Earth and Planetary Science Letters 473 (2017) 269–278

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Barium stable isotopes in the global ocean: Tracer of Ba inputs and utilization

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ARTICLE INFO

Article history:
Received 22 October 2016
Received in revised form 6 June 2017
Accepted 10 June 2017
Available online 28 June 2017
Editor: M. Frank

Keywords:
barium
seawater
barium isotopes
barium utilization
barium oceanic cycle
GEOTRACES

ABSTRACT

Barium has been used as a biogeochemical tracer for alkalinity, productivity, and riverine inputs in the ocean, but its oceanic cycle remains poorly constrained. Barium stable isotope measurements may improve the use of Ba as a tracer and better constrain the cycling of Ba, but data are only available in limited regions of the oceans. In this study, we present dissolved seawater Ba isotopic compositions in a sample collection spanning the North Atlantic, South Atlantic, North Pacific and Southern Oceans. Compiled global upper-ocean [Ba] data show a relatively constant [Ba] (35–45 nM) in the near-surface waters throughout the global ocean, with the exception of areas near river inputs or strong upwelling. The relatively uniform distribution of [Ba] in the upper ocean seawater indicates that Ba removal is slow relative to supply and mixing, and implies that near-surface Ba isotope values are controlled by basin-scale balances rather than by regional or short-term processes. Seawater Ba isotopic compositions show a large variation of $\delta^{138/134}$Ba values ranging from 0.24 to 0.65‰, and a tight relationship with [Ba]. This global relationship can be simply modelled assuming a primary deep Southern Ocean source for Ba to yield a maximum isotope fractionation of $\alpha = 1.00058 \pm 0.00010$ ($\alpha = {}^{138/134}\mathrm{Ba}_{\mathrm{seawater}}/{}^{138/134}\mathrm{Ba}_{\mathrm{particle}}$). This suggested isotope fractionation during Ba removal from seawater is larger than implied by laboratory measurement during barite formation, suggesting additional fractionating phases or a two-stage fractionation process. Riverine input from the Rio de la Plata to the South Atlantic has a signature of $\delta^{138/134}\mathrm{Ba} = -0.06$–0.11‰, which is too light to explain the heavy values (>0.58‰) observed in the surface open ocean. Globally, the Ba isotope composition of the upper ocean waters is correlated with the fraction of Ba utilization at the basin scale (which varies from <15 to 70% at sites studied here). In the deep Atlantic Ocean, distinct $\delta^{138/134}$Ba signals in the northern-sourced (≈0.45‰) and the southern-sourced water (≈0.25‰) trace mixing and allow identification of non-conservative behaviour of Ba, reflecting additional inputs or sinks of Ba during transport (most likely addition from sediment or hydrothermal). Ba isotopes may be useful to trace such inputs in the present and past ocean.

1. Introduction

Barium is actively cycled in the oceans showing a broadly nutrient-like distribution with surface depletion, deep-water enrichment, and an increase of concentration in deep waters as they age from the North Atlantic to the Pacific. Barium is not itself a primary nutrient, so this distribution is somewhat enigmatic. Its marine geochemistry has been extensively investigated, partly to understand the nutrient-like distribution (e.g. Chan et al., 1977; Dehairs et al., 1980), and partly for the applications of Ba excess (e.g. Dymond et al., 1992; McManus et al., 1999) and barite (e.g. Paytan et al., 1996a) as a tracer of past ocean productivity, or seawater alkalinity and ocean circulation (e.g. Lea and Boyle, 1989; Jeandel et al., 1996; Rubin et al., 2003). Due to the chemical similarities between Ba and Ra, Ba has also been used for normalizing ^{226}Ra in seawater for studying large-scale ocean circulation (e.g. Bacon and Edmond, 1972; Chan et al., 1976) and for Holocene marine carbonate chronology (e.g. Paytan et al., 1996b; Staubwasser et al., 2004). Barium has also been used as a water-mass tracer of riverine input to the coastal ocean by directly measuring seawater [Ba] concentrations (Guay and Falkner, 1998) or Ba/Ca ratios in corals (McCulloch et al., 2003) and foraminifera (Lea and Boyle, 1989).

Despite the uses of [Ba] or Ba/Ca ratios in the ocean, the processes controlling Ba distribution and the role of biologically

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http://dx.doi.org/10.1016/j.epsl.2017.06.024

mediated barite formation remain debatable. Decoupling between seawater [Ba] and [Si] in the surface ocean (Chan et al., 1977; Jacquet et al., 2005), and between seawater [Ba] and alkalinity (Thomas et al., 2011) suggests that the Ba oceanic cycle is not directly associated with either the silica or carbonate cycle. Particulate studies have concluded that barite ($BaSO_4$) formation and dissolution play an important role in Ba oceanic cycling (Dehairs et al., 1980; Bishop, 1988), despite the fact that seawater is generally under-saturated with respect to $BaSO_4$. Barite is primarily formed in the mesopelagic zone, where decay of settling organic matter is thought to elevate the level of [Ba] in microenvironments to reach the saturation point of $BaSO_4$ (e.g. Bishop, 1988; Monnin et al., 1999; Ganeshram et al., 2003; Gonzalez-Muñoz et al., 2012). Marine bacteria (e.g. Gonzalez-Muñoz et al., 2012) and Ba absorption onto other particles (e.g. metal oxides, Sternberg et al., 2005) have also been identified as possible contributors to Ba removal and barite formation in the upper ocean. The precise mechanisms and depth of Ba removal and barite formation remain uncertain, however.

Stable Ba isotope fractionation has been investigated recently in experimental materials and various minerals (von Allmen et al., 2010; Bottcher et al., 2012; van Zuilen et al., 2016), igneous rocks (Miyazaki et al., 2014; Nan et al., 2015), soils (Bullen and Chadwick, 2016), corals (Pretet et al., 2015) and seawater (Horner et al., 2015; Cao et al., 2016; Bates et al., 2017). von Allmen et al. (2010) discovered that barite precipitation preferentially incorporates light Ba isotopes into sulphate minerals and leaves heavy isotopes in the remaining solutions. Horner et al. (2015) found substantial variations in Ba isotopic compositions between surface and deep waters, and Bates et al. (2017) investigated the relationship of Ba isotopic compositions with the ocean circulation in the Atlantic Ocean. Cao et al. (2016) also saw variations in the South and East China Seas. These marine studies have shown that seawater Ba isotope fractionation is not a localized signal but a tracer of large-scale Ba oceanic cycling and ocean circulation. Seawater measurements of Ba isotopes are limited, however, preventing assessment of their behaviour at a global scale.

To improve understanding of Ba stable isotope fractionation in seawater and to characterize seawater Ba isotopic compositions in the global oceans, we have analyzed the dissolved Ba isotopic compositions in seawater samples collected from four major ocean basins in the North Atlantic, South Atlantic, North Pacific, and Southern Oceans (Fig. 1).

2. Samples and methods

2.1. Seawater sampling

Seawater samples analyzed in this study were collected from the North Atlantic (Hydrostation S, HydroS), the South Atlantic (UK-GEOTRACES, GA10W), the Southern Ocean (Bonus-GoodHope, GIPY4) and the North Pacific (ALOHA and SAFe stations) (Fig. 1a, Table 1). At each location, between 5 and 12 depths were analyzed. In the South Atlantic, four additional surface samples were analyzed, located from the measured profile towards the coast to the west, approaching the estuary of the Rio de la Plata. These samples cover a wide range of observed Ba concentrations (Fig. 1b). The North Atlantic depth profiles were collected from the Cruise 61183 (September 2011) at Hydrostation S; the South Atlantic samples during the UK-GEOTRACES cruise GA10W in the Argentine Basin (January 2012); the Southern Ocean seawater profile from the Weddell Gyre during the French Bonus-GoodHope expedition (March 2008); and the North Pacific samples from the ALOHA station during the HOE-PhoR-II cruise (September 2013). We also analyzed SAFe intercalibration samples (Johnson et al., 2007). The sampling methods used on these cruises were similar (except for SAFe). Seawater samples were collected from the Niskin bottle rosette, immediately filtered with 0.45-micrometer Acropak cartridge filters, stored in pre-cleaned polypropylene bottles, and acidified to a pH of 1–2 with distilled HCl. For the SAFe samples, seawater samples were collected using the GeoFish and GO-Flo samplers for the surface and deep samples respectively, and filtered with 0.2-micrometer Poretics cartridge filters before acidification and storing.

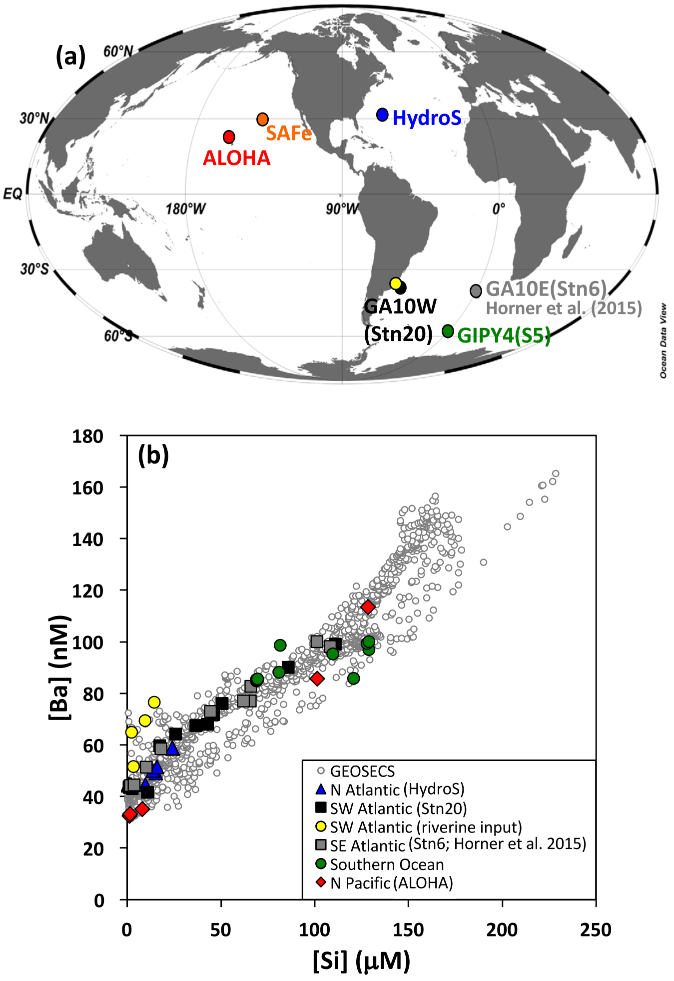

Fig. 1. Map of sampling locations and the distribution of dissolved [Ba] and [Si] in global seawater. (a) The station symbols and data are colour coded consistently for each station throughout this paper. The data for GA10E (Stn6) are taken from Horner et al. (2015). (b) The yellow circles are samples that were collected along the GA10W cruise from Stn20 towards the Rio de la Plata in the SW Atlantic. Latitudes and longitudes are in Table 1. The [Ba] and [Si] concentrations from the GEOSECS Atlantic, Pacific and Southern Ocean dataset are shown in grey open circles (from https://odv.awi.de/en/data/ocean/geosecs/). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2.2. Seawater Ba isotope method

The method of Ba purification used in this study is modified from the method described in Foster et al. (2004) and thus summarized only briefly here. Seawater (50 mL, ~250 ng Ba) was weighed, and spiked with a ^{137}Ba–^{135}Ba double spike to allow correction for mass fractionation during chemical purification and instrument analysis (Text S1). A mixed spike-to-sample ratio of ~0.4 was targeted (ratio of total Ba) based on estimates of [Ba] at seawater sampling point. The double spike was calibrated by measuring the spike, the unspiked standard (NIST3104a), and a series of spike-standard mixtures in different proportions (Table S1).