



Barium-isotopic fractionation in seawater mediated by barite cycling and oceanic circulation

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ARTICLE INFO

Article history:

Received 9 January 2015

Received in revised form 9 July 2015

Accepted 13 July 2015

Available online xxx

Editor: M. Frank

Keywords:

barium

isotopic fractionation

barite

seawater

biogeochemistry

ABSTRACT

The marine biogeochemical cycle of Ba is thought to be controlled by particulate BaSO₄ (barite) precipitation associated with the microbial oxidation of organic carbon and its subsequent dissolution in the BaSO₄-undersaturated water column. Despite many of these processes being largely unique to Ba cycling, concentrations of Ba and Si in seawater exhibit a strong linear correlation. The reasons for this correlation are ambiguous, as are the depth ranges corresponding to the most active BaSO₄ cycling and the intermediate sources of Ba to particulate BaSO₄. Stable isotopic analyses of dissolved Ba in seawater should help address these issues, as Ba-isotopic compositions are predicted to be sensitive to the physical and biogeochemical process that cycle Ba. We report a new methodology for the determination of dissolved Ba-isotopic compositions in seawater and results from a 4500 m depth profile in the South Atlantic at 39.99° S, 0.92° E that exhibit oceanographically-consistent variation with depth. These data reveal that water masses obtain their [Ba] and Ba-isotopic signatures when at or near the surface, which relates to the cycling of marine BaSO₄. The shallow origin of these signatures requires that the substantial Ba-isotopic variations in the bathypelagic zone were inherited from when those deep waters were last ventilated. Indeed, the water column below 600 m is well explained by conservative mixing of water masses with distinct [Ba] and Ba-isotopic compositions. This leads us to conclude that large scale oceanic circulation is important for sustaining the similar oceanographic distributions of Ba and Si in the South Atlantic, and possibly elsewhere. These data demonstrate that the processes of organic carbon oxidation, BaSO₄ cycling, and Ba-isotopic fractionation in seawater are closely coupled, such that Ba-isotopic analyses harbor great potential as a tracer of the carbon cycle in the modern and paleo-oceans.

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1. Introduction

The marine chemistry of Ba (barium) has intrigued geochemists for decades owing to its nutrient-like dissolved profile in seawater (e.g. Chow and Goldberg, 1960), despite lacking a definitive physiological use in phytoplankton. Distributions of dissolved Ba are strongly linearly correlated with those of Si (silicon) throughout much of the global ocean (Fig. 1). Unlike Si however, Ba is rarely quantitatively removed from surface seawater and is around 1000 times less abundant (Wolgemuth and Broecker, 1970; Chan et al., 1977). The near-surface seawater drawdown of Ba has generally been assumed to relate to the precipitation of BaSO₄ (barite; e.g. Dehairs et al., 1980), even though the vast majority of the world's oceans are undersaturated with respect to this

mineral phase (e.g. Monnin et al., 1999). This apparent contradiction is most commonly explained by invoking the existence of ephemeral BaSO₄-supersaturated 'microenvironments' in the water column that favor precipitation of discrete μm-sized BaSO₄ crystals (e.g. Dehairs et al., 1980; Bishop, 1988). The loci of maximum pelagic BaSO₄- and heterotrophic bacterial production are spatially correlated (e.g. Dehairs et al., 2008), suggesting that the development of BaSO₄-forming microenvironments are associated with the microbial oxidation of sinking organic matter (e.g. Chow and Goldberg, 1960). Regeneration of dissolved Ba at deeper depths likely relates to BaSO₄ dissolution in under-saturated seawater, thus closing the open oceans internal Ba cycle and illustrating a remarkable set of linkages between the microbial loop, pelagic BaSO₄ formation, and the cycling and export of BaSO₄ and organic carbon.

Despite these substantial advances in our understanding of Ba biogeochemistry, several important questions persist regarding the modern Ba cycle. For example, the oceanographic processes that

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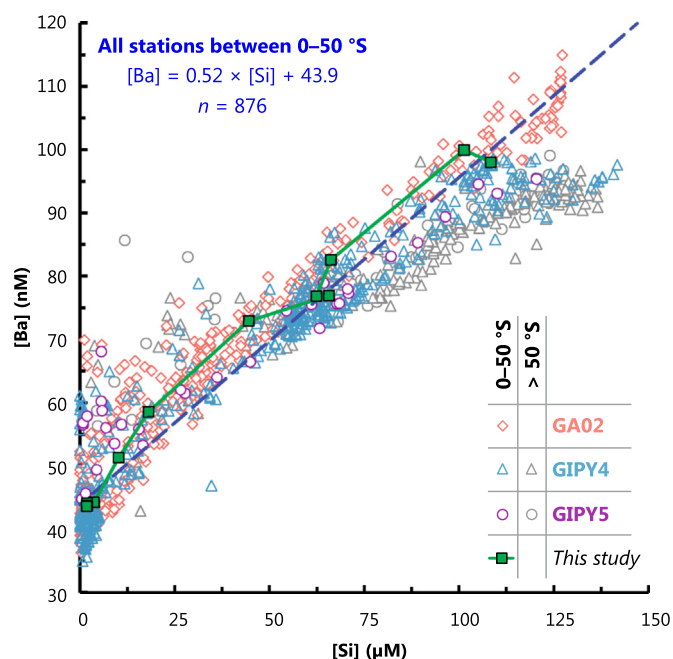


Fig. 1. Co-variation of dissolved [Ba] and [Si] in the South Atlantic. Data sources are *this study* (solid line links profile data) and The GEOTRACES Intermediate Data Product 2014 (Mawji et al., 2015), the latter of which encompasses three separate cruises in the South Atlantic and Southern Oceans (Atlantic Sector) spanning from the Equator to $\approx 70^\circ$ S: GA02 (JC057; diamonds, data courtesy of A. Vilela and J.M. Godoy), GIPY4 (MD166; triangles, data courtesy of F. Dehairs and available from Speich et al., 2008; methods describing how the data were obtained and their interpretation are discussed in Hoppema et al., 2010), and GIPY5 (ANTXXIV/3; circles, data courtesy of T. Roeske and M. Rutgers v. d. Loeff and are available from Roeske and Rutgers v. d. Loeff, 2012; methods describing how the data were obtained are available in Roeske et al., 2012a, 2012b). The best-fit York regression (dashed line) of the 876 GEOTRACES co-located [Ba]–[Si] observations from $< 50^\circ$ S (filled symbols) yields $[\text{Ba}] = 0.52(\pm 0.01) \times [\text{Si}] + 43.9(\pm 0.2)$; regression uncertainties correspond to ± 2 SD. Individual measurements of [Ba] and [Si] were assigned relative uncertainties of $\pm 5\%$, except when [Si] was between 1–10 μM ($\pm 10\%$) and < 1 μM ($\pm 25\%$). Profile data from $> 50^\circ$ S (open symbols) are not regressed in the South Atlantic trend, as data from high latitudes possess significantly gentler slopes and larger intercepts (see e.g. Hoppema et al., 2010).

sustain the linear relationship between dissolved [Ba] and [Si] – but not between Ba and the other major algal nutrients nitrate and phosphate – are poorly understood (Fig. 1; SI; Supplementary Information). Such a strong linear [Ba]–[Si] relationship is perhaps surprising, as BaSO_4 precipitation and dissolution are not diatom-dependent (e.g. Ganeshram et al., 2003), unlike marine Si cycling. Explanations for the correlation between Ba and Si range from local-scale processes that assume that Ba- and Si-bearing carrier phases are remineralized at roughly similar rates during transit through the ocean interior (e.g. Broecker and Peng, 1982) to biogeochemical processes occurring in the surface of the high latitude Southern and Atlantic Oceans that are only communicated to lower latitudes through large-scale oceanic circulation (as suggested for Si, e.g. Sarmiento et al., 2004). Though seawater is likely the ultimate source of Ba ions to marine BaSO_4 , its precipitation is microbially-mediated (e.g. Bertram and Cowen, 1997), such that intermediate Ba sources may be incorporated during BaSO_4 formation. One likely intermediate Ba source to BaSO_4 formation is organic matter, in addition to Ba sourced from dissolved Ba^{2+} in seawater; a continuum between these two end-member sources may also exist (see e.g. Paytan and Griffith, 2007). Finally, the depth ranges over which the most intensive BaSO_4 precipitation occurs in the water column remain inadequately constrained. Estimates of this depth range vary from exclusively in the upper few hundred meters (e.g. Bishop, 1988) to continual formation with depth over several thousand meters (e.g. Van Beek et al.,

2007). Answers to these questions are not only important for understanding the modern biogeochemical cycling of Ba, but also for the application of BaSO_4 -based proxies in paleoceanography (e.g. Dymond et al., 1992; Falkner et al., 1994; Eagle et al., 2003; Griffith and Paytan, 2012; Ma et al., 2014).

Stable isotopic analyses of dissolved Ba in seawater would help address all three of these unresolved issues, as isotopic tracers are a powerful means to probe mineral–fluid reactions, establish mass balances, and study reaction conditions. A handful of recent studies have begun examining Ba-isotopic variability in nature, and have identified significant Ba-isotopic fractionation during mineral precipitation experiments (Von Allmen et al., 2010; Böttcher et al., 2012), between various CaCO_3 minerals (Preter, 2014), and most recently in igneous rocks (Miyazaki et al., 2014). Theoretical predictions support the direction, though not the magnitude, of Ba-isotopic fractionation observed during low-temperature mineral precipitation, which may be related to Ba^{2+} ion desolvation (Hofmann et al., 2012). However, examination of the Ba-isotopic systematics of seawater have hitherto escaped detailed study, largely because of the analytical difficulties associated with the isolation of sufficient quantities of chemically pure Ba from complex matrices such as seawater. Here, we address all of the aforementioned issues by presenting a ≈ 4500 m depth profile of paired Ba-concentration and Ba-isotopic compositions from the South Atlantic Ocean. Our data reveal highly systematic patterns of Ba-isotopic fractionation in the open ocean that are oceanographically consistent with both the direction and magnitude of Ba-isotopic fractionation during BaSO_4 cycling, modulated by basin-scale oceanic circulation.

2. Samples, sampling, and methods

2.1. Hydrographic context

Thirteen water samples were selected for Ba-isotopic analysis from a complete depth profile spanning ≈ 4500 m at Station 6 of GA10E (D357; 39.99° S, 0.92° E; Fig. 2; SI). The water column structure at St. 6, as with much of the 40° S transect, is dominated by the north- and southward advection of water masses that formed at higher latitudes (Fig. 3). Surface waters are a mixture between north-flowing SASW (Sub-Antarctic Surface Water) and south-flowing STSW (Sub-Tropical Surface Water), with surface water macronutrient concentrations significantly greater in SASW than in STSW. Below the surface, northward-flowing AAIW (Antarctic Intermediate Water) is evident around ≈ 600 m from the distinct salinity minimum (~ 34.3), as is the core of southward-flowing UCDW (Upper Circumpolar Deep Water) at 1500 m, which is picked out by the higher macronutrient concentrations (e.g. $\text{PO}_4^{3-} > 2$ μM) and low $[\text{O}_2]$. Salinities > 34.8 and lower macronutrient concentrations between ≈ 2000 – 3500 m are indicative of the southward flow of NADW (North Atlantic Deep Water), whilst abyssal depths are dominated by north-flowing nutrient-rich AABW (Antarctic Bottom Water; Figs. 2 and 3). From the complete profile, 13 samples were selected for analysis so as to include at least one representative end-member from each water mass.

Seawater samples were collected as part of the first UK GEOTRACES 40° S South Atlantic zonal transect in October 2010 (GA10E/D357; Fig. 2). Seawater was sampled using a PTFE-coated OTE (Ocean Test Equipment) 24×10 L bottle CTD system on a ‘trace metal-free’ Ti rosette, deployed from a plasma rope. Following collection, OTE bottles were brought into a clean sampling container for further processing. Water samples were filtered through a 0.2 μm filter capsule and transferred into 1 L HDPE bottles, sealed, and stored inside two zipper storage bags out of direct sunlight. Samples were acidified to pH ~ 2 by addition of 2.4 mL

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