

## Phase associations of barium in marine sediments

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### Abstract

Barium (Ba) is associated with various phases in marine sediments, including carbonates, organic matter, opal, ferromanganese oxyhydroxides, terrestrial silicates and other detrital material, and barite. Using samples representing sediments from a wide variety of sedimentary environments and export production regimes, we show that there is a considerable range in Ba concentrations associated with five operationally defined phases using a sequential extraction procedure (acetic acid, sodium hypochlorite, hydroxylamine hydrochlorite, hydrofluoric–nitric acid mixture, and a final residue dissolution). Distinct regional relationships between the relative abundance of Ba associated with different phases are observed. Since sedimentary Ba is widely used in algorithms to determine past export production, the variability in phase associations of sedimentary Ba shown here should be considered when reconstructing paleo-export productivity.

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### 1. Introduction

Barium (Ba) is associated with various particulate phases in the water column and in marine sediments (e.g., carbonates, organic matter, opal, ferromanganese oxyhydroxides, terrestrial silicates and other detrital material, and barite) (Dehairs et al., 1980; Dymond et al., 1992; Schroeder et al., 1997). The relation between excess Ba ( $Ba_{\text{excess}}$ ) and organic carbon fluxes has been utilized to reconstruct past ocean productivity ( $Ba_{\text{excess}}$  corresponds to the Ba fraction not associated with the terrigenous component as determined by normalization to Al or Ti) (Schmitz, 1987; Dymond et al., 1992; Francois et al., 1995; Murray et al., 2000). The use of

$Ba_{\text{excess}}$  as a paleoproductivity proxy has the underlying assumption that all of the Ba carrying sedimentary fractions composing the so-called  $Ba_{\text{excess}}$  are consistently and predictably related to productivity. However, as many other studies have eluded, Ba may be contained in many phases, some of which are biologically associated (carbonates, organic matter, opal and barite) and others which may not be directly related to biological activity (ferromanganese oxyhydroxides and terrestrial material) (Dehairs et al., 1980; Dymond et al., 1992; Gingele and Dahmke, 1994; Schroeder et al., 1997; McManus et al., 1998; Rutten and de Lange, 2002). Schroeder et al. (1997) found that Ba content in marine sediments correlated with a variety of terrigenous, biogenic and oxide phases, including  $CaCO_3$ , opal, excess Fe and terrigenous matter. They also found correlations between Ba content and bulk sediment accumulation rates, and suggested that sequential extractions might provide further information regarding

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carriers of sedimentary Ba. Rutten and de Lange (2002) performed a sequential dissolution to determine the Ba content associated with a variety of sedimentary phases in eastern Mediterranean sediments and found that the predominant Ba-carriers are clays and barite, however, a small but variable fraction of Ba was found in “other” phases. Likewise, Kryc et al. (2003) performed a sequential extraction of Ba from one marine sediment and one shale sample, and noted Ba in exchangeable, carbonate, opal, oxide, organic and residual phases. Each of these studies uses a different sequential leaching method, however, all demonstrate the potential for Ba to be found in several phases in marine sediments.

When using the  $Ba_{\text{excess}}$  proxy to reconstruct productivity, efforts are made to exclude the terrigenous Ba fraction (e.g., subtraction of terrestrial Ba, see Schenau et al., 2001). A few studies attempted a more thorough approach and tried to evaluate and quantify the concentration of Ba in biogenic material (opal,  $CaCO_3$  and organic matter) and ferromanganese oxyhydroxides based on the average Ba concentrations in these fractions. For example, some studies have found that carbonates contain 30 ppm (Lea and Boyle, 1989) to 200 ppm Ba (Dehairs et al., 1980), opal contains ~120 ppm Ba (Dehairs et al., 1980), organic matter ~60 ppm Ba (Martin and Knauer, 1969; Riley and Roth, 1971), and ferromanganese oxyhydroxides contain ~1000–2000 ppm Ba (Dymond et al., 1984). Here we present a detailed study of Ba associations in various operationally defined sedimentary phases and investigate the variability in these associations using core top sediment samples from a wide range of oceanic locations to test the validity of the assumption that all phases included in excess Ba (also referred to as Bio-Ba) are indeed related in a predictable way to productivity and are not affected by other factors such as sediment composition and mass accumulation rates (MAR). All samples used in this study were treated similarly, with the same sediment to reagent ratios and the same reagent concentrations and reaction times. Therefore, although the Ba dissolved in each phase will to a certain extent depend on the leaching protocol (i.e., operationally defined), since the samples were treated consistently, the variability observed between samples reflects differences in the samples themselves and is not only an artifact of the sequential extraction.

## 2. Methods

### 2.1. Sequential leaching procedure

Sediment samples were chosen to represent a variety of sedimentary environments, including the Southern

Ocean (NBP 9802 and TNO57), equatorial Pacific (JGOFS, MANOP and ERDC), Pacific Coastal Margin (SBB-96) and equatorial Atlantic (INMD) (Table 1). Sediments were treated using an operationally defined five step sequential leaching procedure targeting the sedimentary fractions containing calcium carbonate, labile organic matter, ferromanganese oxyhydroxides, aluminosilicates plus biogenic opal, and a final residue containing barite and other highly refractory minerals such as rutile. The sequential leaching procedure employed includes reaction with acetic acid (25%), sodium hypochlorite (bleach, 5%), hydroxylamine hydrochlorite (0.02% in 25% acetic acid), an HF–HNO<sub>3</sub> mixture, and a final dissolution of all residue with hot HF–HNO<sub>3</sub>–HCl (Table 2, modified from Collier and Edmond, 1984; Eagle et al., 2003). Each of the leaching steps targets one of the major (operationally defined) sedimentary fractions listed above. The sample is rinsed with 18 M-ohm water three times after each leaching step, and this wash is included with the leachate for elemental analysis since significant Ba is removed in the wash (based on analysis of Ba concentrations in leachate solutions and subsequent washes). In addition, bulk dissolution of an aliquot of the same sample in a hot HF–HNO<sub>3</sub>–H<sub>2</sub>O<sub>2</sub> mixture was performed to determine total Ba concentrations ( $Ba_{\text{TotalIBD}}$ ) and extraction yields (Schroeder et al., 1997). All acids and chemicals used were trace metal grade.

### 2.2. Sequential extraction leaching yield and uncertainty

The Ba concentrations of each of the sequential leaching fractions, and the Ba and Al concentrations of bulk dissolution samples, were measured with a TJA Iris Advantage/1000 Inductively Coupled Argon Plasma (ICAP) Spectrometer, fitted with a Solid State Charge Injection Device (CID) detector to analyze multiple elements concurrently, at Stanford University. To reduce matrix effects during ICP-OES analysis, each fraction from the sequential leaching process was dried down, rinsed three times with 8 N trace metal clean nitric acid and reconstituted with 1 N trace metal clean nitric acid. Leachate blanks and total procedure blanks contributed <0.1% of total Ba in all samples. Analytical precision was monitored with internal ICP standards and remained better than 1% throughout the analysis period.

A similar extraction procedure, although with a different reagent to sample ratio, is used for barite separation from marine sediments (e.g., Paytan, 1996; Eagle et al., 2003). The yield of this extraction for barite is ~95% as was determined in a series of recovery experi-



Manop K7905-21BC 0–5 cm	1.053	–138.947	72.0	n/a	14.7	44	13 (1)	49 (3)	222 (13)	775 (44)	710 (40)	1769 (92)	1931
Manop K7905-42BC 10–15 cm	1.063	–138.943	77.9	n/a	14.7	25	4 (0)	24 (2)	226 (23)	404 (42)	313 (32)	971 (81)	1202
Manop K7905-94BC 4–9 cm	11.018	–140.078	0.1	n/a	1.7	11	12 (1)	108 (8)	160 (13)	386 (30)	602 (48)	1268 (88)	1440
ERDC 104 5–10 cm	–3.668	–161.295	85.0	n/a	17	15	7 (1)	73 (14)	40 (7)	60 (11)	363 (67)	543 (79)	686
ERDC 110 5–10 cm	–1.738	–160.487	85.0	n/a	15	25	5 (1)	50 (9)	28 (5)	46 (8)	437 (77)	567 (79)	713
ERDC 125 5–10 cm	–0.003	–160.998	72.0	n/a	14.5	20	4 (1)	56 (9)	28 (4)	68 (11)	469 (75)	625 (93)	675
ERDC 125 10–15 cm	–0.003	–160.998	83.6	n/a	14.5	20	3 (0)	73 (10)	100 (14)	114 (16)	418 (59)	708 (107)	665
Atlantic Ocean													
INMD 104 5–7 cm	4.245	–21.923	70	n/a	16	5	3 (2)	51 (30)	39 (23)	52 (30)	26 (15)	170 (97)	176
INMD 106 10–15 cm	2.732	–20.938	65	n/a	15	4	7 (7)	14 (13)	51 (48)	29 (27)	6 (6)	107 (81)	133
Pacific margin													
SBB-96 Site II 0–10 cm	34.225	–120.033	n/a	n/a	1440	200	3 (1)	18 (3)	16 (3)	102 (20)	382 (73)	521 (107)	485

N/A not available.

<sup>a</sup> Wt.% CaCO<sub>3</sub> for JGOFS TT013 was accessed through the USJGOFS database (<http://usjgofs.whoi.edu>) and wt.% SiO<sub>2</sub> for these samples is from [McManus et al. \(1995\)](#). Wt.% CaCO<sub>3</sub> and SiO<sub>2</sub> for NBP 9802 samples are from [Chase et al. \(2003\)](#), and for TTN0-57 from [King et al. \(2000\)](#). Wt.% CaCO<sub>3</sub> for Manop and ERDC samples were determined by loss on ignition (LOI) in this study. No wt.% SiO<sub>2</sub> data was available for Manop, ERDC, INMD or SBB samples.

<sup>b</sup> Mass accumulation rates were determined by <sup>230</sup>Thorium<sub>ex</sub> for NBP 9802 cores ([Chase, 2001](#)); by C<sup>14</sup> dates ERDC samples ([Berger and Killingsley, 1982](#)); by C<sup>14</sup> dates for TT013 (and K7905) samples ([DeMaster and Pope, 1994](#)); by O<sup>18</sup> stratigraphy for TNO57 (personal communication, Christopher Charles). For the remaining samples, MAR were determined by multiplying sediment AR with DBD. No information was available for SBB-96, so AR ([Behl, 1995](#)) and DBD ([Rack et al., 1995](#)) from a nearby site (ODP 893) were used. For INMD samples, dry bulk density (DBD) was estimated with wt.% CaCO<sub>3</sub>, utilizing Eq. 5 from ([Snoeckx and Rea, 1994](#)), with wt.% CaCO<sub>3</sub> from [Curry and Lohmann \(1990\)](#) and sedimentation rates from [Mix et al. \(1986\)](#).

<sup>c</sup> Productivity values for TT013 and ERDC samples are from [Paytan et al. \(1996\)](#); for TNO57 provided by O. Holm-Hansen (personal communication) based on a 20 year compilation of chlorophyll data for the region and production per chlorophyll unit; and for all other samples productivities are based on satellite measurements of Chl *a*.

<sup>d</sup> Numbers in parentheses are the percentage of Ba in the leachate of the total Ba found in the sequential leaching procedure (Ba<sub>TotalSL</sub>), e.g., Ba<sub>leach</sub>/Ba<sub>TotalSL</sub> × 100 = %.

<sup>e</sup> Bulk dissolution Ba<sub>total</sub> and Al<sub>total</sub> from [Schroeder et al. \(1997\)](#) and [Murray et al. \(2000\)](#).

Table 2

Sequential leaching procedure (modified from Eagle et al., 2003; Collier and Edmond, 1984)

- 1 Weigh 2–3 g sediment
- 2 Acetic-Ba: Remove carbonates with 4 N acetic acid<sup>a</sup> (room temperature, ~12 h).
- 3 Centrifuge and decant leachate, rinse with 40 mL 18 M-ohm water, centrifuge and combine with leachate, repeat 3 times<sup>b</sup>
- 4 Bleach-Ba: Remove organic matter in 5% sodium hypochlorite (50 °C, ~12 h).
- 5 Hydroxylamine-Ba: Remove Fe–Mn oxyhydroxides with 0.2 N hydroxylamine in 25% acetic acid (by volume) (80 °C, ~12 h)
- 6 HF-Ba: Digest aluminosilicates in 1:2 40% hydrofluoric acid:1 N nitric acid (room temperature, ~12 h)
- 7 Residue-Ba: Digest remaining sediment in 2:1 40% hydrofluoric acid:8 N nitric acid, sonicate for 1 h (90 °C, ~12 h), include 8 N hydrochloric acid as needed.

<sup>a</sup> Acid volume is 40 mL for steps 1–5, 30 ml for step 6, and 5 ml for step 7.

<sup>b</sup> Repeat this rinse after each leaching step.

ments discussed in detail in Eagle et al. (2003). In one experiment, a reagent-grade pure barite sample, without a sediment matrix, was subjected to the extraction procedure (Fig. 1). Reagent grade barite crystals are smaller than natural barite found in sediments (0.25  $\mu\text{m}$  compared to 1–5  $\mu\text{m}$ ) and have higher Sr concentrations (Averyt and Paytan, 2003), thus these reagent grade barite crystals are more susceptible to dissolution and mechanical loss, particularly when treated without a

sedimentary matrix. We analyzed the leachates from each step of the sequential dissolution and also determined the residual barite recovered at the end of the procedure. We found that <5% of the total original barite was lost and out of this only 15% was found in solution (e.g., dissolved), while the rest was mechanically lost in the process. Thus mechanical loss of the very small barite crystals during decanting accounted for the majority of barite lost in the sample treated without a sedimentary matrix. Such mechanical loss is expected to be less in sediment samples, but is important, particularly since the amount of barite lost may represent a relatively larger fraction of total barite in samples with low weight percent (wt.%) barite (Eagle et al., 2003). We also determined the Ba concentrations in the leaching solutions after each treatment for a natural sediment sample (NBP 9802 St. 3) and found that similarly little Ba is lost in the process (Fig. 1).

During this experiment, to determine how much Ba is present in sample rinses between treatments, we analyzed the 18 M-ohm water washes separately from the leachates and found they contain dissolved Ba from the previous leaching step (Fig. 1). Thus, the rinse solution was combined with the leachate for analysis, as some of the dissolved fraction comes out of the sample in the rinses between treatments. This step has been added to all samples processed here, thus the only

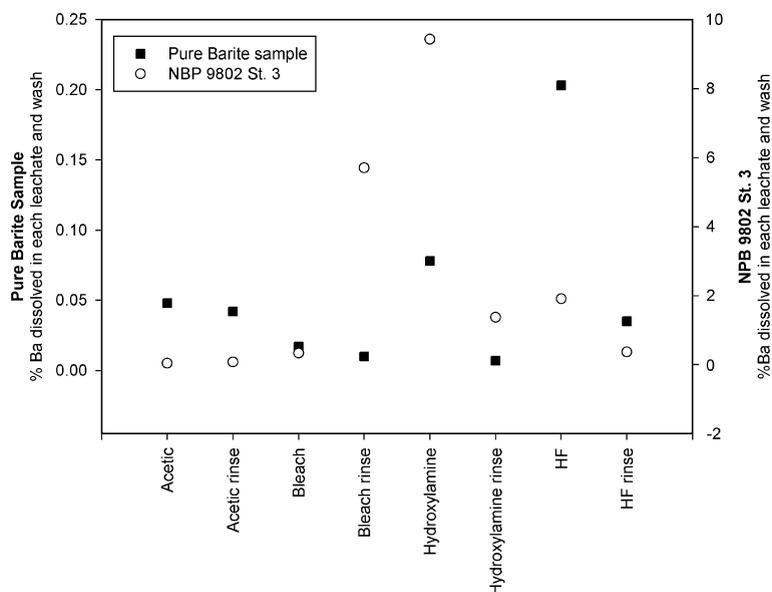


Fig. 1. Sequential leaching procedure yield experiment. A pure barite sample (black squares) and NBP 9802 Station 3 (open circles) were treated with the sequential leaching procedure and Ba was analyzed in all leachates and subsequent washes. Note the different scales for the pure barite (left y-scale) and the sediment samples (right y-scale). The dissolution of the pure barite sample measured in these solutions accounts for <1% of total barite loss, which was <5% overall, with the remaining loss attributed to physical loss during decanting. The Ba dissolved in the sample NBP 9802 Station 3 does not represent Ba lost through barite dissolution (as other Ba containing fractions are included), but rather highlights the amount of Ba found in washes, thus justifying including these washes with the leachates for analysis to reduce loss of Ba.

loss of Ba in this protocol is due to adsorption of dissolved or particulate Ba onto centrifuge tube walls (e.g., all solutions were kept and analyzed).

The overall uncertainty associated with our sequential leaching procedure, including analytical uncertainty (relatively small) and procedural uncertainty (~20%) was determined by comparing  $Ba_{TotalBD}$  measurements (Table 1, Column XIV) to the sum of the Ba from each step of the sequential leaching procedure ( $Ba_{TotalSL}$ , Table 1, Column XIII). This also ensured that the Ba concentrations reported from the sequential leaching procedure were in agreement with the widely used bulk dissolution method.  $Ba_{TotalSL}$  is on average 94% of  $Ba_{TotalBD}$  with a propagated standard error of 11% (Fig. 2). This relatively small but persistent lack of closure is not unexpected and has been observed in other data sets that do not calculate one of the components by difference (Schroeder et al., 1997). As indicated above, this may be partly due to Ba or barite adsorption onto centrifuge tube walls.

### 2.3. Export production

Surface ocean primary productivity for the majority of the samples used here was obtained from multiple year averages of direct measurements of in situ  $^{14}C$  incorporation or Chl *a* measurements; sources are in-

cluded in Table 1. All other primary productivity estimates (when direct measurements were unattainable or were measured infrequently) are based on a numerical algorithm (Arrigo et al., 1998) that was used to estimate daily primary production ( $g\ C\ m^{-2}\ d^{-1}$ ) from Chl *a* fields obtained from Sea-viewing Wide Field-of-view Sensor (SeaWiFS) measurements of ocean color between 1997 and 2001 (see Eagle et al., 2003 for a further discussion). Relatively few multi-year averages of direct new production (equivalent to carbon export here) measurements are available, so we used primary productivity measurements and applied an appropriate *f*-ratio to estimate carbon export fluxes (Table 1, column VII). An *f*-ratio of 0.15 was used for the tropical Pacific (Pena et al., 1992; McCarthy et al., 1996; Aufdenkampe et al., 2001), 0.5 for the Southern Ocean (Metzler et al., 1997), 0.64 for south of the Antarctic Circumpolar Current (Buesseler et al., 2003), and 0.05 for the Atlantic (Wollast and Chou, 2001).

### 2.4. Mass accumulation rates and sediment wt.% $CaCO_3$ and wt.% $SiO_2$

Mass accumulation rates for most of our samples have been previously published. Mass accumulation rates were determined by  $^{230}Th_{ex}$  for NBP 9802

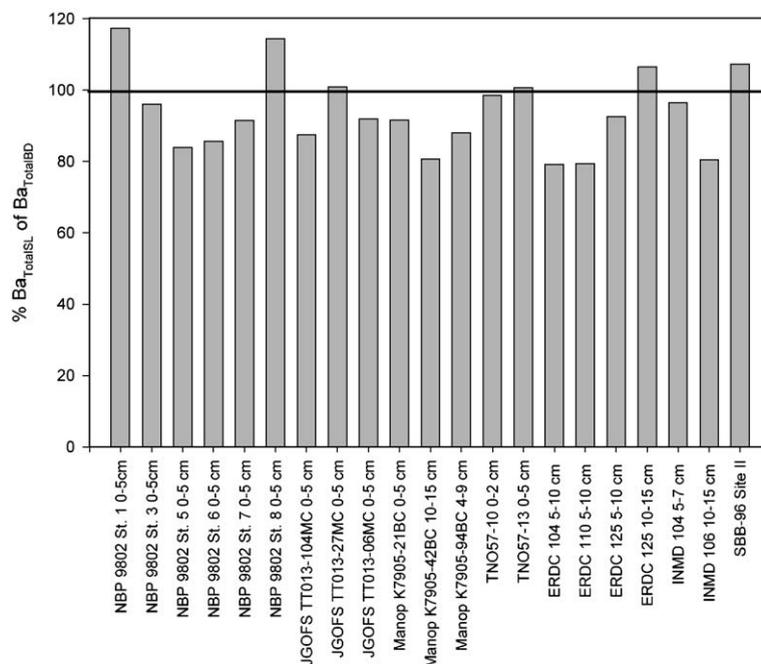


Fig. 2. Plot of the ratio of  $Ba_{TotalSL}$  and  $Ba_{TotalBD}$  to demonstrate the efficiency of the sequential leaching procedure. The dark line marks 100% agreement between  $Ba_{TotalSL}$  and  $Ba_{TotalBD}$ . In most samples, the sequential leaching procedure under recovers Ba as determined using the  $Ba_{TotalBD}$ .

(Chase, 2001), thus accounting for potential sediment focusing which has been demonstrated in this region; by  $C^{14}$  dates for ERDC (Berger and Killingsley, 1982) and JGOFS TT013 (and nearby Manop K7905) cores (DeMaster and Pope, 1994); and by  $O^{18}$  stratigraphy for TNO57 (personal communication, Christopher Charles). For the remaining samples, mass accumulation rates were calculated by multiplying published sedimentation rates with dry bulk density. For INMD samples, dry bulk density was estimated from wt.%  $CaCO_3$ , utilizing Eq. (5) from Snoeckx and Rea (1994), with wt.%  $CaCO_3$  from a nearby location (Curry and Lohmann, 1990) and sedimentation rates from Mix et al. (1986). No information was available specifically for SBB-96, so accumulation rates (Behl, 1995) and dry bulk density (Rack et al., 1995) from a nearby site (ODP 893) were used.

Sediment wt.%  $CaCO_3$  and  $SiO_2$  were previously published for most samples. Wt.%  $CaCO_3$  for JGOFS TT013 was accessed through the USJGOFS database (<http://usjgofs.whoi.edu>) and wt.%  $SiO_2$  data for these samples is from McManus et al. (1995). Wt.%  $CaCO_3$  and  $SiO_2$  for NBP 9802 samples are from Chase et al. (2003), and for TTN0-57 from King et al. (2000). Wt.%  $CaCO_3$  data for Manop and ERDC samples were determined by loss on ignition (LOI) for this study. Wt.%  $SiO_2$  data was not available for Manop, ERDC, INMD or SBB samples.

### 3. Results and discussion

#### 3.1. Ba concentrations in each phase

The Ba concentration and the % of  $Ba_{TotalSL}$  found in each of the five leachates is listed in Table 1 and shown in Fig. 3. Total Ba concentrations range from 133 to 6097 ppm in these samples. The acetic acid leach, targeting carbonates, contains little Ba (0–64 ppm, 0–7% of  $Ba_{TotalSL}$ ). Both the bleach and hydroxylamine leaches, targeting organic matter and ferromanganese oxyhydroxides, respectively, contain considerable, but widely variable Ba (14–316 ppm, 1–30% of  $Ba_{TotalSL}$  for bleach, and 5–275 ppm, 0–48% of  $Ba_{TotalSL}$  for the hydroxylamine leach). The HF leach contains more Ba (29–809 ppm, 2–67% of  $Ba_{TotalSL}$ ) than would be expected based on average shale or other terrigenous material Ba content, as seen by the many high ratios of HF-associated Ba to total aluminum (HF-Ba/ $Al_{Total}$ , Table 3). It is possible that the HF leach dissolved other phases or minerals containing Ba (such as opal), that there are non-terrigenous sources of Al or that the amount of Ba commonly

associated with the terrigenous component is underestimated, i.e., the commonly used ratio of 0.0075 to calculate  $Ba_{excess}$  may be lower than is seen on average in these samples. Since this last statement does not agree with previous work on Ba/Al ratios in marine sediment (Reitz et al., 2004), it is likely that inclusion of Ba from other phases and/or inclusion of Al from non-aluminosilicate phases is responsible for the high HF-Ba/ $Al_{Total}$  seen here. However, high HF-Ba/ $Al_{Total}$  ratios are not observed in all samples, again demonstrating the wide variability in Ba content of the different operationally defined phases. The dissolution of the residue, likely dissolving barite and other resistant phases, contained on average the largest fraction of Ba (0–5777 ppm, 0–87% of  $Ba_{TotalSL}$ ). However, once again the range is very large. This large range in Ba concentrations of the various sedimentary phases indicates that a constant Ba concentration (for example ppm in organic matter) cannot be used to calculate the Ba associated with any of these phases.

#### 3.2. Relationship between Ba phase associations and export production

Accumulation rates of Ba from each phase were correlated with export production (Fig. 4, Table 4). For the equatorial Pacific, Ba accumulation rates of all phases but Bleach-Ba were significantly ( $p$ -value < 0.05) positively correlated with export production. In the Southern Ocean samples, only HF-Ba is significantly (negatively) correlated with export production. Other factors that may also influence Ba distribution in marine sediments include MAR and other sedimentary characteristics such as the abundance of carbonate or biogenic silica. However, wt.%  $SiO_2$  and wt.%  $CaCO_3$  were not found to be direct carriers of Ba, although these sedimentary components do dilute the major Ba carriers.

For the equatorial Pacific, the hydroxylamine-Ba and HF-Ba fractions correlate with export production despite the fact that they target the ferromanganese oxyhydroxides and aluminosilicate/biogenic opal fractions, which are not expected to be simply related to biological activity. The negative correlation between HF-Ba and export production in the Southern Ocean was likewise unexpected. These correlations may be a result of leaching artifacts and/or MAR models (see discussion below). Finally, we note the correlation between the residual fraction (presumably barite) and export production is not strong for the Southern Ocean samples ( $r^2=0.128$ ), despite previous observations with many of the same samples that show a strong

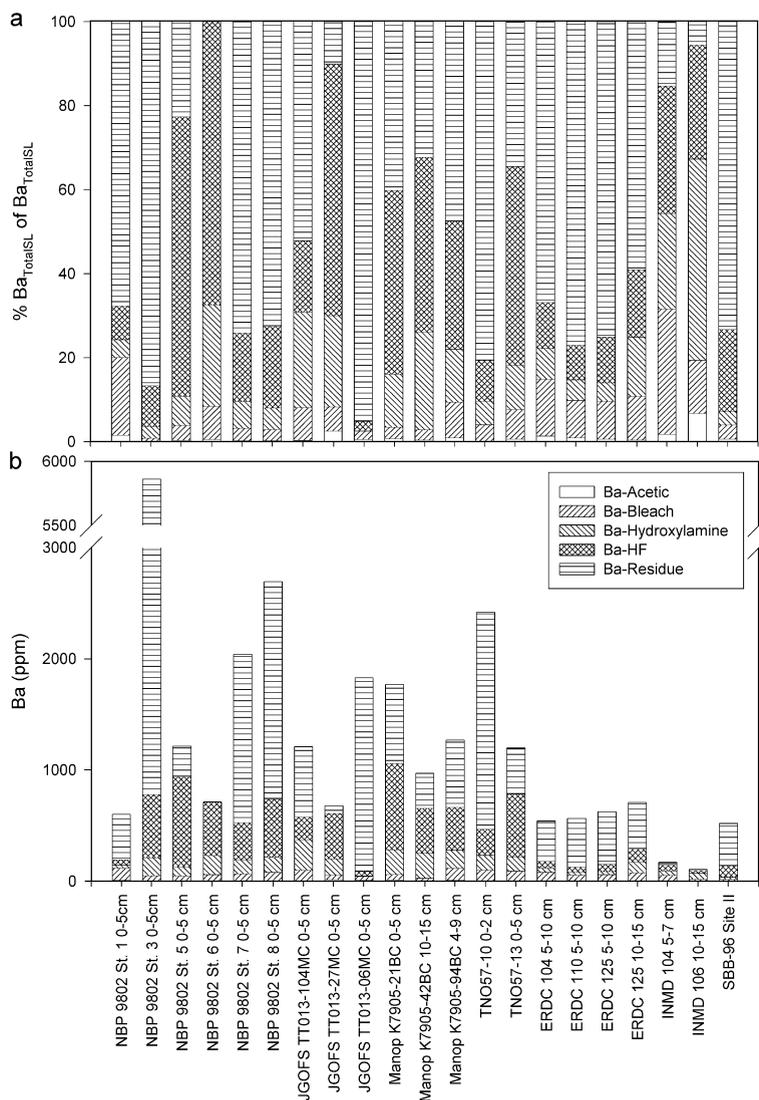


Fig. 3. (a) Plot of % Ba in each leachate of  $Ba_{TotalSL}$  and (b) plot of Ba ppm in each of the five sequential leaching steps, acetic acid, sodium hypochlorite, hydroxylamine hydrochlorite, hydrofluoric–nitric acid mixture, and a final residue. Note the break in scale in (b).

positive correlation between barite accumulation rates and export production (Eagle et al., 2003), thus suggesting that Ba from non-barite sources may be included in this fraction when using this modified leaching protocol.

It is possible that using different age models resulting in different MAR estimates would impact the relationships between Ba accumulation rates and productivity (Paytan et al., 1996); this could also impact the relationship between MAR and sedimentary Ba concentration in the various phases. For example, for the Southern Ocean samples, both  $^{230}\text{Th}_{ex}$  normalization (NBP 9802) and  $\text{O}^{18}$  stratigraphy (TTNO57) were used to calculate MAR, while in the equatorial

Pacific only  $\text{C}^{14}$  based MAR were used (JGOFS TT013, ERDC and Manop). We chose to use  $^{230}\text{Th}_{ex}$  normalization in a region of the Southern Ocean in which sediment focusing had been demonstrated by sedimentary features and not only by the Th data (Chase et al., 2003). This method was not employed for the equatorial Pacific since similar sediment focusing has not been documented and supported by independent sedimentary features (Lyle et al., 2005). Thus, while some error may arise from the use of multiple methods of calculating MAR, we used what we believe to be the most appropriate method available for the cores used in this study. We realize however that MAR are highly dependent on the quality of the age

Table 3  
Total Al concentrations (ppm) and the HF-Ba/Al<sub>Total</sub> ratio

Sample	Total Al	HF-Ba/total Al
NBP 9802 St. 1 0–5 cm	53892	0.0009
NBP 9802 St. 3 0–5 cm	38359	0.0149
NBP 9802 St. 5 0–5 cm	2150	0.3763
NBP 9802 St. 6 0–5 cm	691	0.6961
NBP 9802 St. 7 0–5 cm	5663	0.0588
NBP 9802 St. 8 0–5 cm	22023	0.0237
JGOFS TT013-104MC 0–5 cm	6451	0.0319
JGOFS TT013-27MC 0–5 cm	4066	0.1001
JGOFS TT013-06MC 0–5 cm	20232	<b>0.0019</b>
Manop K7905-21BC 0–5 cm	4164	0.1861
Manop K7905-42BC 10–15 cm	614	0.6580
Manop K7905-94BC 4–9 cm	87066	<b>0.0044</b>
TTNO57-10 0–2 cm	49428	<b>0.0048</b>
TTNO57-13 0–5 cm	8164	0.0695
ERDC 104 5–10 cm	69584	0.0009
ERDC 110 5–10 cm	81295	0.0006
ERDC 125 5–10 cm	67643	0.0010
ERDC 125 10–15 cm	6295	0.0181
INMD 104 5–7 cm	14510	<b>0.0036</b>
INMD 106 10–15 cm	20264	0.0014
SBB-96 Site II 0–10 cm	61820	0.0016

\*Bold samples have HF-Ba/Al<sub>Total</sub> ratios similar to those used to calculate Ba<sub>excess</sub> (0.0045–0.0075, Klump et al., 2000).

models used and that this may impact the relationships reported here.

Because the leaching protocol used here is not identical to the barite separation sequential leaching extraction, there are potential reasons why these experiments might suggest different partitioning of Ba. (1) Here we use only one HF–HNO<sub>3</sub> leaching step (as opposed to 3 for barite extraction), which may result in some variable amount of non-barite material in the residual fraction. (2) The final aluminum chloride leach has been eliminated, thus any variable amount of Ba associated with fluorides that form after the HF step (which is not barite) may be included in the residual fraction. (3) The solution to solid ratio used here is higher than for barite separation, which may result in potentially higher barite dissolution and incorporation of variable amounts of barite-Ba into the non-residual, operationally defined fractions, particularly the HF fraction. This can also explain the positive correlation between this fraction and export production in the equatorial Pacific. Finally, (4) because we use a much smaller sample size, the relative loss of Ba and/or barite due to adsorption onto centrifuge walls (e.g., not 100% yield) may be more significant and affect the calculations (indeed for most samples our total sequential leaching Ba was less than the bulk dissolution Ba expected). It is important to emphasize that despite these methodological artifacts

inherent in all sequential leaching approaches, the data clearly support our major conclusion that variable amounts of Ba exist in the many different components of marine sediment, thus complicating the general use of one excess Ba algorithm to calculate export productivity in all sediments.

#### 4. Summary and conclusions

Ba content in all phases is quite variable, and responds to variations in overlying biological activity, sedimentary provenance, sedimentation rates, and Ba cycling within sediments. Ba associations with various operationally defined sedimentary phases clearly express wide variability, with Ba present in all of the five sedimentary phases targeted with the sequential leaching extraction used here. While our findings indicate that the opal plus alumino-silicate and residual (potentially barite) fractions contain the majority of Ba in these sediments, as suggested by previous studies, other phases contain on average 200 ppm Ba, which may consist of 20% to 40% of total Ba in some sediments. Given the wide variability in Ba phase associations evident from our leaches, it is not realistic to assign an average Ba concentration to a particular phase for the purpose of subtracting this component to derive a modified Ba-excess. Moreover, we did not observe a consistent ratio of HF-Ba (the Ba associated with silicates and other terrestrial material) and total Al. While our assumption that all aluminosilicates dissolve in the HF step may not be valid (i.e., some aluminosilicate in samples with a high terrigenous component may remain in the residue fraction), this variability suggests that the use of one ratio (typically 0.0075) to correct for silicate-associated Ba, may not be appropriate for many samples (as also reported by Klump et al. (2000) and Eagle et al. (2003)).

No consistent correlation between the Ba concentrations associated with the various phases, other than barite, which are included in excess Ba (e.g., carbonate, opal, ferromanganese oxyhydroxides and organic matter) and export production is evident. Accordingly, including Ba from these fractions when using excess Ba to reconstruct past export production may introduce error that cannot be easily evaluated. The correlation between export production and Ba accumulation rates for the various phases was generally poor in the Southern Ocean and generally good in the equatorial Pacific. Our results indicate that the assumptions that all of the fractions composing Ba<sub>excess</sub> are consistently and predictably related to productivity or that a constant Al/Ba

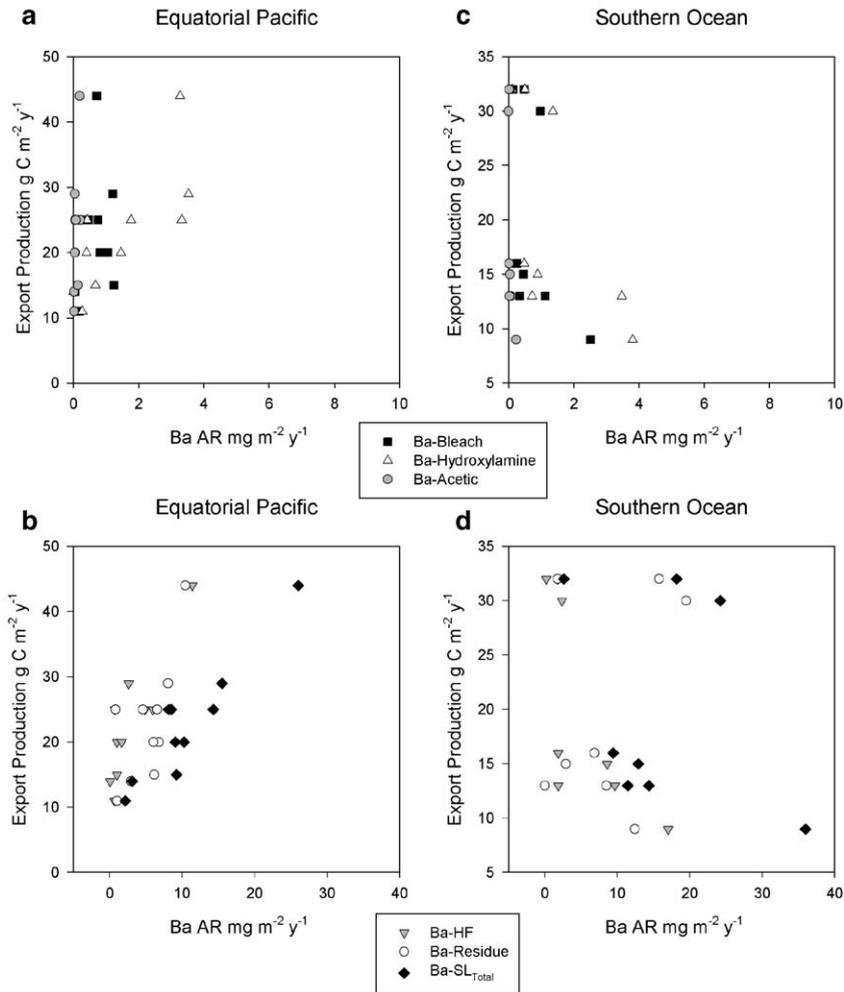


Fig. 4. Ba accumulation rate v. export production for Ba in the five sediment phases and  $Ba_{TotalSL}$  for the equatorial Pacific and Southern Ocean. (a) equatorial Pacific Ba-Bleach, Ba-Hydroxylamine and Ba-Acetic AR, (b) equatorial Pacific Ba-HF, Ba-Residue and  $Ba_{TotalSL}$  AR, (c) Southern Ocean Ba-Bleach, Ba-Hydroxylamine and Ba-Acetic AR, and (d) Southern Ocean Ba-HF, Ba-Residue and  $Ba_{TotalSL}$  AR. Note the different scales of export production between the equatorial Pacific and the Southern Ocean; also note the different scales of Ba AR associated with bleach, acetic and hydroxylamine and HF, residue and total phases. Correlation coefficients ( $r^2$ ) and significance values ( $p$ -values) are in Table 4.

ratio can be used for correction for terrestrial Ba input are not valid, so care must be taken in estimating excess Ba for any purpose, including inference of past export production.

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Table 4

Correlation ( $r^2$ ) and significance ( $p$ -value) between Ba accumulation rate (AR) of each sequential leaching phase and export production

Parameter	Southern Ocean $r^2$	$p$ -value	Equatorial Pacific $r^2$	$p$ -value
Acetic-Ba vs. export production	0.343	0.064	<b>0.310</b>	<b>0.047</b>
Bleach-Ba vs. export production	0.210	0.127	0.062	0.243
Hydroxylamine-Ba vs. export production	0.350	0.061	<b>0.580</b>	<b>0.005</b>
HF-Ba vs. export production	<b>0.476</b>	<b>0.029</b>	<b>0.748</b>	<b>0.001</b>
Residue-Ba vs. export production	0.128	0.192	<b>0.468</b>	<b>0.015</b>
$Ba_{TotalSL}$ vs. export production	0.074	0.258	<b>0.882</b>	<b>&lt;.0001</b>

Values in bold are significantly correlated ( $p < 0.05$ ).

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