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

Lauren E. Kipp^{1,2*}, Matthew A. Charette², Douglas E. Hammond³, and Willard S. Moore⁴

¹Massachusetts Institute of Technology/Woods Hole Oceanographic Institution
Joint Program in Oceanography/Applied Ocean Science and Engineering

²Department of Marine Chemistry and Geochemistry
Woods Hole Oceanographic Institution
Woods Hole, MA, 02543, USA

³Department of Geological Sciences
University of Southern California
Los Angeles, CA, 90089, USA

⁴Department of Earth and Ocean Sciences
University of South Carolina
Columbia, SC, 29208, USA

*Corresponding author
Email: lkipp@whoi.edu
Tel: 1-508-289-3236

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 ^3He dilution model was used to derive a hydrothermal ^{227}Ac end-member activity of $1.5 \times 10^4 - 2.5 \times 10^4$ 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.

KEYWORDS: actinium; hydrothermal; Mid-Atlantic Ridge; GEOTRACES

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., 1983a). 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 years, 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 ($^{227}\text{Ac}_{\text{ex}}$) with depth, with an average open ocean activity of $1.0 \text{ dpm m}^{-3} \text{ } ^{227}\text{Ac}_{\text{ex}}$ (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 , $t_{1/2}=11.4\text{ d}$) 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 (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,b). 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 (Figure 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 hours, 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 ($t_{1/2} = 24.1$ d), 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 and 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 (3M) 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 and Th measured on these samples were compared to those determined on the cartridges. The collection efficiency of Ac was not measured directly, however uptake efficiencies of Ra and Th on to MnO_2 coated fiber are similar to that of Ac (Reid et al., 1979), so the average of the Ra and Th uptake efficiency was used as the efficiency of ^{227}Ac collection at each depth. At station 16 this value ranged from 27.3% to 74.4% between 1500 and 3600 m (Table 1). On the recent US GEOTRACES East Pacific Zonal Transect (October-December 2013), all deep casts involved deployment of two cartridges in series to allow for the direct measurement of ^{227}Ac uptake efficiency; results show that the average efficiency is about 70%, similar to that for Ra and Th.

This also agrees well with the 69% cartridge scavenging efficiency for ^{227}Ac reported in Geibert et al. (2002). Furthermore, there is good agreement between ^{227}Ac and ^{231}Pa activities in regions where equilibrium between these two isotopes is expected (see Results), indicating that the use of Ra and Th efficiencies to calculate ^{227}Ac yields realistic results.

2.2 Particulate ^{227}Ac analysis

On shore, the upper filters from the QMA pairs were analyzed for ^{227}Ac using the Radium Delayed Coincidence Counter (RaDeCC) system (Moore and Arnold, 1996). We used a counting chamber designed for analysis of particulate ^{228}Th via RaDeCC (Maiti et al., 2015). This isotope was measured through its daughter, ^{223}Ra ($t_{1/2} = 11.4$ d), at least two months after sampling to allow for the development of secular equilibrium between ^{227}Ac and ^{223}Ra . We note that this method can detect adsorbed ^{227}Ac that can release ^{219}Rn ; this result should be considered a lower limit, as there may be an additional component tied up in phases that cannot release its radon daughter product. Samples were dampened with 5 mL of Milli-Q (Millipore) water, counted for approximately 24 hours, and then dried in a 55°C oven overnight. Counting efficiency was determined through standard addition of ^{227}Ac to a filter collected at 1200 m (14.00°N , 99.00°E) during the US GEOTRACES East Pacific Zonal Transect, and was found to be 30% on the detector used to count the station 16 samples.

2.3 Dissolved ^{227}Ac analysis

The RaDeCC system was also used to analyze the dissolved ^{227}Ac collected on the MnO_2 coated cartridges. First counts were taken on board the ship less than 24 hours after collection to measure the short-lived ^{223}Ra isotope. Cartridges were then counted again on shore to determine

the ^{227}Ac activity after allowing at least two months for secular equilibrium to develop between ^{227}Ac and ^{223}Ra . The counting efficiency of the RaDeCC system was determined using a set of cartridge standards as described in Henderson et al. (2013). Relative to traditional Mn fiber analysis, RaDeCC efficiencies for the Mn cartridge standards are 15% and ~40% lower for ^{224}Ra and ^{223}Ra , respectively. The lower efficiency for ^{224}Ra is expected based on the larger system volume when a cartridge holder is used; at present, we cannot fully explain the lower efficiency for ^{223}Ra though it may be a combination of the short half life of its ^{219}Rn ($t_{1/2}=4$ s) daughter, incomplete flushing of the full length of the cartridge by the He flow stream, and the kinetics of its release from the cartridge after it has recoiled following ^{223}Ra alpha decay.

3. RESULTS

The transmissometer data from station 16 show a dramatic increase in light attenuation between approximately 3200-3400 m, indicating that the cast was passing through the particle-rich neutrally buoyant plume originating from the TAG vent (Figure 2a). This is also supported by the profile of ^3He , a well-known tracer of hydrothermal activity (Jenkins et al., 1978), which indicates hydrothermal influence at this depth (Figure 2b) (Jenkins et al., 2014).

Profiles of dissolved and particulate ^{227}Ac show the highest activities at 3300-3400 m, corresponding to the depth of the neutrally buoyant plume (Figure 2c). Dissolved ^{227}Ac is reported as the excess ($^{227}\text{Ac}_{\text{ex}}$) of the ^{231}Pa activities measured at corresponding depths; consequently any non-zero value is ^{227}Ac unsupported by decay of its parent in the water column. Dissolved and particulate ^{231}Pa activities were measured by Hayes et al. (2015a, 2015b) and samples of dissolved ^{231}Pa were collected on a separate cast; hence, the depths of the dissolved ^{231}Pa and ^{227}Ac measurements are not exactly the same, but vary by less than 20 m in

all cases. Particulate ^{227}Ac exceeds the activity of its ^{231}Pa parent, and thus its source is not solely from the direct decay of particulate ^{231}Pa , but must also include dissolved ^{227}Ac that has been scavenged onto plume particles. The activities of dissolved and particulate ^{227}Ac and ^{231}Pa , as well as $\delta^3\text{He}$ values, are reported in Table 1.

The dissolved $^{227}\text{Ac}_{\text{ex}}$ activity reached $0.86 (\pm 0.19) \text{ dpm m}^{-3}$ and $0.98 (\pm 0.22) \text{ dpm m}^{-3}$ at 3301 m and 3401 m, respectively, while the particulate activity peaked at $0.14 (\pm 0.02) \text{ dpm m}^{-3}$ and $0.10 (\pm 0.02) \text{ dpm m}^{-3}$ at 3301 m and 3401 m, respectively.

The profiles of dissolved and particulate ^{231}Pa (Figure 3, ^{231}Pa data from Hayes et al., 2015a, 2015b) illustrate a decrease in dissolved ^{231}Pa with a concomitant increase in particulate ^{231}Pa in the plume. This pattern indicates that dissolved ^{231}Pa is not enriched in vent fluids but is being scavenged from the surrounding seawater onto plume particles, as has been observed previously for ^{231}Pa at the East Pacific Rise (Shimmield and Price, 1988). In contrast, the maxima of both the dissolved and particulate ^{227}Ac activities are observed within the core of the plume and are well in excess of its parent ^{231}Pa . Above the plume, the ^{227}Ac returns to secular equilibrium with its parent ^{231}Pa , and below the plume $^{227}\text{Ac}_{\text{ex}}$ is only slightly elevated.

4. DISCUSSION

Because of the increase in both dissolved and particulate ^{227}Ac at the depth of the plume, we contend that high temperature hydrothermal fluids are a source of ^{227}Ac to the deep ocean. In the absence of a hydrothermal source, we would expect the activity of ^{227}Ac to be in secular equilibrium with its parent, ^{231}Pa . A sedimentary flux of $^{227}\text{Ac}_{\text{ex}}$ is unlikely to produce the observed activities because the high activities of ^{231}Pa needed to support this excess not likely to be present in the relatively shallow ridge sediments (3000 m) relative to adjacent abyssal plain

sediments. Furthermore, if sediments were the only source, we would expect to see the highest concentrations close to the bottom. We hypothesize that during seawater circulation through the ridge, nearly all particle reactive ^{231}Pa will be adsorbed onto the basalt. Because ^{227}Ac has a lower particle affinity than ^{231}Pa , it can desorb from basalt surfaces and become dissolved in the circulating hydrothermal fluids. In addition, some ^{227}Ac may be released from the solid phase due to alpha recoil or weathering. The Ac-enriched fluids are then vented back in to the deep ocean, causing the observed peak in dissolved $^{227}\text{Ac}_{\text{ex}}$. As the plume rises, metal-rich particles form and scavenge a fraction of the dissolved ^{227}Ac from both the vent fluids and the surrounding seawater, leading to the peak in particulate ^{227}Ac observed in the plume. As plume particles settle out over the ridge, ^{227}Ac -rich metalliferous sediments become a source of ^{223}Ra to bottom waters.

4.1 Particulate ^{227}Ac in the neutrally buoyant hydrothermal plume

Within the plume, particulate ^{227}Ac makes up 8-12% of the total dissolved ^{227}Ac . The K_d of Ac has been reported to be on the order $\sim 10^5$, which is ten times less than that of Pa and 100 times less than that of Th (Nozaki, 1993; Anderson et al., 1983a; Bacon and Anderson, 1982). In the open ocean, Geibert et al. (2002) found particulate ^{227}Ac to be less than 1.7% of total ^{227}Ac . The scavenging of ^{227}Ac in the plume is similar to the partitioning of La, Ac's closest chemical analogue; particulate La concentrations in the TAG plume have been observed to be up to 14% of ambient seawater dissolved concentrations (German, 1990). Two factors probably cause the particulate fraction of Ac to be larger than in other deep sea settings. One is the higher concentration of particulates in the plume, as indicated by the scattering (Fig. 2). The second factor is the nature of the particulates. The plume particulates are rich in Fe oxyhydroxides,

which have been shown to scavenge trace elements including Th and REEs (Trocine and Trefry, 1988; German et al., 1990, 1991; Klinkhammer et al., 1983, 1994; Mitra et al., 1994). Iron oxyhydroxides account for about half of the suspended particulate material within this neutrally buoyant plume (Lam et al., 2014). The fraction of particulate Ac actually represents a lower limit, because our analytical method only captures the surface bound ^{227}Ac . The difference between the measured and actual activity of particulate ^{227}Ac would depend in part on how much ^{227}Ac is co-precipitated relative to the adsorbed fraction.

4.2 Near bottom ^{227}Ac and ^{223}Ra over the Mid Atlantic Ridge: evidence for ^{227}Ac enrichment in metalliferous sediments

Typical profiles of $^{227}\text{Ac}_{\text{ex}}$ demonstrate an increase in activity with depth (Geibert et al., 2002), but at this station the activity is only $0.20 (\pm 0.07) \text{ dpm m}^{-3}$ near the bottom of the profile (35 m above the seafloor). Here, the presence of Fe-rich metalliferous sediments (German et al., 1993) could inhibit the release of ^{227}Ac from the benthos but at the same time be a source of ^{223}Ra over the ridge. Moore et al. (2008) hypothesized that ^{231}Pa becomes adsorbed on to basalt during the low temperature circulation of seawater through the Puna Ridge, where it can decay to ^{223}Ra and support elevated activities of ^{223}Ra above the ridge. While it is likely that there is a peak of $^{223}\text{Ra}_{\text{xs}}$ at the depth of the TAG plume, it is obscured by a strong bottom source of $^{223}\text{Ra}_{\text{xs}}$ at this station (Charette et al., 2015; Figure 4). This is in contrast to $^{224}\text{Ra}_{\text{xs}}$, which exhibits elevated activities in the plume and is depleted relative to $^{223}\text{Ra}_{\text{xs}}$ at the bottom of the cast (Charette et al., 2015).

The high $^{223}\text{Ra} : ^{224}\text{Ra}$ activity ratio at the bottom of the cast suggests that sediments may be enriched ^{227}Ac , the parent of ^{223}Ra . If diffusion from sediments is the only source of ^{223}Ra and

^{224}Ra to the bottom water below the plume, then the ratio of their water column inventory can be related to their production rates in the sediments (Colbert and Hammond, 2008):

$$\frac{J_{223}}{J_{224}} = \frac{E_{223}}{E_{224}} \sqrt{\frac{\lambda_{224}}{\lambda_{223}}} \quad (1)$$

where J is bottom water inventory or standing crop (dpm m^{-2}), E is the emanation rate of the parent isotope in the sediments ($\text{dpm m}^{-2} \text{ min}^{-1}$) and λ is the decay constant (min^{-1}). Assuming the samples collected below 3500 m are not affected by the hydrothermal plume, integrating the inventories of ^{223}Ra and ^{224}Ra between 3500 m and the seafloor (3635 m) yields an observed $^{223}\text{Ra}:^{224}\text{Ra}$ ratio of 12.4. Rearranging equation (1) to solve for the emanation rate $^{223}\text{Ra}:^{224}\text{Ra}$ ratio in the sediments results in a ratio of 7.0. Typical Mid Ocean Ridge basalts have a $^{231}\text{Pa}:^{232}\text{Th}$ activity ratio of 0.08-0.15 (Bourdon et al., 2000) and the plume particles have a ratio of 0.07-0.10 (computed for data from 3300-3400 m at Station 16 in Hayes et al., 2015b); the upper limit value is approximately 47 times lower than we observed at this station. We suggest that the sediments are enriched in ^{227}Ac , resulting in this unusually high $^{223}\text{Ra}:^{224}\text{Ra}$ activity ratio in the bottom water. Sediments surrounding the TAG mound show REE distributions similar to those in the neutrally buoyant plume, indicating that particles settling out of the plume strongly influence the sediment composition in this region (German et al., 1993). Furthermore, it has been shown that REEs are scavenged by Fe oxyhydroxides in metalliferous ridge crest sediments (Owen and Olivarez, 1988; Olivarez and Owen, 1989; German et al., 1997), and an affinity of ^{227}Ac for Fe oxyhydroxides has previously been noted by Sakamoto et al. (2002). Thus, similar to La, ^{227}Ac settling out of the plume, as well as the ^{227}Ac scavenged by Fe oxyhydroxide rich sediments, can lead to a buildup of this isotope in sediments surrounding TAG and presumably

other vent fields along the Mid-Atlantic Ridge. Radium does not have a strong affinity for Fe oxides (Moore and Reid, 1973; Beck and Cochran, 2013) and Mn oxides are a minor component of the plume particles (Lam et al., 2014), so as the sediment reserve of ^{227}Ac decays, ^{223}Ra is released to bottom waters through diffusion resulting in the high observed $^{223}\text{Ra}:$ ^{224}Ra ratio.

4.3 Estimating the high temperature fluid activity and potential hydrothermal contribution of ^{227}Ac to the deep ocean

Because ^3He is a conservative tracer of hydrothermal activity (Lupton et al., 1977, 1980; Jenkins et al., 1978), the $^3\text{He}/^4\text{He}$ ratio within the neutrally buoyant plume can be used to calculate the dilution factor of hydrothermal fluids and trace element concentrations of end-member vent fluids (e.g. Rudnicki and Elderfield, 1992). The air-normalized $^3\text{He}/^4\text{He}$ ratio (R^*) can be calculated from the helium isotope ratio anomaly ($\delta^3\text{He}$) using Equation (2):

$$R^* = \frac{\delta^3\text{He}}{100} + 1 \quad (2)$$

$\delta^3\text{He}$ was measured at this station by Jenkins et al. (2014), and was $16.8 \pm 0.1\%$ at 3384 m. This most closely matches the depth where the peak in ^{227}Ac is seen, however $\delta^3\text{He}$ is actually highest at 3183 m, reaching $24.4 \pm 0.1\%$, indicating the strongest hydrothermal influence at this depth (Figure 2). The slight depth difference between the peaks in ^{227}Ac activity and $\delta^3\text{He}$ may be because these two species were sampled on separate casts and there was lower sampling resolution for ^{227}Ac around the plume. Short-term fluctuations in plume height and structure are reflected in cast-to-cast differences in the depth of peak particle concentration; the transmissometer on cast 1 recorded the most light attenuation at 3380 m, which more closely

correlates to the peak in Ac, while the transmissometer on cast 2 (which sampled ^3He) indicated the most attenuation at 3200 m. We therefore used $\delta^3\text{He}$ values from both 3400 m and 3200 m in our calculations to represent the range of possible results.

The air-normalized $^3\text{He}/^4\text{He}$ ratio in the neutrally buoyant plume, R_{plume}^* , was calculated to be 1.17 ± 0.01 at 3400 m and 1.24 ± 0.01 at 3200 m. Assuming surrounding deep water is in equilibrium with the atmosphere, the ratio in ambient seawater, R_{sw}^* , equals 1. Because the ratio in vent fluids, R_{h}^* , was not measured on this cruise, we used a value of 7.5 ± 0.9 for TAG from Rudnicki and Elderfield (1992). Assuming an approximately linear relationship between R^* and $[^{227}\text{Ac}]$, Equation (3) relates the change in R^* to the change in $[^{227}\text{Ac}]$ (modified from Rudnicki and Elderfield, 1992):

$$G = \frac{R_{\text{plume}}^* - R_{\text{sw}}^*}{[^{227}\text{Ac}]_{\text{plume}} - [^{227}\text{Ac}]_{\text{sw}}} \quad (3)$$

where $[^{227}\text{Ac}]_{\text{plume}}$ is the activity of dissolved ^{227}Ac in the neutrally buoyant plume, and $[^{227}\text{Ac}]_{\text{sw}}$ is the activity of dissolved ^{227}Ac in ambient seawater that may become entrained in the plume. The peak of dissolved ^{227}Ac (supported plus unsupported) in the plume was $1.27 \pm 0.22 \text{ dpm m}^{-3}$ at 3401 m, and dissolved ^{227}Ac in near-bottom seawater was $0.50 \pm 0.07 \text{ dpm m}^{-3}$ (3600 m). Equation (3) was then substituted in to Equation (4) (Rudnicki and Elderfield, 1992) to estimate the activity of ^{227}Ac in the hydrothermal end-member ($[^{227}\text{Ac}]_{\text{h}}$).

$$[^{227}\text{Ac}]_{\text{h}} = \frac{\chi_{\text{h}}(R_{\text{h}}^* - R_{\text{sw}}^*)}{1.08G} \quad (4)$$

In this expression, χ_h represents the ratio of ^4He in the end-member vent fluids to ^4He in ambient seawater. This ratio was not directly measured on this cruise, so we used a value of 793 ± 85 calculated by Rudnicki and Elderfield (1992) for TAG. Rudnicki and Elderfield (1992) found that calculating χ_h yielded a value that underestimated the true χ_h by 3-13%, so they introduced a correction factor of 1.08 to this equation to redistribute the error to $\pm 5\%$.

Using these equations and the range in R_{plume}^* discussed above, we estimated the activity of ^{227}Ac in end-member vent fluids to be approximately $1.5 \times 10^4 - 2.2 \times 10^4 \text{ dpm m}^{-3}$. By comparing the activity of ^{227}Ac to the conservative tracer ^3He , we are assuming that ^{227}Ac is also behaving conservatively once released to the water column. Although Y has shown conservative behavior during mixing of vent fluids with ambient seawater (Bau and Dulski, 1999), the REEs including La typically are non-conservative and display continuous scavenging on to Fe-oxyhydroxides as the plume disperses (German et al., 1990; Bau and Dulski, 1999). The peak in particulate ^{227}Ac in the neutrally buoyant plume indicates that Ac behaves similarly to the REEs and is also scavenged such that some of the dissolved ^{227}Ac initially present in the vent fluids was lost to the particulate phase. If we assume that all of the particulate ^{227}Ac in the neutrally buoyant plume was originally vented as dissolved ^{227}Ac , the end-member ^{227}Ac activity would be higher ($1.7 \times 10^4 - 2.5 \times 10^4 \text{ dpm m}^{-3}$). Because this calculation does not account for any ^{227}Ac that may have been removed from the plume on particles that are eventually deposited as metalliferous sediments, this endmember activity represents a minimum estimate. We do not consider any loss of ^{227}Ac due to decay, as the age of the neutrally buoyant hydrothermal plume is on the order of days (Rudnicki and Elderfield, 1992) to weeks (based on the fact that the short-lived Ra isotopes are still measureable at the peak of the plume). Hence, over these time scales the decay of ^{227}Ac is not significant.

To determine the potential impact of hydrothermal ^{227}Ac inputs on deep Atlantic Ocean ^{227}Ac inventories, we first need to estimate the hydrothermal fluid flux along the full length of the Mid-Atlantic Ridge (MAR). Slow and ultra-slow spreading ridges like the MAR make up 30,000 km of the global ridge-crest (Sinha and Evans, 2004); here we assumed that the MAR extends from 60°N to 50°S or 12,000 km, equivalent to 40% of slow and ultra slow spreading ridges. The high-temperature fluid flux from these systems is estimated to be $4 \times 10^{12} \text{ kg y}^{-1}$ (German et al., 2010), therefore by this approach we estimate that the flux from the MAR is about $1.6 \times 10^{12} \text{ kg y}^{-1}$. Alternatively, we can estimate this flux by extrapolating the fluid flux of the well-characterized Rainbow hydrothermal vent system. Although vents along slow-spreading ridges are thought to occur every 100 km (Baker et al., 2004), large, tectonically hosted systems like TAG and Rainbow are more likely to occur once every 200 km (German et al., 2010); our estimated length of the MAR then predicts the occurrence of 60 large hydrothermal vents. If each of these vents had a volume flux equal to that of Rainbow ($1.42 \times 10^{10} \text{ kg y}^{-1}$, German et al., 2010), then the high-temperature water flux along the MAR is approximately $8.5 \times 10^{11} \text{ kg y}^{-1}$, which agrees within a factor of two of the previous estimate. Assuming that the hydrothermal fluid flux along the MAR is $8.5 \times 10^{11} - 1.6 \times 10^{12} \text{ kg y}^{-1}$ and that an end-member activity of $1.5 \times 10^4 - 2.5 \times 10^4 \text{ dpm } ^{227}\text{Ac m}^{-3}$ is typical for vents on this ridge, we estimate that the hydrothermal source of ^{227}Ac will contribute $1.2 \times 10^{13} - 3.9 \times 10^{13} \text{ dpm y}^{-1}$ to the deep Atlantic.

As explained above, the only previously recognized source of $^{227}\text{Ac}_{\text{ex}}$ to the deep ocean was the flux from sediments (Nozaki, 1984; Geibert et al., 2002, 2008). Geibert et al. (2008) estimated the global average flux of $^{227}\text{Ac}_{\text{ex}}$ to be $127 \text{ dpm m}^{-2} \text{ y}^{-1}$ by multiplying an average deep ocean $^{227}\text{Ac}_{\text{ex}}$ activity of 1 dpm m^{-3} by the volume of the oceans and assuming this inventory to be supported solely by the flux from sediments. Here, we take a similar approach in

order to compare the relative magnitude of the hydrothermal and sediment sources of $^{227}\text{Ac}_{\text{ex}}$ in the Atlantic basin. The inventory of $^{227}\text{Ac}_{\text{ex}}$ supported by release from sediments was determined from measurements taken at station 20 of the US GEOTRACES North Atlantic Transect, which was in the eastern Atlantic basin (22.34°N, 35.87°W), and did not show any obvious signs of hydrothermal influence based on the transmissometry and $\delta^3\text{He}$ profiles (Figure 5; ^3He data from Jenkins et al., 2014). Excess ^{227}Ac was calculated by subtracting dissolved ^{231}Pa activities from dissolved ^{227}Ac activities. Because $^{227}\text{Ac}_{\text{ex}}$ released from sediments does not typically mix more than 3000 m from the seafloor (Geibert et al., 2008), we used the activities of $^{227}\text{Ac}_{\text{ex}}$ below 1500 m at station 20 to calculate the total integrated $^{227}\text{Ac}_{\text{ex}}$ supported by sediment release. This resulted in an inventory of roughly 300 dpm m^{-2} , which was multiplied by the area of the Atlantic below 3000 m, $69.7 \times 10^6 \text{ km}^2$ (Duxbury and Duxbury, 1991). This depth was chosen because $^{227}\text{Ac}_{\text{ex}}$ is mainly restricted to the deep ocean (Nozaki et al., 1984; Geibert et al., 2002). This calculation yielded an inventory of $2.1 \times 10^{16} \text{ dpm}$, which was then multiplied by the decay constant of ^{227}Ac , 0.0318 y^{-1} , to give a sediment flux of $6.6 \times 10^{14} \text{ dpm y}^{-1}$. Thus, our estimate of the hydrothermal flux of ^{227}Ac is 1.9 – 5.8% of the sediment flux in the Atlantic.

Previous studies have used ^{227}Ac as a tracer for diapycnal mixing in the deep ocean by assuming that there is a single source of $^{227}\text{Ac}_{\text{ex}}$ at the seafloor (Nozaki, 1984; Geibert et al., 2002). Given our evidence that hydrothermal vents are a source of ^{227}Ac to the ocean, the use of ^{227}Ac as a tracer of near-bottom mixing in areas near hydrothermal activity must be carefully evaluated. This hydrothermal source may lead to new applications of ^{227}Ac in hydrothermal systems, such as constraining the residence time of circulating fluids in the crust.

5. CONCLUSIONS

Profiles of particulate and dissolved ^{227}Ac in the neutrally buoyant TAG hydrothermal plume indicate that hydrothermal vents are a source of this element to the deep ocean. The activity of particulate ^{227}Ac in the plume was 8-12% of the activity of total dissolved ^{227}Ac , indicating moderate scavenging on to Fe-oxyhydroxide rich plume particles. The hydrothermal endmember activity of ^{227}Ac was estimated to be $1.5 \times 10^4 - 2.5 \times 10^4 \text{ dpm m}^{-3}$, which, if multiplied by our estimate of the hydrothermal fluid flux along the Mid-Atlantic Ridge, is approximately 1.9 – 5.8% of the ^{227}Ac flux from Atlantic sediments. While this hydrothermal source may not have a significant impact on the ^{227}Ac inventory in the ocean, it will complicate the use of this isotope as a tracer of deep ocean diapycnal mixing in regions where hydrothermal activity is present.

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Table 1. Data collected from cast 3 (pumps) and cast 2 (bottles) at U.S. GEOTRACES North Atlantic station 16. Cartridge scavenging efficiencies for Ra and Th were calculated as described in Section 2.1. Errors on Ac activities are propagated from 1 σ counting errors. “nd” indicates that no data were collected at this depth; “bdl” indicates that the activity is below detection. ¹Protactinium-231 data from Hayes et al., 2015a, 2105b. ²Helium-3 data from Jenkins et al., 2014.

Pump depth (m)	Ra cartridge scavenging efficiency	Th cartridge scavenging efficiency	Total dissolved ²²⁷ Ac (dpm m ⁻³)	Particulate ²²⁷ Ac (dpm m ⁻³)	Particulate ²²⁷ Ac (dpm m ⁻³)
1500.9	0.38 ± 0.02	0.40 ± 0.01	0.25 ± 0.04	0.013 ± 0.005	0.0014 ± 0.0005
2100.9	0.78 ± 0.03	0.72 ± 0.03	0.46 ± 0.06	0.035 ± 0.010	0.0031 ± 0.0010
3001.4	0.73 ± 0.02	0.58 ± 0.01	0.79 ± 0.15	0.045 ± 0.011	0.0106 ± 0.0035
3301.4	0.74 ± 0.03	0.61 ± 0.02	1.16 ± 0.19	0.143 ± 0.020	0.0345 ± 0.0050
3401.4	0.30 ± 0.01	0.25 ± 0.01	1.27 ± 0.22	0.106 ± 0.017	0.0201 ± 0.0030
3504.9	0.43 ± 0.02	0.41 ± 0.02	0.73 ± 0.09	0.067 ± 0.013	0.0079 ± 0.0013
3600.0	0.67 ± 0.03	0.59 ± 0.01	0.50 ± 0.07	0.035 ± 0.009	0.0060 ± 0.0010

Bottle depth (m)	Dissolved ²³¹ Pa ¹ (dpm m ⁻³)	$\delta^3\text{He}^2$ (%)	Nominal depth (m)	Dissolved ²²⁷ Ac _{ex} (dpm m ⁻³)
1492.8	0.284 ± 0.018	6.54 ± 0.14	1500	bdl
1793.2	nd	7.30 ± 0.14	2100	0.17 ± 0.06
2092.5	0.289 ± 0.016	6.23 ± 0.14	3000	0.49 ± 0.15
2690.4	nd	5.77 ± 0.14	3300	0.86 ± 0.19
2986.6	0.287 ± 0.013	6.35 ± 0.14	3400	0.98 ± 0.22
3183.8	0.247 ± 0.008	24.38 ± 0.14	3500	0.42 ± 0.09
3283.9	0.261 ± 0.011	22.48 ± 0.14	3600	0.20 ± 0.07
3383.8	0.273 ± 0.012	16.79 ± 0.14		
3487.4	0.298 ± 0.006	6.09 ± 0.14		
3605.3	0.297 ± 0.012	4.66 ± 0.14		

Table 2. Data collected from cast 7 (pumps) and casts 4 and 9 (bottles) at U.S. GEOTRACES North Atlantic station 20. Cartridge scavenging efficiencies for Ra and Th were calculated as described in Section 2.1. Errors on Ac activities are propagated from 1 σ counting errors. “nd” indicates that no data were collected at this depth; “bdl” indicates that the activity is below detection. ¹Protactinium-231 data from Hayes et al., 2015a, 2105b. ²Helium-3 data from Jenkins et al., 2014.

Pump depth (m)	Ra cartridge scavenging efficiency	Th cartridge scavenging efficiency	Total dissolved ²²⁷ Ac (dpm m ⁻³)	Particulate ²³¹ Pa ¹ (dpm m ⁻³)
1060.4	0.35 ± 0.01	0.53 ± 0.04	0.16 ± 0.04	0.0018 ± 0.0002
2300.4	0.46 ± 0.07	0.69 ± 0.06	0.40 ± 0.08	0.0029 ± 0.0003
3500.4	0.48 ± 0.02	0.51 ± 0.02	0.43 ± 0.06	0.0024 ± 0.0002
4701.4	0.51 ± 0.03	0.55 ± 0.04	0.34 ± 0.05	0.0023 ± 0.0002
5266.4	0.55 ± 0.02	0.45 ± 0.03	0.81 ± 0.10	0.0036 ± 0.0003
5316.4	0.99 ± 0.15	0.59 ± 0.04	1.28 ± 0.23	0.0038 ± 0.0003
5370.9	0.99 ± 0.05	0.66 ± 0.05	1.41 ± 0.17	0.0043 ± 0.0004
5420.2	0.43 ± 0.01	0.43 ± 0.01	0.95 ± 0.10	0.0041 ± 0.0004

Bottle depth (m)	$\delta^3\text{He}^2$ (%)	Bottle depth (m)	Dissolved ²³¹ Pa ¹ (dpm m ⁻³)	Nominal depth (m)	Dissolved ²²⁷ Ac _{ex} (dpm m ⁻³)
1195	2.74 ± 0.14	1055.2	0.278 ± 0.005	1060	bdl
1493.7	2.30 ± 0.14	2288.6	0.470 ± 0.009	2300	bdl
1888.6	1.62 ± 0.14	3482.5	0.418 ± 0.008	3500	0.005 ± 0.001
2288.6	2.00 ± 0.14	4675.6	0.336 ± 0.007	4700	0.003 ± 0.001
2685.6	2.16 ± 0.14	5253.5	0.303 ± 0.005	5265	0.507 ± 0.078
3084.4	2.52 ± 0.14	5303.6	0.281 ± 0.005	5315	0.995 ± 0.202
3482.5	2.79 ± 0.14	5375.5	0.290 ± 0.005	5370	1.118 ± 0.165
4281.7	3.05 ± 0.14	5435.3	0.289 ± 0.005	5420	0.658 ± 0.094
4675.6	3.00 ± 0.14				
5077.6	3.43 ± 0.14				
5768.1	3.67 ± 0.14				

FIGURE CAPTIONS

Figure 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.

Figure 2. Profiles of (a) light transmission, (b) $\delta^3\text{He}$, and (c) dissolved $^{227}\text{Ac}_{\text{ex}}$ and particulate ^{227}Ac at station 16. ^{227}Ac and ^3He were sampled on casts 2 and 3, respectively; light transmission from cast 2 is shown.

Figure 3. Activities of dissolved and particulate ^{227}Ac and ^{231}Pa at the depths influenced by the TAG hydrothermal plume. ^{231}Pa data from Hayes et al., 2015a, 2015b. Excess ^{227}Ac is the difference between dissolved ^{227}Ac and dissolved ^{231}Pa .

Figure 4. Excess ^{223}Ra at station 16. The deepest sample collected was 35 m above the seafloor.

Figure 5. Profiles of (a) light transmission, (b) $\delta^3\text{He}$, and (c) dissolved ^{227}Ac and ^{231}Pa at station 20, a location with no significant hydrothermal influence. ^{231}Pa data from Hayes et al., 2015a, 2015b. Excess ^{227}Ac is the difference between dissolved ^{227}Ac and dissolved ^{231}Pa . See Figure 1 for location of station 20 relative to station 16.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5