorption onto particles. Dissolved uranium is conservative in the ocean and the distribution of uranium isotopes is well-mixed (Andersen et al., 2010), so the production rates of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  are well-known, and nearly constant throughout the ocean. Scavenging residence times for  $^{231}\text{Pa}$  (50–200 years) and  $^{230}\text{Th}$  (10–40 years) (Henderson and Anderson, 2003) are much shorter than their respective half-lives of 32,760 years (Robert et al., 1969) and 75,584 years (Cheng et al., 2013) so their removal from the water column can be treated as being quantitatively equal to their known production rates. Water column variations in the activities of  $^{231}\text{Pa}$  and  $^{230}\text{Th}$  are the result of factors related to their removal, redistribution, or partitioning between phases – factors such as particle flux, particle composition, advection, and diffusion.

Much like iron, early studies on the scavenging of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  in hydrothermal plumes were focused on sites nearby ridge crest sources. Ridge flank sediments showed enhanced removal of  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  associated with downcore peaks in Fe and Mn content, reflecting hydrothermal scavenging (German et al., 1997, 1993; Shimmiel and Price, 1988). However, peaks in  $^{230}\text{Th}$  and  $^{231}\text{Pa}$  activity were not always associated with hydrothermal metal anomalies in these cores.

Other studies focused on the signature of hydrothermal scavenging in the water column. German et al. (1991) found a positive, linear correlation between total (dissolved plus particulate)  $^{230}\text{Th}$  and particulate Fe in samples within two kilometers of an active vent site at the TAG hydrothermal vent field. This is slightly unexpected, given that high concentrations of sinking particles would be expected to generate a deficit of  $^{230}\text{Th}$ . The authors argued that the elevated total  $^{230}\text{Th}$  was the result of re-entrainment of particles that had previously sunken out of the hydrothermal plume.

German et al. (2002) measured particulate  $^{230}\text{Th}$  in sediment trap samples from within 20 m of an active hydrothermal vent site at  $13^\circ\text{N}$  on the East Pacific Rise, and found  $^{230}\text{Th}$  fluxes three times greater than in the overlying water column. This was explained by adsorption of dissolved  $^{230}\text{Th}$  onto particles setting up a strong dissolved  $^{230}\text{Th}$  gradient away from vent activity, with the resulting diffusive transport

causing  $^{230}\text{Th}$  on sinking particles to be greater than what was produced in overlying waters. The spatial extent of this lateral diffusive input flux is not well understood. Only recently have mid-depth  $^{230}\text{Th}$  deficits at sites thousands of kilometers away from ridge systems been attributed to hydrothermal scavenging. Lopez et al. (2015) found a depletion in dissolved and total  $^{230}\text{Th}$  in  $\sim 2500$  m depth waters in the Central Equatorial Pacific, 5000 km downstream of the East Pacific Rise (EPR). These authors attributed their signal to depletion of  $^{230}\text{Th}$  from the water column by near-axis hydrothermal scavenging, and subsequent advection of the depletion signal westward towards their site.

Here we present dissolved and particulate  $^{230}\text{Th}$ ,  $^{231}\text{Pa}$ , and  $^{232}\text{Th}$  data from a hydrothermal plume in the South Pacific Ocean extending over 4000 km away from the EPR. We use the radioactive disequilibrium of these nuclides in the dissolved phase and enrichment in the particulate phase to understand the particle dynamics and scavenging behavior of trace metals in regions of intense hydrothermal activity.

## 2. Materials and methods

### 2.1. Cruise setting and sample collection

GEOTRACES cruise GP16 took place between Manta, Ecuador and Papeete, Tahiti aboard the RV Thomas G. Thompson between 25 October and 20 December 2013 (Fig. 1). Sampling for dissolved and particulate protactinium and thorium isotopes took place at 20 stations, 10 of which are downstream of the South East Pacific Rise (SEPR) ridge axis, and one of which (Station 18) lies directly above the ridge axis. The SEPR is one of the fastest-spreading ridge systems in the world, with a spreading rate of roughly  $14.5 \text{ cm yr}^{-1}$  (Feely et al., 1996). Hydrothermal activity along the SEPR is well-documented by anomalously high mantle-derived  $^3\text{He}$  ( $^3\text{He}_{\text{xs}}$ ) downstream of the ridge axis throughout the Pacific Basin (Lupton and Craig, 1981), as well as the areal extent of metalliferous sediments surrounding the ridge system (Boström et al., 1969). Along  $11\text{--}15^\circ\text{S}$ , independent lines of evidence point towards topographically-steered westward flow between 2000 and 3000 m depth above the ridge axis (Faure and Speer, 2012; Hautala and Riser, 1993; Reid, 1986), placing the GP16 stations west of the SEPR downstream of the hydrothermal activity along the ridge axis.

### 2.2. Sample collection and analysis

Radionuclide samples were collected according to standard GEOTRACES protocols (Anderson et al., 2012), then analyzed by two intercalibrated labs: Lamont-Doherty Earth Observatory of Columbia University (LDEO) and University of Minnesota (UMN). For dissolved samples, 4–5 l of seawater were filtered through a  $0.45 \mu\text{m}$  Acropak capsule filter at sea and acidified to  $\text{pH} = 2$  using 6 M hydrochloric acid. Particulate samples were collected with McLane Research Laboratories in-situ pumps, using a  $51 \mu\text{m}$  polyester screen to collect particles  $> 51 \mu\text{m}$ , followed by two stacked  $0.8 \mu\text{m}$  filters to collect small particles ( $0.8\text{--}51 \mu\text{m}$ ). Details of the sampling methodology for collecting particulate samples for radionuclide analysis can be found in Hayes et al. (2015a). The full procedure describing analysis of particulate samples for composition can be found in Lam et al. (this issue).

Download English Version:

<https://daneshyari.com/en/article/7698874>

Download Persian Version:

<https://daneshyari.com/article/7698874>

[Daneshyari.com](https://daneshyari.com)