Marine Chemistry xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Marine Chemistry

journal homepage: www.elsevier.com/locate/marchem

Radium isotopes as tracers of hydrothermal inputs and neutrally buoyant plume dynamics in the deep ocean

Lauren E. Kipp[a,b,*], Virginie Sanial[b], Paul B. Henderson[b], Pieter van Beek[c], Jean-Louis Reyss[d], Douglas E. Hammond[e], Willard S. Moore[f], Matthew A. Charette[b]

[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] Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (CNRS/CNES/IRD/UPS) Observatoire Midi Pyrénées, 14 Avenue Edouard Belin, 31400 Toulouse, France
[d] Laboratoire des Sciences du Climat et de l'Environnement, Université de Versailles Saint-Quentin CEA-CNRS, avenue de la terrasse, 91198 Gif-sur-Yvette Cedex, France
[e] Department of Earth Sciences, University of Southern California, Los Angeles, CA 90089, USA
[f] Department of Earth and Ocean Sciences, University of South Carolina, Columbia, SC 29208, USA

ARTICLE INFO

Keywords:
Radium
Hydrothermal
GEOTRACES
Iron

ABSTRACT

Radium (Ra) isotopes are enriched in hydrothermal fluids, have a wide range of half-lives and are minimally impacted by scavenging removal processes; therefore, they have the ability to provide key information on the fate of trace elements in both near- and far- field hydrothermal plumes. To expand our understanding of Ra isotopes and their usefulness as tracers of hydrothermal activity, we measured Ra isotopes in both high and low temperature vent fluids, and in neutrally buoyant plumes. The time scales of plume transport were derived from Ra isotopes in neutrally buoyant plumes emanating from 15°S on the East Pacific Rise (EPR) and the TAG vent field on the Mid Atlantic Ridge (MAR) relative to their source ratio in high-temperature vent fluids. In near-field (< 100 km from vent) neutrally buoyant plumes, the short-lived Ra isotopes (^{223}Ra: $t_{1/2}$ = 11.4 d, ^{224}Ra: $t_{1/2}$ = 3.66 d) suggest plume ages of ~1 month and ~5 d over the EPR and MAR, respectively. Farther afield (> 100 km from vent), the distribution of the longer-lived ^{228}Ra ($t_{1/2}$ = 5.75 y) is indicative of hydrothermal plumes with different points of origin along the EPR. Radium-228 derived plume ages were used to calculate the residence time of hydrothermal dissolved Fe, which was in the range of 9–20 y (with an upper limit of 50 y depending on model assumptions). These are shorter than typical deep ocean Fe residence times, a result of scavenging removal of Fe from the neutrally buoyant plume during transport. This study highlights the utility of Ra isotopes in providing time-scales of hydrothermally derived trace element cycling in the deep ocean.

1. Introduction

Since their discovery in 1977, seafloor hydrothermal vents have been recognized as important sources and sinks for elements in the deep ocean (Corliss et al., 1978; Edmond et al., 1979). During the hydrothermal circulation of seawater through the crust, water-rock reactions enrich circulating fluids in certain metals, gases, and radionuclides (Campbell et al., 1988; Edmond et al., 1982; Jenkins et al., 1978; Kadko and Moore, 1988; Von Damm et al., 1985). Radionuclide enrichment processes include the alteration of basalt by hydrothermal fluids, in-situ decay of parent isotopes, and recoil effects from the decay of parents in the basalt (Hammond et al., 1988; Kadko and Moore, 1988; Krishnaswami et al., 1982). These properties have been used to constrain the time scales of processes such as the circulation of fluids through the crust, formation of chimneys, and particle scavenging and settling rates (see Kadko, 1996 for a review).

In the case of radium isotopes, elevated activities of ^{228}Ra ($t_{1/2}$ = 5.75 y) and ^{226}Ra ($t_{1/2}$ = 1600 y) have been observed in high-temperature hydrothermal fluids of the Mid-Atlantic Ridge (MAR; Rudnicki and Elderfield, 1992), and the Endeavour Segment (Kadko and Moore, 1988) and Cleft Segment (Kadko, 1996) of the Juan de Fuca Ridge (JDFR). As high-temperature, low-pH modified seawater interacts with basalt, Ra may be released into the circulating fluids. The activity observed in vented fluids is determined by fluid residence time, circulation depth in the crust, and composition of the host rock.

For example, the activity ratio of ^{228}Ra/^{226}Ra has been used to measure fluid crustal residence times (e.g. Kadko and Moore, 1988; Kadko et al., 2007). Because they are solubilized during basalt

* Corresponding author at: Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA
E-mail address: lkipp@whoi.edu (L.E. Kipp).

http://dx.doi.org/10.1016/j.marchem.2017.06.011
Received 14 December 2016; Received in revised form 16 June 2017; Accepted 23 June 2017

alteration, radium isotopes are useful in constraining the time elapsed between the onset of high-temperature basalt-seawater interaction and venting at the seafloor. The half-life of ^{228}Ra makes it an appropriate tracer for this process, which has been estimated to occur on time scales of < 5 y. Normalizing the activity of ^{228}Ra to the long-lived ^{226}Ra corrects for any secondary chemical reactions or removal processes that may occur during circulation (Kadko and Moore, 1988; Kadko et al., 2007).

There have been fewer studies involving the short-lived isotopes ^{223}Ra ($t_{1/2}$ = 11.4 d) and ^{224}Ra ($t_{1/2}$ = 3.66 d) in hydrothermal systems. Moore et al. (2008) observed activities of ^{223}Ra well in excess of its parent ^{227}Ac ($t_{1/2}$ = 21.8 y) above the Puna Ridge (Hawaii, USA), a site with low-temperature hydrothermal activity, and used the inventory of this isotope to quantify the fluid flux through the ridge. They proposed that excess ^{223}Ra may be useful in assessing the relative importance of low-temperature hydrothermal venting to ocean chemistry. Kadko et al. (2007) used the ^{224}Ra/^{223}Ra activity ratios in fluids in the Reykjanes hydrothermal system to conclude that mixing and secondary precipitation reactions during upwelling were minimal, which permitted a tighter constraint on the water-rock ratio in the Reykjanes system.

Above hydrothermally active ridges, neutrally buoyant plumes are an important source of trace elements and isotopes (TEIs) to the deep ocean (e.g. Lilley et al., 1995). The scavenging and oxidation processes that occur within the plume can affect the concentrations of TEIs that are eventually delivered farther afield (Edmond et al., 1979; German et al., 1991a, 1991b; German et al., 1990). Therefore, in order to understand the ultimate impact of hydrothermal vents on deep ocean chemistry, it is important to constrain neutrally buoyant plume transport rates away from the ridge as well as the removal rates of TEIs from the plume.

In the past, ^{222}Rn has been used to estimate spreading rates of neutrally buoyant plumes; using this method Rudnicki and Elderfield (1992) found that plume material sampled 1 km away from the TAG hydrothermal vent field was 1–10 d old. The half-lives of ^{223}Ra and ^{224}Ra, being similar to that of ^{222}Rn, make these isotopes another possible tool for dating young (days–months) plume material. For older plumes (years–decades), ^{228}Ra can be used in a similar manner. In both applications, the Ra isotope is normalized to either a longer-lived Ra isotope (e.g. ^{226}Ra) or a conservative tracer (e.g. ^{3}He) in order to correct for the effects of dilution such that any decrease in Ra activity is primarily due to decay. Most importantly, these Ra ages can be applied to determine the transport rates and residence times of trace metals in the plume.

Here we add to and review measurements of the Ra quartet in both high and low temperature vent fluids. We then combine the measurements of Ra in high-temperature hydrothermal vent fluids with recent measurements of the Ra quartet in neutrally buoyant plumes over the East Pacific Rise (EPR) and MAR to investigate the utility of Ra isotopes as tracers of hydrothermal plume dynamics.

2. Methods

2.1. Sample collection

Samples of the Trans Atlantic Geotraverse (TAG) neutrally buoyant plume were collected aboard the *R/V Knorr* at Station 16 of the 2011 US GEOTRACES North Atlantic Transect (GA03; 26.136 N, 44.826 W), 0.15 km northeast from the TAG active hydrothermal mound (26.135 N, 44.825 W; Fig. 1a). Results of the Ra measurements conducted on this cruise have been previously reported in Charette et al. (2015). Samples from the EPR were collected on the *R/V Thomas Thompson* during the 2013 US GEOTRACES East Pacific Zonal Transect (GP16). This transect was designed to capture the large hydrothermal plume known to emanate from this ridge at 15°S (e.g. Lupton, 1998; Lupton and Craig, 1981) and follow its westward transport. The station locations of the western half of the GP16 transect are shown in Fig. 1c.

On both GA03 and GP16, samples were collected using McLane in situ pumps (McLane WRT-LV) deployed on a 3/8″ plastic coated Vectran line. Seawater was pumped through 1 μm filters to remove particles, and then passed through a MnO_2 coated cellulose cartridge to collect dissolved Ra, Th, and Ac isotopes (see Henderson et al., 2013 for details of cartridge preparation). Pumps were programmed to run for 4 h, filtering 1500–1700 L of seawater at an average flow rate of 6.5 L min^{-1}. After collection, cartridges were rinsed with Ra-free water and dried with filtered compressed air to remove excess moisture. To determine the cartridge scavenging efficiency, smaller volume samples of ^{226}Ra (15–25 L) were collected using a Niskin bottle mounted above the pumps, and the activities of Ra measured on these samples were compared to those determined on the cartridges.

Because it was not possible to sample endmember vent fluids on the GA03 and GP16 cruises, fluids used for this study were collected from other hydrothermal systems on several cruises in the northeast Pacific (Fig. 1b). Specific locations include vents within the High Rise vent field (HRF), Main Endeavour Field (MEF), and Clam Bed site, all on the Endeavour Segment of the Juan de Fuca Ridge (Delaney et al., 1992; Robigou et al., 1993), from Axial Seamount (Embley et al., 1990), and from off-axis vents at Baby Bare Seamount and Ocean Drilling Program (ODP) Hole 1026B (Davis and Becker, 1998; Davis et al., 1992). All high temperature vent samples were collected with a 1-liter titanium syringe following the procedure of Edmond et al. (1979). Low temperature, large volume samples were collected by pumping water into a 120 L barrel originally filled with deionized water. Radium was concentrated from the large volume samples by passing the sample through a column of MnO_2 coated fiber at a flow rate < 1 L min^{-1}.

Vent fluids were also collected during a 1991 voyage of the *R/V Atlantis* (AII-125, Leg 33) using the *HOV Alvin* include high-temperature vent fluids from the Godzilla, Boardwalk, Park Place, Ventnor, and Fairycastle edifices (HRF) and samples of diffuse flow from the Clam Bed site, located between the Main Endeavour and High Rise fields. Additional fluid samples were collected during a 2002 expedition of the *R/V Atlantis* (ATV7L20) using the *ROV Jason II*. At the MEF, high temperature fluids were sampled at the Dudley edifice, and low temperature fluids were sampled from the Dudley edifice and the Easter Island area (just north of the Peanut edifice). Low temperature fluids were also collected from Axial Seamount (Bag-city area), Baby Bare Seamount and ODP Hole 1026B, located about 6 km north of the Baby Bare Seamount. On the Baby Bare Seamount, basalt groundwater was sampled by driving a piston core barrel into the weathered basalt (Johnson, 2003). The ROV attached a hose to the end of the probe and allowed the water flow to flush a 120 L barrel originally filled with DI water. These samples are designated as Probe 3 and Probe 4 and were re-sampled in 2003 using the same procedures.

2.2. Sample analysis

2.2.1. Analysis of Ra isotopes on large volume water column samples

Dissolved Ra isotopes were measured using the Radium Delayed Coincidence Counter (RaDeCC) system (Moore and Arnold, 1996). Samples were first counted on board the ship < 24 h after collection to measure the short-lived ^{223}Ra and ^{224}Ra. Cartridges were then re-analyzed after 4 weeks and again after 2 months to determine the activities of ^{224}Ra and ^{223}Ra supported by ^{228}Th ($t_{1/2}$ = 1.91 y) and ^{227}Ac, respectively. The efficiency of the RaDeCC system was determined using a set of cartridge standards as described in Henderson et al. (2013).

After RaDeCC analysis was complete, the cartridges were ashed in a muffle furnace at 820 °C for 48 h. The cartridge ash was then transferred to polystyrene vials, sealed with epoxy (to prevent ^{222}Rn loss), and counted on high purity, well-type germanium detectors to measure ^{228}Ra using the lines of ^{228}Ac (338, 911, and 969 keV) and ^{226}Ra using the lines of ^{214}Pb (295 and 352 keV) and ^{214}Bi (609 keV). Gamma analyses for the GP16 water column samples were conducted at the