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Hydrothermal vents: A previously unrecognized source of actinium-227 to the deep ocean

Lauren E. Kipp [a,b,*], Matthew A. Charette [b], Douglas E. Hammond [c], Willard S. Moore [d]

[a] Massachusetts Institute of Technology/Woods Hole Oceanographic Institution, Joint Program in Oceanography/Applied Ocean Science and Engineering, USA
[b] Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
[c] Department of Geological Sciences, University of Southern California, Los Angeles, CA 90089, USA
[d] Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA

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ABSTRACT

Actinium-227 ($t_{1/2} = 21.77$ y) is produced by decay of protactinium-231 ($t_{1/2} = 32{,}760$ y). Abyssal sediments are enriched in ^{231}Pa and thus provide a source of the more soluble ^{227}Ac to the deep-sea, where it can be used as a tracer of deep ocean diapycnal mixing. In this study, we examine the distribution of dissolved and particulate ^{227}Ac within a neutrally buoyant hydrothermal plume overlying the TAG vent field (26.14°N, 44.83°W, Mid-Atlantic Ridge) collected during the U.S. GEOTRACES North Atlantic Transect (2011). Elevated activities of both particulate and dissolved ^{227}Ac within the plume indicate that hydrothermal vents may be a previously unrecognized source of this isotope to the marine environment. We contend that vent fluids are the main source of the ^{227}Ac enrichment. Based on the activities of dissolved and particulate ^{227}Ac within the plume, a ^{3}He dilution model was used to derive a hydrothermal ^{227}Ac end-member activity of 1.5×10^4–2.5×10^4 dpm m^{-3}. Assuming that TAG is characteristic of all vents along the Mid-Atlantic Ridge, the hydrothermal source of ^{227}Ac to the deep Atlantic is estimated to be 1.9–5.8% of the flux from Atlantic sediments. Although this hydrothermal flux may not have a large impact on the total oceanic inventory of ^{227}Ac, it must be considered when using this isotope as a tracer of deep ocean mixing in areas where hydrothermal activity is present.

1. Introduction

The longest-lived isotope of actinium, ^{227}Ac ($t_{1/2} = 21.77$ y), is produced by the decay of ^{231}Pa ($t_{1/2} = 32{,}760$ y) in the ^{235}U decay series. Uranium-235 exhibits a long half-life ($t_{1/2} = 7.04 \times 10^8$ y) and fairly uniform oceanic distribution (Weyer et al., 2008), leading to constant production of ^{231}Pa throughout the water column. Because of its particle affinity, virtually all of the ^{231}Pa produced in the open ocean water column is scavenged onto particles and accumulates in sediments (Anderson et al., 1983). Actinium-227 is more soluble than its parent (Nozaki, 1993; Anderson, 1980), thus ^{227}Ac produced through the decay of sediment-bound ^{231}Pa is released to the overlying water column.

Although ^{227}Ac is in equilibrium with its parent ^{231}Pa in the upper water column, this sedimentary source results in activities in excess of ^{231}Pa extending up to several thousand meters from the sea floor (Nozaki, 1984; Geibert et al., 2002). Bottom water inventories of ^{227}Ac are therefore a function of decay of ^{231}Pa in sediments, ^{227}Ac release to bottom waters through diffusion and bioturbation, and vertical transport via diapycnal mixing processes (Nozaki, 1984; Nozaki et al., 1990). The sediment source of ^{227}Ac makes it a useful tracer of deep water mass mixing on time scales of about 100 y, both on its own and in tandem with ^{228}Ra, which has a similar sediment source (Nozaki, 1984; Nozaki and Yang, 1987). Observed open ocean profiles of ^{227}Ac exhibit an increase in excess ^{227}Ac (^{227}Ac$_{ex}$) with depth, with an average open ocean activity of 1.0 dpm m^{-3} ^{227}Ac$_{ex}$ (Nozaki, 1984; Geibert et al., 2002, 2008). The chemistry of Ac closely resembles that of lanthanum (La) due to similarities in their ionic radii and electron configuration (Kirby and Morss, 2011).

Hydrothermal systems exhibit conditions much different than the open ocean; the percolation of seawater through oceanic crust produces vent fluids that are reduced, acidic, and enriched in many trace elements and isotopes (Edmond et al., 1979, 1982; Campbell et al., 1988). Other elements such as uranium, which is tightly correlated with magnesium, are depleted in vent fluids (Michard et al., 1983; Seyfried et al., 2003). Recent evidence suggests that during the circulation of seawater through the crust, particle reactive ^{231}Pa is stripped out of the seawater and retained on mineral surfaces (Moore et al., 2008). High activities of ^{223}Ra (daughter of ^{227}Ac, $t_{1/2} = 11.4$ days) measured above the Puna Ridge, Hawaii, a site with low temperature hydrothermal circulation, suggest that ^{227}Ac is adsorbed onto mineral surfaces along with ^{231}Pa, which would allow for the buildup of ^{223}Ra that is needed to support the high observed ^{223}Ra activities

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* Corresponding author at: Massachusetts Institute of Technology/Woods Hole Oceanographic Institution, Joint Program in Oceanography/Applied Ocean Science and Engineering, USA.
E-mail address: lkipp@whoi.edu (L.E. Kipp).

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(Moore et al., 2008). Measurements of ^{227}Ac at this same region of low temperature circulation were not elevated compared to typical deep water activities (Geibert et al., 2008). However, there have been no previous studies of ^{227}Ac at high temperature vent sites, yet rare earth elements (REEs), which demonstrate similar seawater chemistry to Ac, can be enriched in hydrothermal fluids by factors of 10–10,000 above ambient seawater concentrations (Michard et al., 1983; Michard, 1989; Mitra et al., 1994).

Radionuclides like Th, as well as the REEs, are scavenged by the iron (Fe) oxyhydroxides present in hydrothermal plume particles (German et al., 1990, 1991). High activities of particulate ^{231}Pa have been observed on plume particles (Shimmield and Price, 1988; German et al., 1991; Hayes et al., 2015a, 2015b). Elevated concentrations of La, the closest chemical analog to Ac, have also been observed in neutrally buoyant plume particles (German et al., 1990; Sherrell et al., 1999; Edmonds and German, 2004), and REE:Fe ratios in metalliferous ridge crest sediments suggest that REEs are scavenged by Fe oxyhydroxides that settle out of the plume (Owen and Olivarez, 1988; Olivarez and Owen, 1989; German et al., 1997). Work by Sakamoto et al. (2002) suggests that Ac also has an affinity for Fe oxyhydroxides. Although the few existing measurements of particulate ^{227}Ac in the open ocean suggest that it is not particle reactive (Anderson, 1980; Geibert et al., 2002), Moore (1992) suggests that ^{227}Ac may be more particle reactive than Ra in particle-rich environments. In this study we examine the activities of both dissolved and particulate ^{227}Ac in a hydrothermal plume emanating from the high temperature TAG hydrothermal vent.

2. Methods

2.1. Sample collection

Samples were taken at station 16 of the US GEOTRACES North Atlantic Transect cruise, designated as GEOTRACES section GA03, which took place aboard the R/V Knorr from October- December 2011. This station (26.14°N, 44.83°W) was located directly above the TAG hydrothermal vent field (Fig. 1). The water depth at this station was 3635 m; the deepest sample was collected 35 m above the seafloor at 3600 m.

Suspended (1–51 μm) particles were collected via dual-flowpath in situ pumps (McLane WRT-LV) hung on a 3/8″ plastic coated Vectran line. Eight pumps were deployed on each of the casts (surface and deep), and were programmed to run for 4 h, pumping 1500–1700 L of seawater at an average flow rate of 6.5 L min^{-1}. Both flowpaths included 51 μm polyester mesh prefilters (Sefar 07–51/33) to collect sinking particles. The higher volume flowpath (typical filtered volume ~1100 L) was passed through paired 1 μm quartz fiber (Whatman QMA) filters while the lower volume flowpath (typical filtered volume ~500 L) was passed through paired 0.8 μm polyethersulfone (Pall Supor800) filters (see Lam et al., 2014 for more detailed pump filtration methods). The QMA filters were used to collect less contamination-prone trace elements and isotopes, including ^{234}Th ($t_{1/2} = 24.1$ days), and ^{227}Ac, while the Supor filters collected the more contamination-prone species, including ^{230}Th ($t_{1/2} = 7.5 \times 10^4$ y) and ^{231}Pa ($t_{1/2} = 3.28 \times 10^4$ y) (see Hayes et al., 2015a, 2015b for a more detailed description of ^{230}Th and ^{231}Pa sampling procedures). Each cast also included "dipped blank" filters, which were exposed to seawater for the entirety of the cast and analyzed following the same procedures as the samples in order to determine the seawater blank. After collection, QMA filters were dried at 50 °C for later analysis on shore.

Downstream of the QMA and Supor filter heads, the flowpaths were joined and passed through a grooved acrylic cartridge (3 M) impregnated with MnO_2 (see Henderson et al., 2013 for details of cartridge preparation) to collect dissolved Ra, Th, and Ac isotopes. After collection, cartridges were rinsed with Ra-free water and dried to 30–50% moisture using filtered compressed air. To determine the cartridge scavenging efficiency, smaller volume samples of ^{226}Ra (15–25 L) and ^{234}Th (4 L) were collected using a Niskin bottle mounted either on the CTD rosette (shallow cast) or above the pumps (deep cast), and the activities of Ra

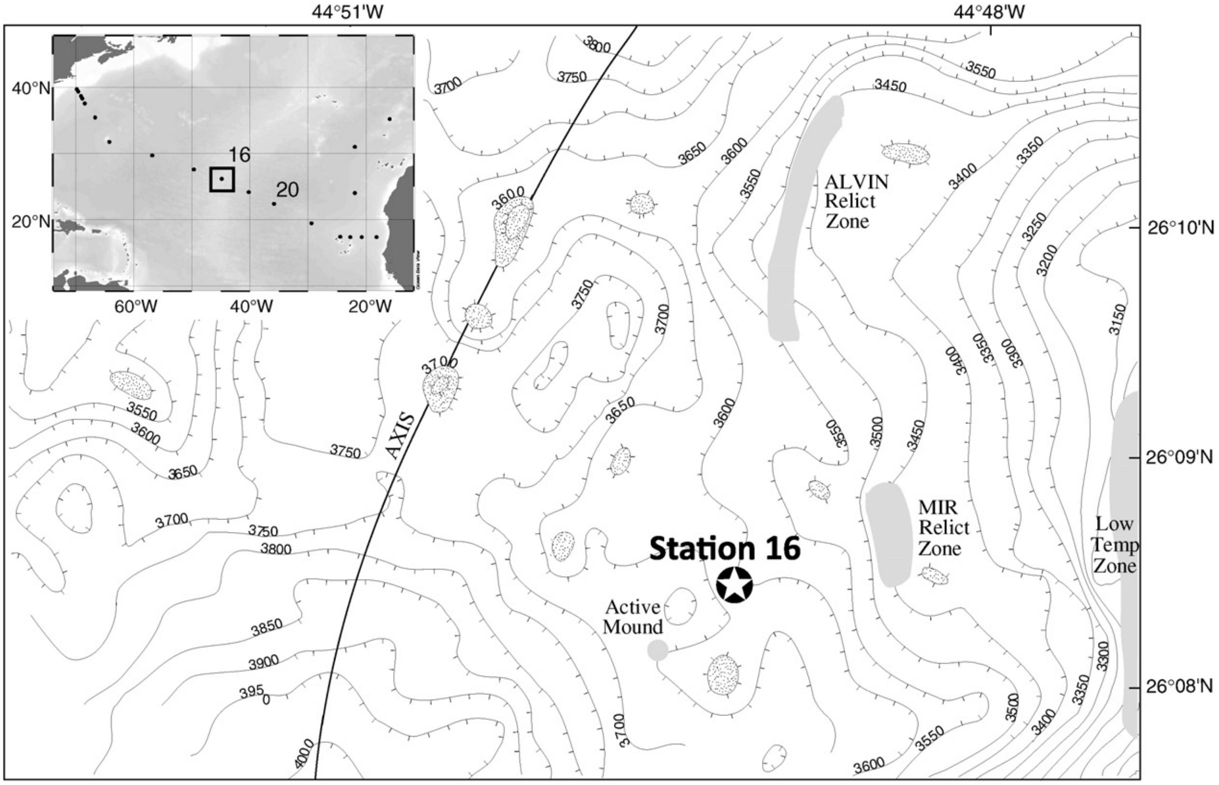

Fig. 1. Bathymetry of the TAG hydrothermal field, modified from White et al. (1998). The location of station 16 is highlighted with a star, and the inlayed map shows the location of all the stations occupied on the US GEOTRACES North Atlantic Transect.