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High latitude controls on dissolved barium isotope distributions in the global ocean

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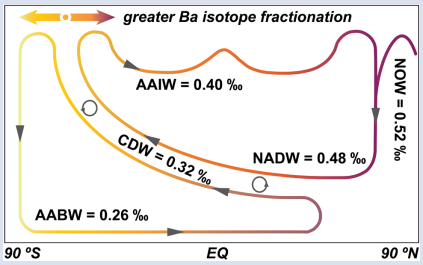
Abstract



The high latitude regions play a key role in regulating the marine biogeochemical cycling of barium (Ba) and the pre-formed Ba isotope compositions in the global ocean. In this study, we present 17 new depth profiles of dissolved Ba concentrations ([Ba]) and isotope compositions (δ^{138}Ba) from the high latitude Atlantic, Pacific and Southern Oceans to trace the ventilation of deep waters in the Southern Ocean and their subsequent transport throughout the global ocean. Our data reveal how biogeochemical processes in the Southern Ocean generate distinct δ^{138}Ba signatures of upper ocean water masses, and that large scale ocean circulation constrains the meridional gradient of δ^{138}Ba distributions in the deep Atlantic Ocean. The significant increase in [Ba] of deep waters in the North Pacific is mainly achieved through dissolution of sinking particles which adds a δ^{138}Ba signal comparable to the deep Pacific Ocean.

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Introduction

Barium (Ba) is a bio-intermediate element in the ocean, whose dissolved concentrations ([Ba]) in the water column have a nutrient-like depth profile with a [Ba] depletion in the upper ocean resulting from removal *via* marine particles (*e.g.*, barite) and [Ba] enrichment at depth due to particulate matter decomposition and remineralisation (Lea and Boyle, 1991). Recent studies presenting novel dissolved Ba isotope compositions (δ^{138}Ba) have provided additional insights into the processes driving the oceanic cycling of Ba (*e.g.*, Horner *et al.*, 2015; Cao *et al.*, 2016; Hsieh and Henderson, 2017). In the uppermost water column, Ba isotope fractionation is likely induced by preferential adsorption of the light isotopes onto biogenic particles (Cao *et al.*, 2020). Although laboratory experiments of adsorption to silica hydrogel exhibited Ba isotope fractionation in the opposite direction, with heavy Ba isotopes being preferentially adsorbed (van Zuilen *et al.*, 2016), field observations consistently reveal lighter isotope enrichment in surface water particles (Horner *et al.*, 2017; Cao *et al.*, 2020). During sinking and decomposition of these particles, barite formation with a preference for the assimilation of light isotopes (von Allmen *et al.*, 2010) leads to high dissolved δ^{138}Ba values in subsurface seawater (Horner *et al.*, 2015; Bates *et al.*, 2017). In contrast, δ^{138}Ba values of deep waters appear to be mainly controlled by barite dissolution and large scale ocean circulation (Hsieh and Henderson, 2017).

Given that the oceanic residence time of dissolved Ba (~3.5 to 5 kyr; Rahman *et al.*, 2022) is longer than the global ocean mixing time, but short enough to prevent complete homogenisation, studies have focused on the importance of advection and mixing on determining dissolved δ^{138}Ba within water masses in the deep Atlantic Meridional Overturning Circulation (AMOC; Bates *et al.*, 2017; Hsieh and Henderson, 2017). The distribution of deep water δ^{138}Ba is overall consistent with two end member mixing between North Atlantic Deep Water (NADW) and Antarctic Bottom Water (AABW). However, the lack of δ^{138}Ba data from high latitude regions where these water masses form results in uncertain end member δ^{138}Ba signatures. Additionally, despite several studies in the Atlantic Ocean, the stable Ba isotope distribution in global seawater, in particular in the Indo-Pacific, remains largely unconstrained. The still poor spatial coverage of available data has so far prevented a robust identification of the mechanisms controlling the distribution of dissolved Ba isotopes in the global ocean.

Here, we examine the spatial and vertical distribution of δ^{138}Ba and [Ba] in 17 new water depth profiles from the high latitude Atlantic, Pacific and Southern Oceans (Fig. 1). These data reveal how NADW and AABW acquire their respective Ba isotope signatures in the polar and subpolar regions. In combination with previously reported low and mid-latitude δ^{138}Ba profiles (Horner *et al.*, 2015; Bates *et al.*, 2017; Hsieh and

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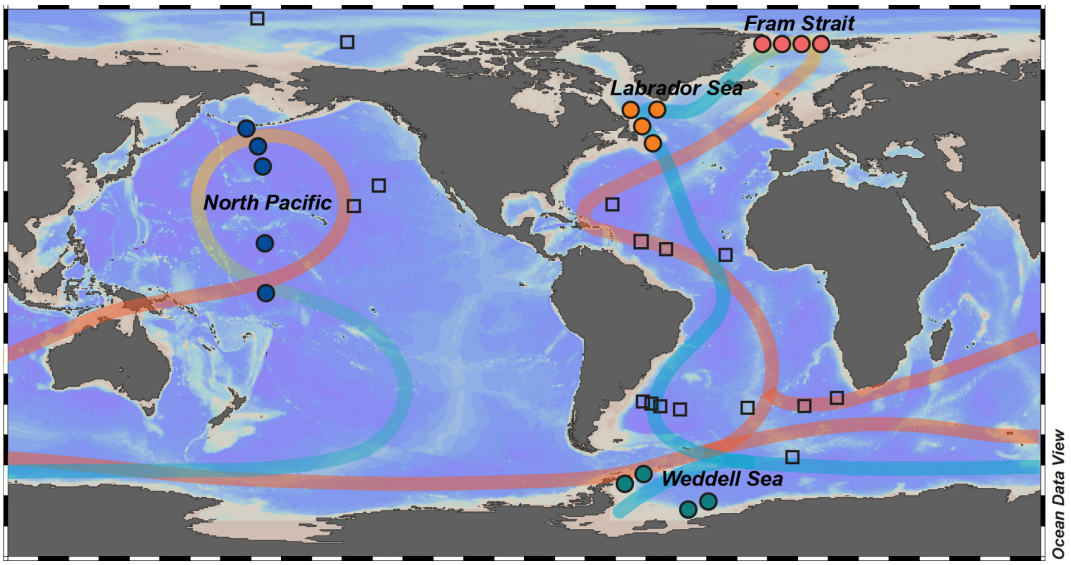

Figure 1 Simplified global overturning circulation with locations of seawater profile stations of this study (coloured circles). Open squares denote published profiles (Horner *et al.*, 2015; Bates *et al.*, 2017; Hsieh and Henderson, 2017; Bridgestock *et al.*, 2018; Geyman *et al.*, 2019; Whitmore *et al.*, 2022). Produced using Ocean Data View (Schlitzer, 2022).

Henderson, 2017; Bridgestock *et al.*, 2018; Geyman *et al.*, 2019), we are now able to better constrain Ba isotope fractionation in the upper ocean and to obtain a more complete picture of the δ^{138}Ba systematics within the global overturning circulation.

Ba Isotope Fractionation in the Upper Ocean

Seawater samples for dissolved [Ba] and δ^{138}Ba were measured at GEOMAR, Kiel, applying methods detailed in Yu *et al.* (2020) and the Supplementary Information. The depth profiles of δ^{138}Ba from the Fram Strait, the Labrador Sea and the Weddell Sea are shown together with two low and mid-latitude Atlantic δ^{138}Ba profiles, overlain by [Ba] data in Figure 2. The samples in the surface and subsurface Weddell Sea have relatively high [Ba] (~90 nmol kg^{-1}) and low δ^{138}Ba (~0.3 ‰), suggesting that the southward intrusion of Circumpolar Deep Water (CDW) was associated with little Ba depletion and isotope fractionation relative to the AABW end member. Previous studies have suggested that the low availability of light and micronutrients (*e.g.*, iron) limits phytoplankton growth in the upper Weddell Sea despite the large inventory of major nutrients available for phytoplankton growth (Sunda and Huntsman, 1997). The minor Ba isotope fractionation in the upper Weddell Sea, as a result of limited barite formation, is consistent with the relatively low productivity of this well known high nutrient low chlorophyll (HNLC) region. The strong upwelling of CDW from below, on

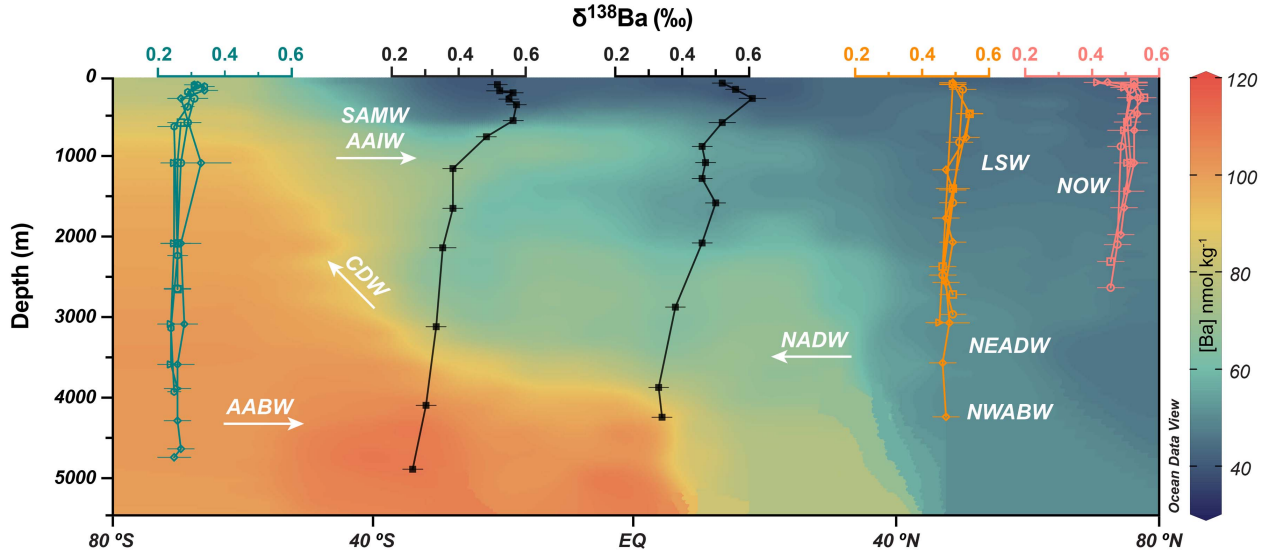

Figure 2 Depth profiles of dissolved δ^{138}Ba in the Weddell Sea (green), the Labrador Sea (orange), the Fram Strait (pink), and the low and mid-latitude Atlantic Ocean (black, Bates *et al.*, 2017). Dissolved [Ba] data are from the GEOTRACES intermediate data product 2017 (Schlitzer *et al.*, 2018) and this study. SAMW, Subantarctic Mode Water; AAIW, Antarctic Intermediate Water; CDW, Circumpolar Deep Water; AABW, Antarctic Bottom Water; NADW, North Atlantic Deep Water; LSW, Labrador Sea Water; NEADW, Northeast Atlantic Deep Water; NWABW, Northwest Atlantic Bottom Water; NOW, Northern Overflow Water. Produced using Ocean Data View (Schlitzer, 2022).

the other hand, further diminishes the degree of Ba isotope fractionation, resulting in a homogenous water column δ^{138}Ba signature that is indistinguishable from that of CDW.

In contrast, the upwelled CDW that moves northwards by Ekman transport undergoes strong Ba isotope fractionation due to high diatom productivity resulting in Ba adsorption to particles in the surface and barite precipitation at intermediate depths (Horner *et al.*, 2015; Cao *et al.*, 2016). As Subantarctic Mode Water (SAMW) and Antarctic Intermediate Water (AAIW) flow northwards from the Subantarctic Zone, surface and subsurface dissolved δ^{138}Ba values increase from ~0.3 to ~0.6 ‰ and ultimately reach high δ^{138}Ba values observed in the Labrador Sea and the Fram Strait (Fig. 2). This meridional upper ocean contrast along the upper limb of the AMOC reflects the combined effects of biologically mediated isotope fractionation at high southern latitudes and the role of large scale ocean circulation.

In the tropical and subtropical Pacific Ocean, [Ba] and δ^{138}Ba exhibit larger gradients between the surface and deep waters than those in the Atlantic Ocean (Fig. 3). The stronger Ba depletion (~30 nmol kg^{-1}) and associated greater Ba isotope fractionation (~0.62 ‰) likely result from the weak vertical mixing in the North Pacific Gyre (Emery and Dewar, 1982), allowing more time for Ba removal associated with particle adsorption and barite formation in the upper ocean. In contrast, upper ocean Ba isotope fractionation becomes less pronounced northwards, where [Ba] slightly increases in the sub-Arctic Pacific (Fig. 3). These less fractionated Ba isotope signatures reflect the limited biological productivity of the HNLC region in the upper sub-Arctic Pacific, similar to that of the Weddell Sea.

Ba Isotope Distribution in the Deep Ocean

The [Ba] and δ^{138}Ba signatures pre-formed in the surface are subducted by deep water formation at high latitudes (*e.g.*, Weddell Sea and Labrador Sea). Due to the vigorous circulation of the Weddell Sea, four depth profiles in the southern and western Weddell Sea (Fig. S-2) are indistinguishable from each other in their δ^{138}Ba values, which defines the end member Ba isotope composition of AABW at 0.26 ± 0.03 ‰. In the Labrador Sea, Labrador Sea Water (LSW), Northeast Atlantic Deep Water (NEADW) and Northwest Atlantic Bottom Water (NWABW) have essentially invariant δ^{138}Ba values and thus define the end member Ba isotope composition of NADW as 0.48 ± 0.05 ‰ (Fig. S-2).

The distinctive Ba isotope signatures of deep waters originating in the Weddell Sea and those in the high latitude North Atlantic (*i.e.* Nordic Seas and Labrador Sea) constrain the meridional gradient of Ba isotope compositions in the deep ocean. The deep ocean δ^{138}Ba and [Ba] data obtained here are compiled with previously reported profiles in a δ^{138}Ba against 1/[Ba] plot (Fig. 4). The high latitude dissolved δ^{138}Ba and 1/[Ba] data display a linear correlation (black dashed line) suggesting conservative mixing between the Northern Overflow Waters (NOW) with low [Ba] and high δ^{138}Ba and AABW characterised by elevated [Ba] and low δ^{138}Ba. The δ^{138}Ba signature of NADW (0.48 ± 0.05 ‰) in the Labrador Sea is only slightly lower than that of NOW (0.52 ± 0.07 ‰), and a clear δ^{138}Ba-1/[Ba] mixing relationship is observed between NOW, NADW and the waters from the deep subtropical North Atlantic (Fig. 4). This suggests that the pre-formed Ba isotope signature of NOW in the Fram Strait represents the northernmost end member of the global deep ocean mixing trend, which is modified along its pathway to the production sites of NADW due to the entrainment of Lower Deep Water (LDW) at greater depth.

It could be argued that the coupled changes in 1/[Ba] and δ^{138}Ba can also be explained by a regeneration model, in which light Ba isotopes are progressively regenerated from sinking particles driving the deep oceans towards a higher [Ba] and lower δ^{138}Ba values. The results of such a model are shown in Figure 4 and the Supplementary Information. As outlined by Bridgestock *et al.* (2018) and Hsieh and Henderson (2017), the continuous addition of Ba from sinking particles along the southward flow of deep Atlantic water masses is unlikely to generate significant deviations from the mixing line, confirmed by the similarity with the regeneration model (Fig. 4). In contrast, some low and mid-latitude data clearly deviate towards heavier δ^{138}Ba values, which requires the involvement of a third mixing end member. Hsieh *et al.* (2021) presented Ba isotope measurements

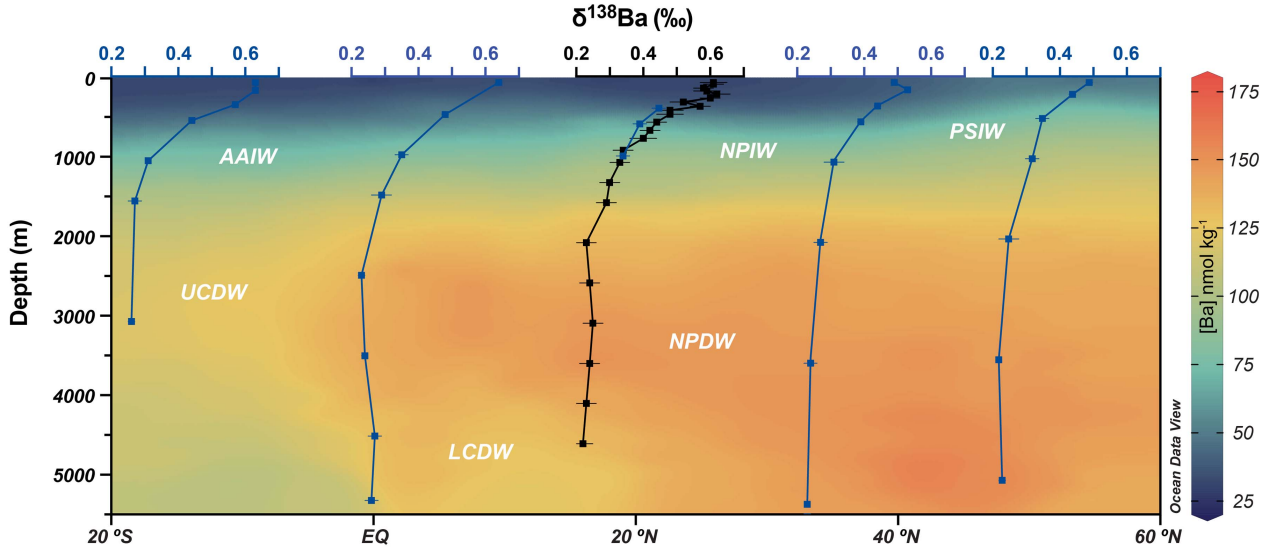

Figure 3 Depth profiles of dissolved δ^{138}Ba in the Pacific Ocean (blue). The depth profile of δ^{138}Ba in the mid-latitude North Pacific (SAFe station, black) is from Geyman *et al.* (2019). Dissolved [Ba] data are from the GEOTRACES intermediate data product 2017 (Schlitzer *et al.*, 2018) and this study. UCDW, Upper Circumpolar Deep Water; LCDW, Lower Circumpolar Deep Water; NPIW, North Pacific Intermediate Water; NPDW, North Pacific Deep Water; PSIW, Pacific Subpolar Intermediate Water. Produced using Ocean Data View (Schlitzer, 2022).

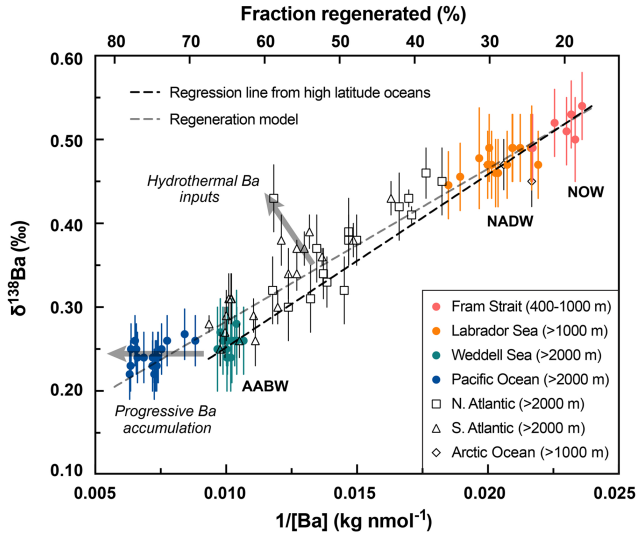

Figure 4 Deep ocean mixing line (black dashed line; data from this study) of δ^{138}Ba against 1/[Ba] and results of a regeneration model assuming a pre-formed [Ba] of 35 nmol kg^{-1} and a δ^{138}Ba value of 0.62 ‰ (grey dashed line). Literature dissolved δ^{138}Ba and [Ba] data (black) are from Horner *et al.* (2015), Bates *et al.* (2017), Hsieh and Henderson (2017), Bridgestock *et al.* (2018), Geyman *et al.* (2019), and Whitmore *et al.* (2022). The potential impacts of hydrothermal Ba input in the Atlantic and progressive Ba accumulation in the deep Pacific are denoted by bold light grey arrows.

in several hydrothermal vent fluids and suggested that significant inputs of hydrothermal Ba contribute significant amounts of Ba with high δ^{138}Ba to the deep ocean, which causes deviations from the high latitude end member mixing line and the regeneration model (Fig. 4). By excluding these deep water masses that are potentially influenced by hydrothermal inputs, a conservative mixing model was applied to quantify the variability of dissolved δ^{138}Ba not related to conservative mixing in the low and mid-latitude Atlantic Ocean. However, the lack of deviations of the δ^{138}Ba values from conservative mixing indicates any effects of particle regeneration are within analytical uncertainties and non-conservative contributions originating from biogeochemical cycling are small in this case (Fig. S-3 and the Supplementary Information).

In the deep Pacific, water masses below ~2000 m depth are characterised by light Ba isotope compositions indistinguishable from those of the deep Weddell Sea, though with significantly higher [Ba] (Fig. 4). A higher fraction of regenerated Ba in the deep Pacific would be expected to cause deviations from the observed mixing relationship at higher [Ba] accompanied by slightly elevated δ^{138}Ba values (Fig. 4). The substantially high proportion of regenerated Ba (~75 %) in the deep Pacific, along with the high Ba 'utilisation' (~70 %) in the upper North Pacific indicated by Hsieh and Henderson (2017), demonstrates that biogeochemical Ba cycling plays a more important role in regulating the deep Pacific δ^{138}Ba signatures than in the Atlantic Ocean. In contrast to the regeneration model, the uniformity of deep water δ^{138}Ba signatures in the Southern Ocean and the North Pacific indicates little or no Ba isotope fractionation during progressive accumulation of Ba along the conveyor belt in the deep Pacific. A homogeneity similar to that of δ^{138}Ba signatures is also observed in the dissolved δ^{30}Si and δ^{114}Cd distribution in the deep Pacific, where both isotope values are indistinguishable from those of the deep Southern Ocean (de Souza *et al.*, 2014; Janssen *et al.*, 2017; Xie *et al.*, 2019). Using a simple mass balance calculation developed for stable Cd isotopes by Janssen *et al.* (2017), the net accumulated Ba originating from dissolution of sinking particles in the deep North Pacific is characterised by an average δ^{138}Ba value of 0.22 ± 0.24 ‰ (Supplementary Information), which is consistent with the deep Pacific δ^{138}Ba signature of 0.25 ± 0.04 ‰. Pacific deep water δ^{138}Ba thus reflects a mixture of biogeochemical Ba cycling and large scale ocean circulation considering its similarity to AABW (0.26 ± 0.03 ‰). This new detailed view of the oceanic Ba cycle will facilitate the use of Ba concentrations and stable isotopes as tracers for ocean circulation globally and for biogeochemical processes in specific regions.

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Additional Information

Supplementary Information accompanies this letter at https://www.geochemicalperspectivesletters.org/article2242.

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