



Constraining the oceanic barium cycle with stable barium isotopes



Zhimian Cao^{a,b,*}, Christopher Siebert^a, Ed C. Hathorne^a, Minhan Dai^b, Martin Frank^a

^a GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstrasse 1-3, Kiel 24148, Germany

^b State Key Laboratory of Marine Environmental Science, Xiamen University, Xiang'an District, Xiamen 361102, China

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ABSTRACT

The distribution of barium (Ba) concentrations in seawater resembles that of nutrients and Ba has been widely used as a proxy of paleoproductivity. However, the exact mechanisms controlling the nutrient-like behavior, and thus the fundamentals of Ba chemistry in the ocean, have not been fully resolved. Here we present a set of full water column dissolved Ba (DBa) isotope ($\delta^{137}\text{Ba}_{\text{DBa}}$) profiles from the South China Sea and the East China Sea that receives large freshwater inputs from the Changjiang (Yangtze River). We find pronounced and systematic horizontal and depth dependent $\delta^{137}\text{Ba}_{\text{DBa}}$ gradients. Beyond the river influence characterized by generally light signatures (0.0 to +0.3‰), the $\delta^{137}\text{Ba}_{\text{DBa}}$ values in the upper water column are significantly higher (+0.9‰) than those in the deep waters (+0.5‰). Moreover, $\delta^{137}\text{Ba}_{\text{DBa}}$ signatures are essentially constant in the entire upper 100 m, in which dissolved silicon isotopes are fractionated during diatom growth resulting in the heaviest isotopic compositions in the very surface waters. Combined with the decoupling of DBa concentrations and $\delta^{137}\text{Ba}_{\text{DBa}}$ from the concentrations of nitrate and phosphate this implies that the apparent nutrient-like fractionation of Ba isotopes in seawater is primarily induced by preferential adsorption of the lighter isotopes onto biogenic particles rather than by biological utilization. The subsurface $\delta^{137}\text{Ba}_{\text{DBa}}$ distribution is dominated by water mass mixing. The application of stable Ba isotopes as a proxy for nutrient cycling should therefore be considered with caution and both biological and physical processes need to be considered. Clearly, however, Ba isotopes show great potential as a new tracer for land–sea interactions and ocean mixing processes.

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1. Introduction

The nutrient-like distribution of dissolved barium (DBa) in seawater, resembling that of silicate ($\text{Si}(\text{OH})_4$) with low surface and elevated deep water concentrations (Bacon and Edmond, 1972; Lea and Boyle, 1989; Jeandel et al., 1996; Jacquet et al., 2005; Roeske et al., 2012), is commonly attributed to the biologically mediated incorporation of DBa in or adsorption onto biogenic particles in the upper ocean and regeneration via particle dissolution and/or degradation at depth (Dehairs et al., 1980; Paytan and Griffith, 2007). Importantly, within this cycle, a maximum of excess (or biogenic) particulate Ba (Ba_{xs}), most likely resulting from barite (BaSO_4) precipitation in oversaturated microenvironments generated by degradation of sinking organic aggregates, is frequently observed in the mesopelagic zone between 100 and 600 m water depth (Dehairs et al., 1997;

Jacquet et al., 2005). Therefore, Ba_{xs} or barite fluxes to the deep ocean and their accumulation rates in sediments have been widely applied to reconstruct export productivity (Paytan et al., 1996; Nürnberg et al., 1997; Paytan and Griffith, 2007). However, the exact mechanisms controlling the behavior of DBa and the mesopelagic Ba_{xs} maximum are not fully understood (Ganeshram et al., 2003; Jacquet et al., 2005). Moreover, the poor preservation of barite in sediments under suboxic conditions complicates the interpretation of its paleoceanographic record (McManus et al., 1998).

Recently, the first measurements of mass-dependent stable Ba isotope fractionation have been reported (von Allmen et al., 2010; Böttcher et al., 2012; Miyazaki et al., 2014; Horner et al., 2015; Nan et al., 2015), which provide a new avenue to better understand the biogeochemistry of Ba in the ocean and thus to extend and improve its applicability as a paleoproxy. This pioneering work showed that measurable differences of Ba isotopic compositions (−0.5 to +0.1‰) exist between natural Ba minerals of various origins. Lighter Ba isotopes are enriched in Ba precipitates produced in the laboratory relative to the corresponding aqueous solutions, probably due to reaction kinetics or sur-

* Corresponding author at: GEOMAR Helmholtz Center for Ocean Research Kiel, Wischhofstrasse 1-3, Kiel 24148, Germany. Tel.: +49 431 6002254; fax: +49 431 6002925.

E-mail address: zcao@geomar.de (Z. Cao).

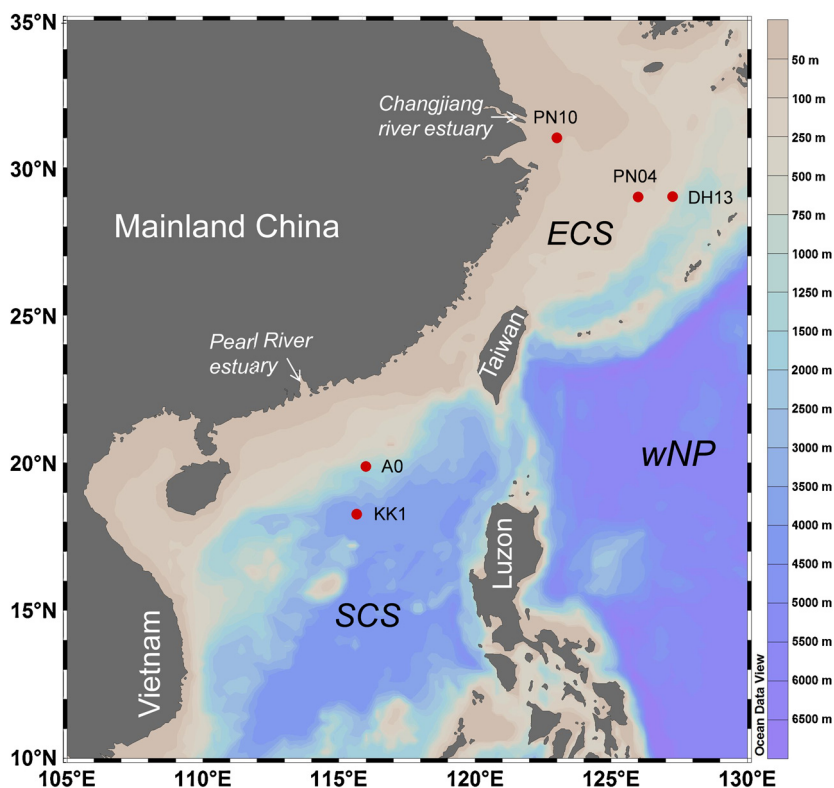


Fig. 1. Bathymetric map of the East China Sea (ECS) and the South China Sea (SCS) showing the locations of sampling stations. The bottom depths of stations PN10, PN04, DH13, A0, and KK1 are ~50 m, ~120 m, ~600 m, ~1450 m, and ~3800 m, respectively. The Changjiang (Yangtze River) and the Pearl River are two of the world's largest river systems feeding the ECS and the northern SCS, respectively. wNP: western North Pacific. The map was created with ODV (Schlitzer, 2015). (For interpretation of the colors in this figure, the reader is referred to the web version of this article.)

face entrapment of the lighter isotopes (Immenhauser et al., 2010; von Allmen et al., 2010). A seawater profile in the South Atlantic showed that Ba isotopic compositions generally decrease with water depth (Horner et al., 2015). Consequently, given the direct involvement of Ba in various biological and chemical processes, fractionation of stable Ba isotopes in seawater has the potential to provide information on nutrient cycling, productivity and water mass mixing.

With the goal to establish a framework for the use of oceanic Ba isotope fractionation as a proxy, we analyzed dissolved Ba isotopic compositions ($\delta^{137}\text{Ba}_{\text{DBa}}$) from different marine regimes in four seawater profiles collected in the East China Sea and the South China Sea, extending from the inner shelf influenced by a large river plume (Zhai and Dai, 2009) to the deep South China Sea basin, which is analogous to an open ocean setting (Cao and Dai, 2011). $\delta^{137}\text{Ba}$ signatures of Ba_{xs} in suspended particles ($\delta^{137}\text{Ba}_{\text{Baxs}}$) were also determined for the upper 150 m of the water column at one station in the South China Sea (Fig. 1; Tables 1 and 2). In addition, $\delta^{137}\text{Ba}_{\text{DBa}}$ was measured in samples collected from eight rivers around the world to assess the isotopic composition of the major Ba source to the ocean (Table 3). Given the close relationship between DBa and $\text{Si}(\text{OH})_4$ concentrations generally observed in the world's oceans (Bacon and Edmond, 1972; Lea and Boyle, 1989; Jeandel et al., 1996; Jacquet et al., 2005; Roeske et al., 2012), we compared our seawater $\delta^{137}\text{Ba}_{\text{DBa}}$ data with the corresponding dissolved Si isotope signatures ($\delta^{30}\text{Si}_{\text{Si}(\text{OH})_4}$; Cao et al., 2012, 2015). We also compared our Ba results with the distribution of other major nutrient (nitrate (NO_3) and phosphate (PO_4)) concentrations in order to further constrain the biological effects on seawater Ba isotopic compositions.

2. Materials and methods

2.1. Sampling

In August 2009, seawater samples for DBa concentration and $\delta^{137}\text{Ba}_{\text{DBa}}$ analyses were collected at stations PN10 (located on the inner shelf), PN04 (mid-shelf), and DH13 (continental slope) of the East China Sea (Cao et al., 2015). In January 2010, this sample set was extended by station KK1 located in the north basin of the South China Sea (Fig. 1). 60–250 mL of seawater was collected with Niskin bottles attached to a Rosette sampler and filtered through 0.45 μm nitrocellulose acetate filters into acid pre-cleaned polyethylene bottles immediately after sampling. Samples were subsequently acidified to $\text{pH} \sim 2$ with distilled concentrated HCl (0.1% v/v) and stored at room temperature in the dark until analysis in the laboratory. In addition, filtered and acidified water samples were collected from various global rivers (Table 3).

In August 2009, suspended particle samples for Ba_{xs} concentration and isotopic composition ($\delta^{137}\text{Ba}_{\text{Baxs}}$) analyses were obtained at station A0 in the South China Sea (Fig. 1) by filtering ~6 L of seawater through 0.4 μm polycarbonate membranes. The membranes were dried at 50 °C overnight and stored in polycarbonate dishes until analysis in the laboratory.

2.2. Ba isotope analyses

Here we summarize the method for Ba isotope measurements using a double spike technique. Further details are provided in the Supplementary Material.

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