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Coastal barium cycling at the West Antarctic Peninsula

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ABSTRACT

Barium cycling in the ocean is associated with a number of processes, including the production and recycling of organic matter, freshwater fluxes, and phenomena that affect alkalinity. As a result, the biogeochemical cycle of barium offers insights into past and present oceanic conditions, with barium currently used in various forms as a palaeoproxy for components of organic and inorganic carbon storage, and as a quasi-conservative water mass tracer. However, the nature of the oceanic barium cycle is not fully understood, particularly in cases where multiple processes may be interacting simultaneously with the dissolved and particulate barium pools. This is particularly the case in coastal polar regions such as the West Antarctic Peninsula, where biological drawdown and remineralisation occur in tandem with sea ice formation and melting, glacial meltwater input, and potential fluxes from shelf sediments.

Here, we use a high-precision dataset of dissolved barium (Ba_d) from a grid of stations adjacent to the West Antarctic Peninsula in conjunction with silicic acid ($Si(OH)_4$), the oxygen isotope composition of water, and salinity measurements, to determine the relative control of various coastal processes on the barium cycle throughout the water column. There is a strong correlation between Ba_d and $Si(OH)_4$ present in deeper samples, but nevertheless persists significantly in surface waters. This indicates that the link between biogenic opal and barium is not solely due to barite precipitation and dissolution at depth, but is supplemented by an association between Ba_d and diatom tests in surface waters, possibly due to barite formation within diatom-dominated phytodetritus present in the photic zone. Sea-ice meltwater appears to exert a significant secondary control on barium concentrations, likely due to non-conservative biotic or abiotic processes acting as a sink for Ba_d within the sea ice itself, or sea-ice meltwater stimulating non-siliceous productivity that acts as a Ba_d sink. Meteoric water input, conversely, exerts little or no control on local barium levels, indicating that glacial meltwater is not a significant coastal source of barium to the West Antarctic Peninsula shelf waters.

1. Introduction

Records of dissolved and particulate barium (Ba) have been applied as proxies for several past and present oceanic variables and processes such as export production, alkalinity, and meltwater input (Hall and Chan, 2004; Jacquet et al., 2007; Lea and Boyle, 1989). The reliability of such proxies can be improved through an enhanced understanding of the oceanic Ba cycle. Current understanding of oceanic Ba dynamics is limited, particularly in regions where multiple factors may influence the dissolved barium pool.

Barium is a bio-intermediate element found in trace concentrations (30–160 nM) in the ocean (Chan et al., 1976; Dehairs et al., 1980;

Wolgemuth and Broecker, 1970). Sourced from continental weathering, the main input of barium to the oceans is fluvial run-off (Guay and Falkner, 1998). A secondary source is dissolved barium from hydrothermal vent systems, which is thought to precipitate locally (Edmond et al., 1979; Von Damm et al., 1985).

Dissolved barium (Ba_d) in the ocean has a biointermediate nutrient-like distribution, with low concentrations at the surface that do not reach complete depletion, and increased concentrations at depth. A connection between surface water depletion of Ba_d and phytoplankton productivity has been established by numerous observations throughout the global ocean (Esser and Volpe, 2002; Hoppema et al., 2010; Nozaki et al., 2001), although the exact nature of this biologically-

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related uptake is yet to be established. Very few, if any, marine organisms actively take up barium directly (Bertram and Cowen, 1997; Griffith and Paytan, 2012). Whilst there is evidence for the presence of barium within phytoplankton (Ganeshram et al., 2003), either associated with organic material, incorporated into calcite (CaCO₃) or celestite (SrSO₄) tests (Bernstein and Byrne, 2004; Bernstein et al., 1992; Dymond and Collier, 1996; Lea and Spero, 1992), or adsorbed onto oxyhydroxides associated with opaline silica (Sternberg et al., 2005), the relative importance and viability of each of these associations is still under debate.

The involvement of barium in biological processes is reflected in its co-variance in global ocean waters with silicic acid and alkalinity (Dehairs et al., 1980; Lea and Boyle, 1989). An important factor in the nutrient-like behaviour of barium is thought to be the biologically-mediated nature of barium sulphate (barite) precipitation, which does not occur in bulk seawater because barite is undersaturated in most of the global ocean (Monnin and Cividini, 2006). It has been suggested that the formation of barite occurs by supersaturation resulting from elevated barium or sulphate within microenvironments created by decaying organic matter (Bishop, 1988; Dehairs et al., 1980). This causal link is supported by observations of the distribution of particulate barium in the water column (correlation with rates of oxygen consumption and bacterial respiration (Dehairs et al. 1980; Bishop 1988; Jacquet et al. 2007; 2011; Thomas et al. 2011), association of barite crystals with bio-aggregates (Stroobants et al., 1991) and in sediments (correlation with organic carbon fluxes (Dymond and Collier, 1996; Dymond et al., 1992). The exact mechanism behind this precipitation, and the level of bacterial involvement, is still unclear (Gonzalez-Muñoz et al. 2012; Gonzalez-Muñoz et al. 2003).

As a result of its association with organic matter, biogenic barite has been established as a proxy for export productivity both in the modern ocean (Jacquet et al., 2007; Thomas et al., 2011) and in sediment cores representing past oceanic conditions (Nürnberg et al., 1994; Thompson and Schmitz, 1997). Records of the ambient marine concentration of dissolved barium (usually measured via the Ba/Ca ratio preserved in biogenic calcite or aragonite) can also yield pertinent information about past oceanic conditions, thanks to its co-variance with important parameters such as alkalinity, silicic acid, or riverine fluxes (Hall and Chan, 2004; LaVigne et al., 2016; Lea and Boyle, 1989; Plewa et al., 2006). However, the current limited understanding of the oceanic barium cycle can make it difficult to distinguish the influences of these various processes on the barium stocks of the water masses investigated.

Here, we investigate the controls on the distribution of dissolved barium in shelf-slope waters of the West Antarctic Peninsula (WAP), in order to improve our understanding of barium cycling in seawater and to improve the robustness of productivity proxy interpretations. Along the WAP, coastal processes such as sea ice formation and meltwater discharge can be observed alongside biological activity and ocean mixing, making it an ideal natural laboratory to study the relative controls that these processes exert on dissolved barium in seawater.

2. Materials and methods

Seawater samples were collected from stations covering the Palmer Long Term Ecological Research (PalLTER) grid (Fig. 1) during annual cruises of the ARSV *Lawrence M. Gould* in two consecutive austral summers: LMG11-01 (2nd January 2011 – 6th February 2011) and LMG12-01 (30th December 2011 – 7th February 2012). Water was sampled either from surface water using a trace metal-clean towfish or at depth using Niskin bottles deployed on a CTD (Conductivity-Temperature-Depth) rosette. Dissolved barium concentration data reported here are publicly available within the PAL-LTER data system (dataset #266): <http://oceaninformatics.ucsd.edu/datazoo/data/pall-ter/datasets>.

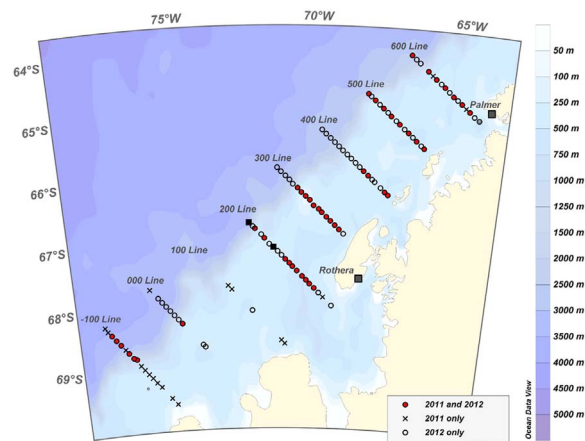


Fig. 1. Map showing the Palmer Long Term Ecological Research grid (PalLTER) covering waters adjacent to the West Antarctic Peninsula. Black circles and crosses indicate surface sample sites from cruises LMG11-01 (02/01/2011 – 06/02/2011) and LMG12-01 (30/12/2011 – 07/02/2012): red filled circles represent stations occupied in both years, crosses/open circles stations occupied only in 2011/2012 respectively. Location of two depth profiles at grid stations 200.100 and 200.160 in 2012 shown by filled black squares. Grid lines are labelled from -100 to 600, stations denoted by grid line plus approximate kilometres from the base tangent of the grid (e.g. 200.100 – station 100 km along grid line 200). Grey squares indicate the location of Palmer Station on Anvers Island and the Rothera Station on Adelaide Island.

2.1. Dissolved barium

The dissolved barium concentrations of 0.2 μm filtered (Acropak-200, Pall) seawater samples were analysed using isotope dilution inductively coupled plasma mass spectrometry (ID ICP-MS) (Klinkhammer and Chan, 1990). Samples were prepared for isotope dilution (ID) as follows: 250 μL aliquots of seawater were spiked gravimetrically with 200 μL of a ¹³⁵Ba-enriched solution (10 μg/mL ¹³⁵Ba, Inorganic Ventures, Christiansburg, VA, USA, gravimetrically diluted to 0.013 μg/mL ¹³⁵Ba [96 nM] using high purity 3% HNO₃) to achieve a ¹³⁸Ba/¹³⁵Ba ratio of 0.7–1.0 to minimise error propagation (Klinkhammer and Chan, 1990). The concentration of the spike solution was calibrated via reverse isotope dilution using a commercial Ba natural standard solution from High-Purity Standards. Spiked solutions were then diluted 20 times with high purity 3% HNO₃ and homogenised.

Isotope ratios (¹³⁸Ba/¹³⁵Ba) were measured in spiked samples using a Thermo-Finnigan Element XR (Cardiff University) or Element-1 (Rutgers University) ICP-MS in low resolution mode, with dissolved barium concentrations subsequently calculated using Eq. 1. A mass bias correction coefficient (K) was calculated each time samples were analysed by measuring the ratio of ¹³⁸Ba/¹³⁵Ba in a 1 ppb Ba natural standard solution prepared in 5% (v/v) seawater (NASS-6 seawater standard of 5 ppb ± 0.15 Ba), and comparing this to the average natural ratio reported in the literature (10.88) (Eq. 2). The isotope ratio determined in this solution varied between 10.5 and 11.1, with measured uncertainty across each sample run never exceeding 1.5% (2*RSD). This uncertainty was consistently less than the mass bias determined for each sample run, which was on average a 1.9% deviation from the literature value.

$$Conc_{sample} = Conc_{spike} \times \frac{m_{spike}}{m_{sample}} \times \left(\frac{R_{spike} - KR_{sample}}{KR_{sample} - R_{naturalstandard}} \right) \times \frac{f_{spike}}{f_{naturalstandard}} \quad (1)$$

Where: $Conc_{sample}$ = concentration of barium in sample

$Conc_{spike}$ = concentration of barium in spike.

m = mass.

R = ratio of ¹³⁸Ba/¹³⁵Ba in sample, spike, or natural standard.

f = abundance of ¹³⁵Ba in spike or natural standard.

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