Geochimica et Cosmochimica Acta 395 (2025) 238–247

Contents lists available at ScienceDirect

Geochimica et Cosmochimica Acta

journal homepage: www.elsevier.com/locate/gca

Barium uptake and isotope fractionation by a marine diatom: Implications for oceanic barium cycle

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ARTICLE INFO

Associate editor: Susan Halsall Little

Keywords:
Barium
Isotope fractionation
Diatom
Biological uptake
Barite

ABSTRACT

Barium (Ba) is a nutrient-type element in the ocean and is commonly used as a tracer for reconstructing marine productivity. Despite recent developments in Ba stable isotope analysis and growing research interest, the controls on biological Ba uptake and isotope fractionation remain largely unknown. This study presents a series of culture experiments using the model marine diatom *Thalassiosira weissflogii* to explore biological Ba uptake contributing to pelagic barite ($BaSO_4$) formation and its associated isotope fractionation for the first time. The results show that Ba cell quotas (Ba/P) are positively correlated with Ba concentrations in the culture medium, with slopes influenced by diatom-specific growth rates under high and low light levels. Similar trends in Ba, Ca, and Sr uptake suggest that Ba is likely taken up passively through Ca transporters, as a leakage of seawater Ba into the cells. This study also investigates Ba/C ratios in *Thalassiosira weissflogii* for the first time, revealing significantly lower ratios (down to 43500-fold) compared to those observed in marine field particles. This finding suggests that additional Ba sources are required to sustain particulate Ba flux associated with export production in marine water columns. The Ba isotope compositions of the cultured species indicate preferential uptake of isotopically lighter Ba from seawater, with isotope fractionation $\Delta^{138}Ba_{bio\text{-}sw}$ values ranging from −0.47 ‰ to −0.14 ‰ as Ba concentrations in the medium increase from 90 to 200 nmol/kg. The fractionation pattern is independent of the growth rates. The Ba isotope results from cultured diatoms provide the first evidence explaining the mismatch between Ba isotope fractionation factors in pelagic and laboratory-precipitated barite, suggesting that initial isotope fractionation from seawater through biological uptake can lead to a more negative fractionation factor in pelagic barite than that observed in laboratory-precipitated barite. Considering the Ba/C ratios between cultured diatoms and sediment traps, biological uptake is unlikely to be the sole or primary source of Ba for pelagic barite formation. This study provides the first constraint on marine diatom Ba cell quotas and their isotope fractionation factors, emphasizing the need to investigate the contribution of Ba from other sources (e.g., microbial processes) and the associated isotope fractionation during pelagic barite formation.

1. Introduction

Barium (Ba) has been commonly used as a marine biogeochemical proxy tracing some critical processes (e.g., Horner and Crockford, 2021), including riverine inputs (e.g., Charbonnier et al., 2020; Gou et al., 2020; Cao et al., 2021; Bridgestock et al., 2021), upwelling (e.g., Lea et al., 1989; Mohan et al., 2018), alkalinity (e.g., Jeandel et al., 1996), and productivity (e.g., Dymond et al. 1992; Paytan and Griffith, 2007; Carter et al., 2020). Pelagic barite ($BaSO_4$) plays an important role in the marine Ba cycle, but the mechanisms of its formation remain debated, especially given that upper ocean seawater is mostly undersaturated with respect to barite precipitation (Monnin et al., 1999). Several studies have shown that the degradation of phytoplankton debris and organic matter provides microenvironments conducive to pelagic barite precipitation (e.g., Dehairs et al., 1980; Bishop, 1988; Stroobants et al., 1991; Ganeshram et al., 2003). Recent studies also suggest that microbial processes enhance barite nucleation in these microenvironments, as evidenced by Ba enrichment on phosphate groups found on cell surfaces and extracellular polymeric substances (EPS) in bacterial biofilms (Martinez-Ruiz et al., 2018). However, the sources of Ba for this enrichment in microenvironments remain unclear.

Although Ba is not an essential element for microbial organisms, its

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https://doi.org/10.1016/j.gca.2025.03.006
Received 17 November 2024; Accepted 8 March 2025
Available online 13 March 2025

close association with major nutrient cycling (e.g., Si) in the ocean has prompted several studies to investigate its biological uptake. For example, the marine Ba cycle is influenced by diatom accumulations (e.g., Bacon and Edmond, 1972; Dehairs et al., 1980). Acantharians, with $SrSO_4$ skeletons, may also play a key role in marine Ba cycle (e.g., Bernstein et al., 1998; Steiner et al., 2025). Fisher et al. (1991) and Sternberg et al. (2005) conducted diatom culturing experiments to study biological Ba uptake under varying [Ba] conditions in culture medium. Sternberg et al. (2005) highlighted that high Fe concentration in culture medium can lead to Ba adsorption onto Fe-oxyhydroxides on diatom frustules, which suggests that Ba uptake in Fisher et al. (1991) may have been overestimated.

Recent developments in marine Ba stable isotope analysis provide a new approach to studying the marine Ba cycle (e.g., Horner et al. 2015; Bates et al., 2017; Hsieh and Henderson, 2017; Bridgestock et al., 2018; Cao et al., 2020). Seawater Ba concentration and isotope profiles show that both parameters are controlled by barite removal in the upper ocean and barite dissolution in the deep ocean. Pelagic barite exhibits consistent Ba isotope fractionation, with a preferential uptake of isotopically light Ba from seawater (Horner et al., 2017; Cao et al., 2020). However, current Ba isotope studies have raised a major question regarding the oceanic Ba isotope budget, as summarized by Horner and Crockford (2021): why is the average Ba isotope fractionation factor in pelagic barite more negative than the values derived from inorganic barite precipitation experiments (von Allmen et al., 2010)?

Ganeshram et al. (2003) have shown that the respiration of organic matter can contribute at least 50 % of the Ba precipitated in pelagic barite, highlighting the role of organic-matter-associated Ba in its formation. The differences in barite Ba isotope fractionation between inorganic experiments and field studies likely reflect the involvement of organic matter in pelagic barite formation in marine environments. However, there is a lack of Ba isotope data for marine phytoplankton. This missing information of Ba isotope fractionation in organic matter may explain the mismatch between the field- and lab-based estimates of barite isotope fractionation (Horner et al., 2015; Horner and Crockford, 2021). Barium isotope studies in corals (e.g., Hemsing et al., 2018; Geyman et al., 2019; Hsieh et al., 2022; Yu et al., 2022), bivalves (Fobra et al., 2024), and cyanobacteria (Mehta et al., 2023) have shown that organisms with biogenic calcium carbonates formation preferentially take up isotopically light Ba compared to ambient seawater. Similarly, Ba isotope studies in soils and rivers suggest that plants may also take up isotopically light Ba (Bullen and Chadwick, 2016; Charbonnier et al., 2020).

To better understand the impact of phytoplankton biological uptake on the marine Ba cycle and isotope fractionation in organic-matter-associated Ba prior to barite formation, we have conducted a series of marine diatom culture experiments using the model diatom species *Thalassiosira weissflogii* (*T. weissflogii*). In these culture studies, we have regulated [Fe] conditions in culture medium to minimize the effects of Fe-oxyhydroxides. The goal of this study is to provide the first constraint on Ba isotope fractionation during biological uptake and its contribution to pelagic barite formation, while also helping to assess the limitations of using Ba isotopes as a tracer for ocean productivity.

2. Methods

2.1. Diatom culturing experiments

The marine diatom *T. weissflogii* CCMP 1587 was selected for Ba uptake and isotope fractionation studies in culturing experiments because the genus *Thalassiosira* is one of the most dominant species in marine diatom blooms (Harris et al., 1995). Additionally, *T. weissflogii* has been studied for its metal quotas (Ho et al., 2003) and Ba uptake (Sternberg et al., 2005). The culture methods followed those described by Ho et al. (2003) and Sternberg et al. (2005). Briefly, all experiments were initiated after at least a 14-day acclimatization period. *T. weissflogii* was transferred from a high-Ba background medium to a low-Ba background medium (natural surface seawater) prior to the start of the experiments. The diatoms were grown in polycarbonate bottles (Nalgene) at 20 °C under a 12:12 light cycle in a growth chamber (GC-1065, FIRSTEK). Two different experiment setups were used: (High Light Experiment) 0.1 L bottles at 260 μmol photons/m^2/s and (Low Light Experiment) 1 L bottles at 150 μmol photons/m^2/s. All culture experiments were conducted in triplicate.

A natural surface seawater sample was used to provide a low Ba background for the experiments. The sample was collected during cruise LGD2211 (2022/08/30–2022/09/05) in the Pacific Ocean (21.9°N, 123.3°E) and filtered through a Polycap filter (0.22 μm, Whatman), following metal-free sampling procedures (Cutter et al., 2010). Its trace element concentrations, including Ba, were determined by ICP-MS (Table S1). Compared to the added trace elements in the culture medium, the seawater background was negligible. However, the Ba concentration in the seawater sample (34 ± 1 nmol/kg; 1SD, n = 3) was factored into the final Ba concentration of each culture medium.

Nutrient and trace metal solutions (except for Ba and Fe) were prepared and added to the culture medium with the chelator ethylenediaminetetraacetic acid (EDTA) (100 μmol/kg), following the Aquil recipe (Price et al., 1989). Since the primary variable in these experiments was [Ba], Ba solutions were independently prepared from an ICP Ba standard (Part# 10004–1-100, High Purity Standards) and added to the culture medium in concentrations ranging from 34 to 200 nmol/kg. The Fe solution was also added separately to maintain a low Fe concentration (< 100 nmol/kg) to avoid Fe-oxide formation and Ba adsorption (Sternberg et al., 2005). The concentrations of nutrients, vitamins, and trace elements in the culture medium are summarized in Table S2.

Diatom growth was monitored using a Multisizer 3 Coulter Counter (Beckman Coulter) for particle sizes between 3 and 15 μm, expressed as cell density (cells/mL). Typically, between days 2 and 5, the growth curve of *T. weissflogii* showed an exponential phase, characterized by a high specific growth rate (Fig. S1). Specific growth rate was calculated using the equation: specific growth rate = $(LnN_2 - LnN_1)/(T_2 - T_1)$, where LnN_2 and LnN_1 are the natural logarithms of cell densities at time points T_1 and T_2, respectively.

Cells were harvested as the growth curve approached the late-exponential phase. They were separated from the culture medium by centrifugation. After removing the supernatant, cells were rinsed three times with 20 mL of Milli-Q water to eliminate residual culture medium. The cell samples were then transferred into Teflon vials and digested for cell quota analysis. A 4 mL digestion solution containing 50 % HNO_3 + 10 % HF (v/v, ULTREX II Ultrapure Reagent, J.T. Baker) was added to the vials, which were then heated on a hotplate at 140 °C.

2.2. Elemental and Ba isotope analysis

A sector field high-resolution ICP-MS (Element XR, Thermo Fisher Scientific) at the Research Center for Environmental Changes, Academia Sinica, was used for elemental cell quota analysis. In all experiments, the diatom reference material BCR-414 (European Commission) was used for accuracy. The measured BCR-414 [Ba] concentration was 30 ± 2.1 mg/kg (1 SD, n = 7), consistent with the reported value of 34 ± 4 mg/kg (1 SD) (Van Horsten et al., 2022). The Ba concentration of some culture medium was also measured before and after experiment.

For the low light experiment, the particulate organic carbon (POC) and nitrogen (PON) content of *T. weissflogii* was measured using a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer. These results were used to calculate the diatom C/N and Ba/C ratios.

Due to the low quantity of Ba in the cultured diatom samples, triplicate samples from each culture medium Ba concentration were combined for Ba isotope analysis. Several sample pretreatments were performed prior to analysis, following methods established by Hsieh and Henderson (2017) and Hsieh et al. (2022), with modifications from

Table 1
Cultured *T. weissflogii* cellular Ba/P, Sr/P, Ca/P, Fe/P and Ba isotope compositions.

Medium [Ba]	μ	Ba/P	Mean	Sr/P	Mean	Ca/P	Mean	Fe/P	Mean	$\delta^{138}Ba_{bio}$	$\delta^{138}Ba_{sw}$	$\Delta^{138}Ba_{bio\text{-}sw}$
(nmol/kg)	(d^{-1})	(μmol/mol)	±1SE	(mmol/mol)	±1SE	(mol/mol)	±1SE	(mmol/mol)	±1SE	±2SD (n = 3)	±2SD (n = 3)	±2SD (n = 3)
High Light Experiment (container: 0.1 L; light: 260 μmol photons/m^2/s)												
	0.72	29		7.7		1.4		6.2				
34	0.84	29	28.7 ± 0.4	11.3	9 ± 1	1.3	1.4 ± 0.1	6.7	6.4 ± 0.2	n/a	+0.66 ± 0.05	n/a
	0.73	28		8.5		1.6		6.2				
	0.69	60		6.3		0.8		5.3				
90	0.64	67	61 ± 3	7.6	6.9 ± 0.4	1.1	1.0 ± 0.1	5.2	5.27 ± 0.03	–0.25 ± 0.10	+0.22 ± 0.05*	–0.47 ± 0.11
	0.66	55		6.9		0.9		5.3				
	0.81	81		6.1		0.8		4.9				
149	0.75	79	79 ± 1	9.1	7.3 ± 0.9	1.8	1.2 ± 0.3	4.4	4.9 ± 0.3	–0.14 ± 0.05	+0.13 ± 0.05*	–0.26 ± 0.07
	0.85	77		6.7		1.0		5.3				
	0.64	112		9.4		1.3		4.6				
189	0.62	118	113 ± 2	11.1	10.1 ± 0.5	1.7	1.5 ± 0.1	4.1	4.3 ± 0.2	–0.04 ± 0.10	+0.09 ± 0.05*	–0.14 ± 0.11
	0.64	111		9.8		1.4		4.1				
Low Light Experiment (container: 1 L; light: 150 μmol photons/m^2/s)												
	0.98	6		1.9		0.18		5.4				
34	0.99	8	7.2 ± 0.6	1.8	1.8 ± 0.1	0.15	0.16 ± 0.01	7.8	6.6 ± 0.7	n/a	+0.66 ± 0.05	n/a
	0.92	8		1.7		0.14		6.5				
	0.93	16		3.0		0.33		6.8				
100	0.94	17	15.9 ± 0.9	2.4	2.5 ± 0.3	0.24	0.26 ± 0.03	6.6	6.6 ± 0.1	–0.13 ± 0.15	+0.20 ± 0.07	–0.33 ± 0.10
	0.83	14		2.1		0.21		6.4				
	0.64	20		2.3		0.23		5.7				
150	0.85	29	27 ± 4	2.7	2.4 ± 0.1	0.28	0.25 ± 0.02	5.8	5.4 ± 0.4	–0.19 ± 0.05	+0.07 ± 0.08	–0.26 ± 0.09
	0.96	33		2.4		0.23		4.7				
	0.89	64		3.6		0.37		5.7				
200	0.88	36	43 ± 10	2.6	2.8 ± 0.5	0.27	0.28 ± 0.05	5.5	5.4 ± 0.2	–0.09 ± 0.09	+0.10 ± 0.05	–0.20 ± 0.10
	0.87	30		2.0		0.20		5.1				

*Calculated $\delta^{138}Ba_{sw}$ values, using a mixing model between natural seawater and an added Ba standard (Fig. S2).

Table 2
Cultured *T. weissflogii* cellular Ba/C, C/P and C/N ratios.

Medium [Ba]	Ba/C	Mean	C/P	Mean	C/N	Mean
(nmol/kg)	(10^{-6}g/g)	±1SE	(mol/mol)	±1SE	(mol/mol)	±1SE
Low Light Experiment						
	1.2		56		7.6	
34	1.1	1.3 ± 0.1	79	66 ± 7	7.6	7.6 ± 0.1
	1.5		61		7.4	
	3.0		60		7.9	
100	3.1	3.0 ± 0.1	63	61 ± 1	7.5	7.7 ± 0.1
	2.8		58		7.6	
	3.7		60		7.8	
150	5.0	5.7 ± 1.4	65	57 ± 6	7.4	7.5 ± 0.1
	8.3		46		7.5	
	11.6		63		7.4	
200	5.3	7.4 ± 2.1	76	69 ± 4	7.3	7.9 ± 0.6
	5.3		67		9.0	

Matecha et al. (2021). In brief, double spikes of ^{137}Ba-^{135}Ba were added to the samples to monitor mass fractionation during pretreatment. For seawater (culture medium) samples, the Ca(Ba)CO_3 co-precipitation technique was used to preconcentrate Ba before cation exchange chromatography. Both the co-precipitated and digested cell samples were dissolved in 1 mL of 3 N HCl before being loaded onto a chromatography column (2 mL Bio-Rad® AG 50 W-X8 200–400 mesh). The column was cleaned twice with 10 mL of H_2O and 10 mL of 6 N HCl, then conditioned with 10 mL of 3 N HCl. After loading the sample (dissolved in 1 mL of 3 N HCl), 11 mL of 3 N HCl was used to clean the sample matrix, followed by 14 mL of 4 N HNO_3 to elute Ba. The Ba recovery from the column, tested with BCR-414 (~200 ng Ba), was 114 ± 13 % (1 SD, n = 3). The overall procedural blank for Ba was < 0.2 ng, which is negligible compared to the total Ba content (> 50 ng) in each cultured phytoplankton sample.

Ba isotope compositions were determined using a multicollector inductively coupled plasma mass spectrometer (MC-ICP-MS, Nu Plasma HR) at the Institute of Oceanography, National Taiwan University. During each analysis, ion beams of Ba isotopes (^{138}Ba, ^{137}Ba, ^{135}Ba, and ^{134}Ba) and interferences (^{140}Ce, ^{139}La and ^{131}Xe) were monitored simultaneously over 40 cycles, with an integration of 8 s per cycle. Baselines were measured by ESA deflection (20 s) at the beginning of each analysis and subtracted from the measured ion beam signals. The sample-standard bracketing method (standard-three different samples-standard) was used to monitor instrumental drift, including a thorough cleaning procedure (60 s in 10 % HNO_3 – 60 s in 2 % HNO_3 – 60 s in another pot of 2 % HNO_3) between standards and samples. Each sample was analyzed three times independently. The Ba isotopic compositions are expressed in δ-notation as δ^{138}Ba (‰) relative to the reference standard NIST 3104a: δ^{138}Ba (‰) = [($^{138/134}Ba_{sample}$/$^{138/134}Ba_{NIST3104a}$)-1]x1000. Standards and samples typically showed an internal precision between 0.04 and 0.06 ‰ (± 2 SE) during isotope analysis. The long-term (external) precision and accuracy were monitored with a secondary Ba standard (NBS-127) over two years, yielding δ^{138}Ba = -0.29 ± 0.05 ‰ (2 SD, n = 44), consistent with published values from previous studies (Horner et al., 2017; Crockford et al., 2019; Hsieh et al., 2022). Additionally, natural seawater collected from the Pacific Ocean for culturing experiment showed [Ba] = 34 nmol/kg and δ^{138}Ba = +0.66 ± 0.05 ‰ (2SD, n = 3), following the global seawater δ^{138}Ba and [Ba] trend (Hsieh and Henderson, 2017). The Ba isotope composition of the diatom reference material BCR-414 was measured and reported for the first time as δ^{138}Ba = -0.17 ± 0.05 ‰ (2 SD, n = 4).

It is worth noting that the culturing experiments conducted at natural seawater [Ba] levels in this study did not yield Ba isotope data due to insufficient diatom Ba mass at low [Ba] in culture medium. The mean [Ba] in the top 250 m of the global ocean is generally below 45 nmol/kg (Mete et al., 2023). Nevertheless, the experiments conducted at [Ba] around 100 nmol/kg are still comparable to surface concentrations in the Southern Ocean. Despite some limitations, this study provides the first dataset to explore the role of biological uptake in the marine Ba isotope cycle and its implications for pelagic barite Ba isotope fractionation.

3. Results

The results of specific growth rates, elemental cell quotas (Ba/P, Sr/P, Ca/P, and Fe/P), and δ^{138}Ba values (including those for the culture medium) from the two sets of *T. weissflogii* culturing experiments are summarized in Table 1. The elemental quotas are normalized to P for comparisons. The specific growth rates of cultured *T. weissflogii* in this study range from 0.62 to 0.99 day^{-1}. Generally, the specific growth rates during the high light experiment were slower than those observed in the low light experiment. In the high light experiment, the cellular Ba/P ratios increased from 28.7 to 113 μmol/mol as the culture medium [Ba] rose from 34 to 189 nmol/kg, while the cellular Sr/P, Ca/P, and Fe/P remained relatively constant. In contrast, the low light experiment also showed an increase in cellular Ba/P ratios from 7.2 to 43 μmol/mol within a similar range of culture medium [Ba] (34 to 200 nmol/kg). However, this increase was noticeably lower than in the first set, which seems to correlate with the specific growth rates and trends observed for

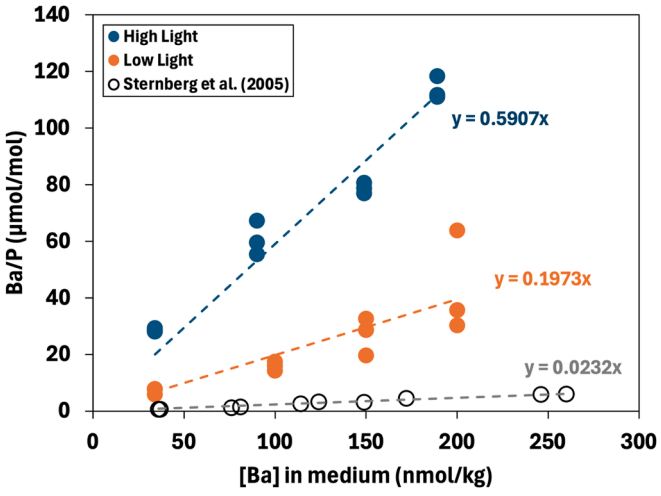

Fig. 1. Cellular Ba/P ratios in T. weissflogii at different Ba concentrations in the culture medium. The open circles show data from Sternberg et al. (2005) for comparison. The dashed lines represent the slopes of each experiment.

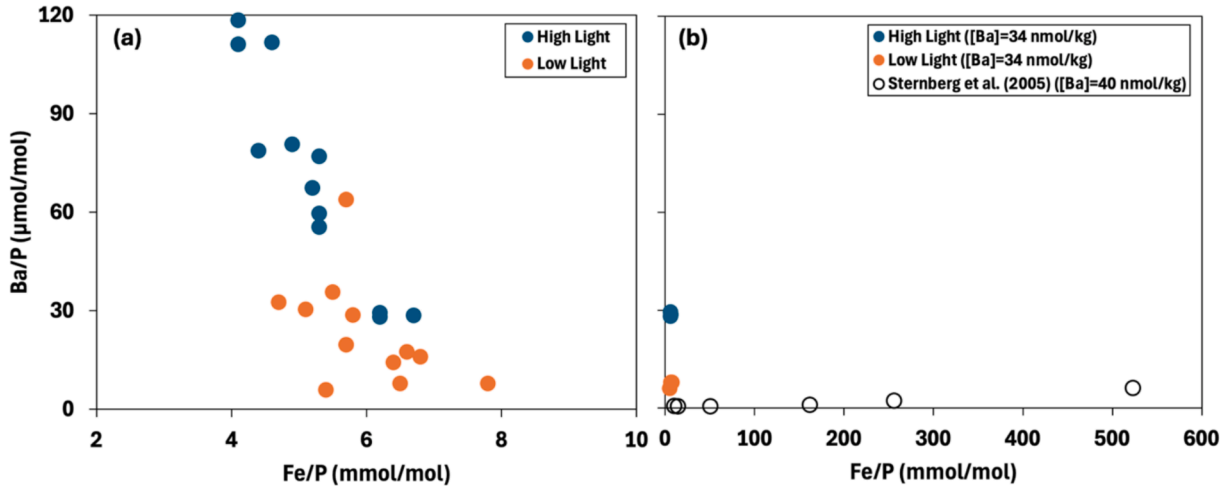

Fig. 2. Cellular Ba/P and Fe/P ratios in *T. weissflogii* for (a) all data from the high and low light experiments in this study and (b) data from the culture medium with [Ba] = 34 nmol/kg in this study and [Ba] = 40 nmol/kg in Sternberg et al. (2005). All cellular Fe/P ratios in this study are below 8 mmol/mol, which is significantly lower than the recommended value (100 mmol/mol) to prevent extracellular Fe oxyhydroxide precipitation and Ba adsorption.

other Group II elements (discussed later).

The cellular C/P and C/N ratios of cultured *T. weissflogii* in the low light experiment were consistent, ranging from 46 to 79 mol/mol and 7.3 to 9.0 mol/mol, respectively (Table 2). These values align with those reported in previous studies (*T. weissflogii* C/P: 86 ± 7 mol/mol; C/N: 6.3 ± 0.8 mol/mol, Ho et al., 2003). The cellular Ba/C ratios of cultured *T. weissflogii*, ranging from 1.1×10^{-6} to 11.6×10^{-6} g/g, are reported for the first time, offering useful comparisons with sediment trap particulate data from previous studies.

Barium isotope compositions revealed a wide range of measured $\delta^{138}Ba_{bio}$ values, from −0.25 to −0.04 ‰, in the cultured *T. weissflogii* samples (triplicates combined for each culture medium [Ba] experiment) (Table 1). Some culture medium $\delta^{138}Ba_{sw}$ and $[Ba]_{sw}$ compositions were also measured or calculated for the initial and final compositions before and after culturing experiment. Natural seawater had $[Ba]_{sw}$ = 34 nmol/kg and $\delta^{138}Ba_{sw}$ = +0.66 ± 0.05 ‰ (2SD, n = 3), while the ICP Ba standard (used to adjust culture medium [Ba]) had $\delta^{138}Ba$ = -0.02 ± 0.05 ‰ (2SD, n = 3). The measured and calculated Ba compositions in the culture medium were consistent (Fig. S2).

Changes in the culture medium [Ba] and $\delta^{138}Ba$ compositions were carefully monitored throughout the experiments. For example, in the low light experiment with natural seawater [Ba], the final culture medium maintains $[Ba]_{sw}$ at 34 nmol/kg and $\delta^{138}Ba_{sw}$ at + 0.64 ± 0.05 ‰ (2SD, n = 3) at the end of the experiment. Similarly, in the experiment with a culture medium $[Ba]_{sw}$ of 200 nmol/kg, the initial and final $\delta^{138}Ba_{sw}$ values ranged between + 0.08 ± 0.06 ‰ (2SD, n = 3) and + 0.14 ± 0.04 ‰ (2SD, n = 3), with $[Ba]_{sw}$ remaining around 195 nmol/kg. The changes in both $\delta^{138}Ba_{sw}$ and $[Ba]_{sw}$ in the culture medium during the experiments were minimal (<0.2 % of the total Ba pool), suggesting that biological uptake did not significantly alter the $[Ba]_{sw}$ or $\delta^{138}Ba_{sw}$ compositions in the dissolved pool. Therefore, the isotope fractionation between the diatoms and the corresponding culture medium ($\Delta^{138}Ba_{bio\text{-}sw}$) can be directly calculated as: $\Delta^{138}Ba_{bio\text{-}sw} \approx \delta^{138}Ba_{bio} - \delta^{138}Ba_{sw}$, which is approximately equal to $1000 \times \ln(\alpha_{bio\text{-}sw})$, based on the isotope fractionation factor ($\alpha_{bio\text{-}sw} = {}^{138/134}Ba_{bio}/{}^{138/134}Ba_{sw}$). The $\Delta^{138}Ba_{bio\text{-}sw}$ results range from −0.14 to −0.47 ‰ (Table 1).

4. Discussion

4.1. Ba uptake in marine diatom

The increase in cellular Ba/P ratios observed in cultured *T. weissflogii*

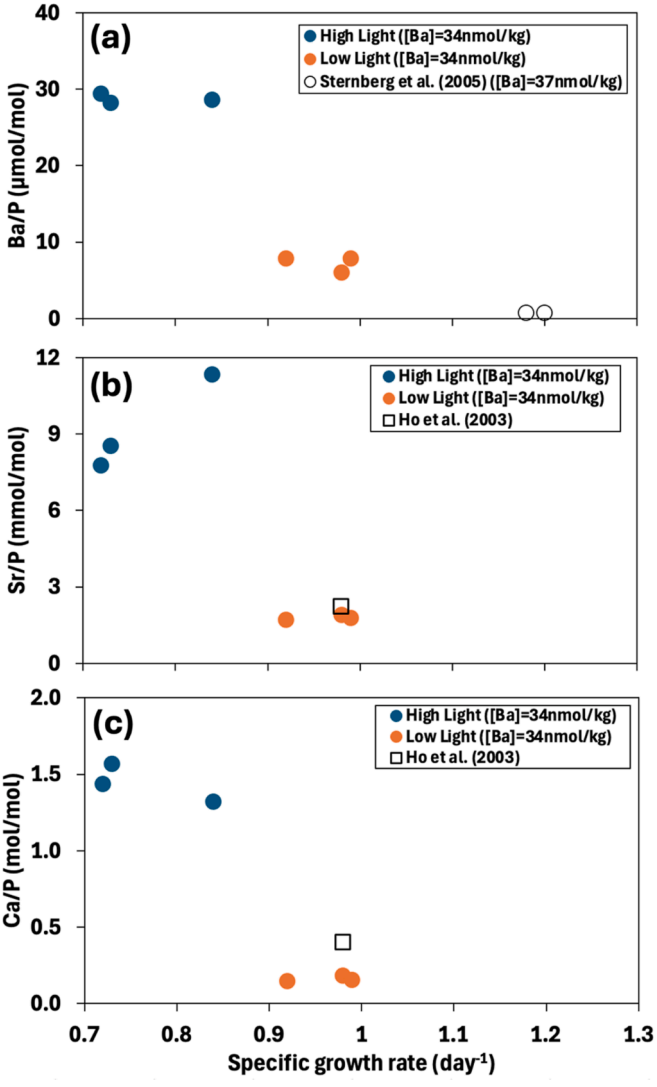

Fig. 3. Cellular (a) Ba/P, (b) Sr/P, and (c) Ca/P ratios in *T. weissflogii* grown in a culture medium with [Ba] = 34 nmol/kg, plotted against specific growth rates. The open circles and squares represent data from Sternberg et al. (2005) (culture medium [Ba] = 37 nmol/kg) and Ho et al. (2003), respectively.

samples demonstrates the uptake of Ba under elevated Ba concentrations in the culture medium (Fig. 1). While similar observations of Ba uptake in marine diatoms have been reported in previous studies (Fisher et al., 1991; Sternberg et al., 2005), the underlying mechanisms controlling this process remain unresolved. Fisher et al. (1991) conducted a leaching experiment and suggested that most Ba accumulation is accociated with diatom frustules, while Sternberg et al. (2005) emphasized that such high accumulation of Ba may result from the adsorption of Ba onto Fe hydroxides on the cell surface under high Fe culturing conditions. In a compilation of cultured diatom cellular Ba data from different species, Stenberg et al. (2005) found that cellular [Ba] (3 ~ 95 μg/g dry weight) reported across species in previous studies (e.g., Reiley and Roth, 1971; Fisher et al., 1991) is one to two orders of magnitude higher than the values (0.1 ~ 0.4 μg/g dry weight) obtained under low-Fe culture conditions. These high cellular [Ba] data should be carefully re-evaluated.

Following Sternberg et al.'s (2005) recommendations to avoid Fe hydroxide precipitation by maintaining low culture medium [Fe] (< 100 nmol/kg), our results clearly show that cultured *T. weissflogii* samples can take up varying amounts of Ba under different culture medium [Ba] conditions (Fig. 1). However, the slopes of Ba uptake between the two sets of experiments differ significantly, and both are much steeper than those reported by Sternberg et al. (2005). Given that the cell quota Ba/P and Fe/P ratios do not show any positive correlation (Fig. 2a), this difference is unlikely attributed to Ba adsorption onto Fe hydroxide precipitation. In addition, the Fe/P ratios (4.1 to 7.8 mmol/mol) are much lower than the recommended value of 14.6 ± 1.33 mmol/mol (1SD) by Sternberg et al. (2005) for avoiding Ba adsorption onto Fe hydroxides in culture experiments (Fig. 2b).

We found that the slopes of Ba uptake in cultured *T. weissflogii* were associated with specific growth rates. In Fig. 1, the slope of Ba uptake in the high light experiment was nearly three times steeper than the low light experiment, and the specific growth rates of the high light experiment (0.72 ± 0.08 day^{-1}) were lower than those in the low light experiment (0.89 ± 0.09 day^{-1}) (Table 1). Given the importance of growth rates in determining cell physiology in culture experiments, the relationship between growth rates and cellular Ba/P quotas (using data from culture medium [Ba] of 34 nmol/kg) was explored in Fig. 3, which include data from Sternberg et al. (2005) under similar culture conditions (20°C, 2 L bottles and 150 μmol photons/m^2/s). The results show that higher growth rates are associated with lower Ba/P cell quotas in cultured *T. weissflogii* samples.

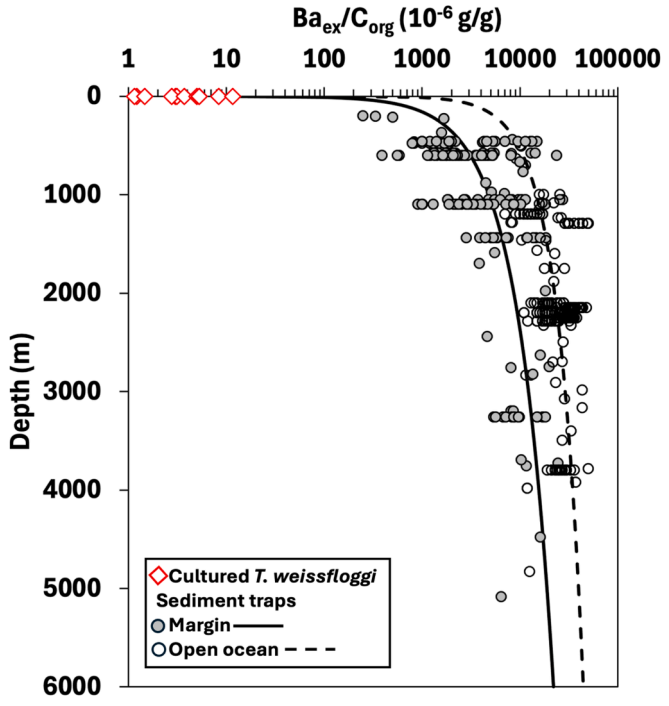

Fig. 4. Comparison of cellular Ba/C ratios in cultured *T. weissflogii* from this study (red open diamonds) with organic C to excess Ba (Ba_{ex}/C_{org}) ratios from sediment traps in previous studies on continental margins (gray circles) and open ocean sites (open circles) (Dymond et al., 1992; Francois et al., 1995; Dymond and Collier, 1996; Dehairs et al., 2000; McManus et al., 2002; Fagel et al., 2004; Sun et al., 2013). The dashed and solid lines show the relationship between Ba_{ex}/C_{org} ratios and water depth in the open ocean (Francois et al., 1995) and continental margins (Fagel et al., 2004), respectively.

Since Ba is not known to have any physiological function in phytoplankton, the variation of Ba concentration in culture medium is unlikely to influence the growth rates of the diatom directly. To explore this further, we measured not only Ba but also the uptake of chemically similar Group II elements (i.e., Ca and Sr). These additional measurements allowed us to evaluate whether shared uptake pathways might explain Ba incorporation. In Fig. 3, the cellular Ca/P and Sr/P quotas in the model diatom show a similar trend to the Ba/P quota, with higher Ca/P and Sr/P accumulation at lower specific growth rates, even though the concentrations of Ca and Sr in the culture medium are fixed.

Diatom Ba uptake can occur through biological cellular uptake and/or physical adsorption onto the cell surface (Sternberg et al. 2005). Although this study does not provide direct evidence to determine the exact mechanism controlling the uptake, by comparing the trends of Ba, Ca, and Sr uptake across different experimental conditions, we identified consistent patterns that pointed toward a common mechanism. Given that Ca and Sr uptake varies despite their fixed concentrations in the cluture medium (Fig. 3), the mechanism is more likely driven by biological processes. Therefore, we propose that the similar chemical properties to Ca may allow Ba to be taken up via phytoplankton Ca transporters or Ca pumps. It is well known that Ca serves important structural, metabolic, and signaling functions in marine phytoplankton (Falciatore et al., 2000; Demidchik et al., 2018; Helliwell et al., 2021). A similar mechanism has been proposed for Sr uptake in coccolithophores (Stevenson et al., 2014). Due to the negative potential in the cytoplasm, Ba^{2+} ions can passively enter cells through these transporters or channels, even in the absence of a specific Ba transport system (Sternberg et al., 2005). Accidental uptake of Ba through Ca channels on cell membranes is likely a major mechanism influencing the intracellular Ba quota.

The efficiency of nutrient and trace element uptake depends on surface area, enzyme activity, and transporter concentrations (Finkel et al., 2010). At higher growth rates, phytoplankton cells require more substantial supplies of major nutrients and essential trace elements (e.g., Fe). Therefore, the number of specific transporters for these nutrients and elements should proportionally increase within a given area of cell surface, while those for Ca may decrease on the surface. We propose that the negative correlation between the uptake of Group II elements and specific growth rates in marine diatoms are attributed to limited space on major and minor nutrient transporters available on the cell surface. As a result, the uptake of Group II elements by marine diatoms decreases at higher growth rates. In Fig. 2a, the slightly negative relationship between cellular Fe/P and Ba/P ratios appears to support the hypothesis that an increase in Fe uptake may be accompanied by a decrease in Ba (Group II element) uptake under higher growth rates. Although further studies are needed to fully understand the controls on biological uptake of Group II elements in marine phytoplankton, the results of this study emphasize the need to investigate the roles of biological uptake and phytoplankton growth in the marine Ba cycle. Changing micronutrient concentrations can also be considered as a controlling factor for testing the hypothesis of transporter space limitation.

4.2. Comparisons of Ba/C ratios between cultured diatom and sinking particles

Our study found that the measured cellular Ba/C ratios in the model

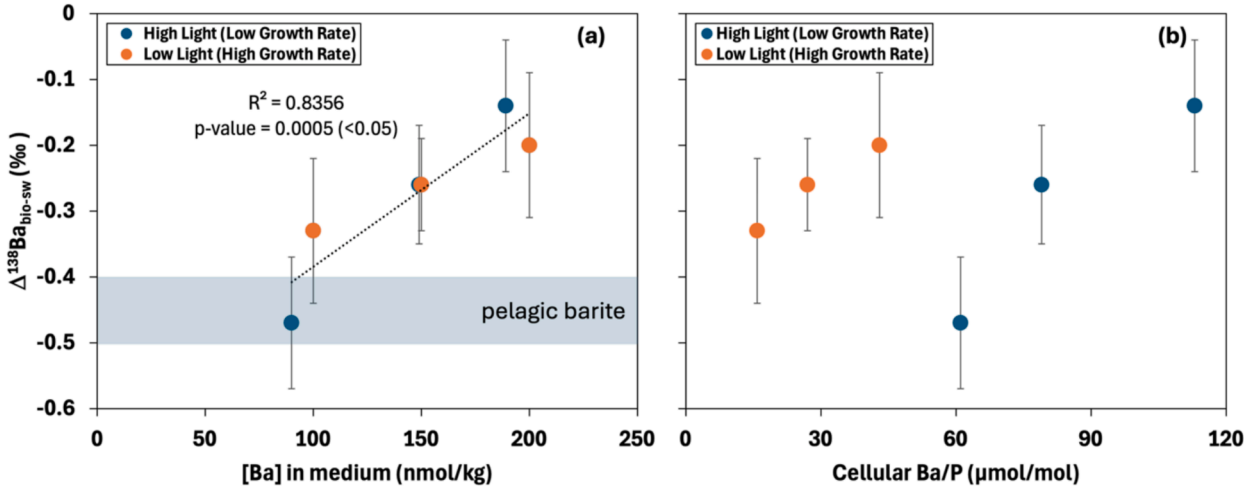

Fig. 5. Ba isotope fractionation ($\Delta^{138}Ba_{bio\text{-}sw}$) by biological uptake in *T. weissflogii* under (a) different Ba concentrations in the culture medium and (b) different cellular Ba/P ratios. The dashed line represents a linear regression through the six data points, along with its R-squared and p-value. The blue shading indicates the range of previously reported Ba isotope fractionation in pelagic barite ($\Delta^{138}Ba_{bar\text{-}sw}$).

diatom show much lower values ($1.1 \times 10^{-6} - 11.6 \times 10^{-6}$ g/g) than particulate excess Ba to organic C ratios (corrected for lithogenic fraction) (Ba_{ex}/C_{org}) observed in the field (Table 2, Fig. 4). The ratios of Ba_{ex}/C_{org} are commonly used to reconstruct marine export production and paleoproductivity (Dymond et al., 1992). However, these ratios can vary significantly, from 250×10^{-6} to $50{,}000 \times 10^{-6}$ g/g, in sediment traps across different oceanic settings, such as between the open ocean and continental margins (Fig. 4). This huge variability highlights the challenge of using Ba as a productivity proxy. Despite the large variation in particulate and sediment Ba_{ex}/C_{org} values throughout water columns, the measured cellular Ba/C ratios can be down to 22 ~ 43,500 times smaller than the Ba_{ex}/C_{org} ratios observed in the field.

Dymond et al. (1992) proposed that the increase in particulate Ba_{ex}/C_{org} values with depths are primarily driven by (1) the decrease in organic carbon flux due to degradation and (2) the increase in Ba sinking flux due to uptake and preservation in microenvironments within water columns. Considering global average surface ocean productivity (205 to 410 mg C/m^2/d) and the global median POC flux at 100 m depth (~100 mg C/m^2/d) (Mouw et al., 2016; Webb, 2021), the 2-4-fold decrease in POC flux from the surface to around 100 m depth cannot explain the large difference between particulate and cellular Ba/C ratios.

Using global average surface ocean productivity (205 to 410 mg C/m^2/d) and the average cultured diatom Ba/C ratio (2.7×10^{-6} g/g) from this study, we estimate an average biological Ba uptake rate in the surface ocean to be around 0.02 – 0.04 μg Ba/cm^2/yr. Dehairs et al. (1980) estimated a biogenic particulate Ba sinking flux of ~ 1.35 μg Ba/cm^2/yr, and Paytan and Kastner (1996) estimated an average ocean particulate Ba sinking flux of ~ 4.12 μg Ba/cm^2/yr. Comparing these results, it is clear that phytoplankton Ba uptake alone cannot account for the particulate Ba sinking flux below the euphotic zone, indicating a 34- to 206-fold increase in particulate Ba sinking flux.

Several previous studies have demonstrated similar arguments using a stoichiometric approach, relating particulate Ba to macronutrient ratios to assess the contribution of phytoplankton on the particulate Ba sinking flux. Horner et al. (2015) used Ba:P:O_2 ratios to examine the role of phytoplankton organic matter in the South Atlantic Ba cycling, showing that the proportion of Ba regenerated from the respiration of organic matter is insignificant (< 1.5 %). A similar observation was also reported in the North Pacific by Steiner et al. (2024). The low particulate Ba/P ratios in the photic zone ocean are insufficient to account for the observed increase in particulate Ba flux with depth, suggesting that phytoplankton organic matter is unlikely to be the primary source of Ba for barite formation.

The sources of Ba contributing to this increased particulate Ba sinking flux and their enrichment mechanisms remain unclear. Several studies have emphasized the importance of microbial processes during organic matter degradation and barite formation (Gonzalez-Muñoz et al., 2012; Torres-Crespo et al., 2015; Martinez-Ruiz et al., 2018). Further research is required to understand the additional Ba from other processes that contribute to this enrichment in microenvironments (e.g., carbonate, Fe-Mn oxides, or ambient seawater). Nevertheless, this study provides the first estimate of the phytoplankton Ba/C cell quota and offers quantitative evidence supporting the hypothesis that phytoplankton Ba uptake is not the major source of Ba driving the increased particulate Ba sinking flux.

4.3. *Ba isotope fractionation in marine diatom: implications for oceanic Ba isotopes*

The cultured marine diatom *T. weissflogii* exhibited significant Ba isotope fractionation between cellular uptake and seawater. The cellular $\delta^{138}Ba$ values are isotopically lighter than those of the culture medium (Table 1), consistent with most phytoplankton results observed for other metal isotope systems (e.g., Si isotopes: de La Rocha et al., 1997; Zn isotopes: John et al., 2007; Köbberich and Vance, 2019; Samanta et al., 2018). The calculated isotope fractionation $\Delta^{138}Ba_{bio\text{-}sw}$ values range from −0.14 ‰ to −0.47 ‰ under different Ba concentrations in the culture medium (Fig. 5).

What effect may control the changes of isotope fractionation $\Delta^{138}Ba_{bio\text{-}sw}$ values during the biological uptake? Mehta et al. (2023) conducted a series of culture experiments studying Ba isotope fractionation during the formation of intracellular carbonates in cyanobacteria. The intracellular carbonate shows an consistent isotope fractionation $\Delta^{138}Ba$ of −0.33 ‰ from the culture medium. However, an outflux of Ba from the cells to the culture medium was observed at the end of their experiments, possibly due to intracellular carbonate dissolution in response to cellular stress. This behaviour is not observed in our study given the different culture conditions (e.g., cultur medium [Ba], biological species and biominerals). In another unlikely event that Ba uptake was influenced by Ba adsorption onto Fe oxyhydroxides on the cell surface, as discussed in Section 4.1, the isotope fractionation factor may range from −0.2 ‰ to −0.3 ‰, based on the estimates of Ba adsorption onto Fe oxyhydroxides by Knight et al. (2024), which could contribute to our data (−0.14 ‰ to −0.47 ‰). However, this requires future studies with high Fe culturing conditions to evaluate the additional Ba isotope fractionation induced by Ba adsorption.

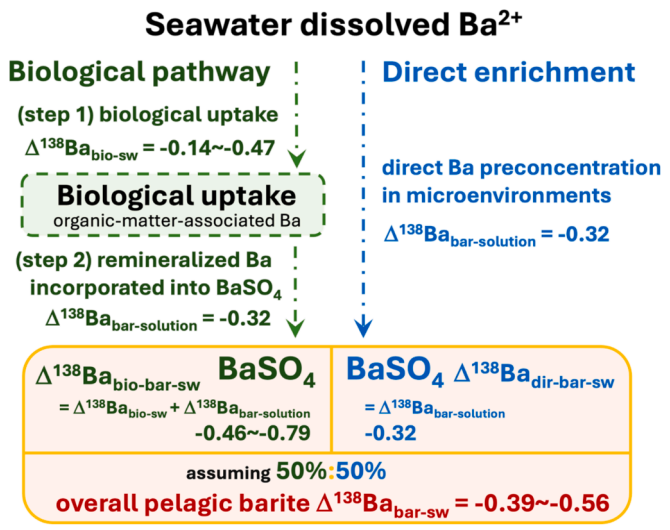

Fig. 6. Schematic diagram illustrating the two pathways by which seawater dissolved Ba is incorporated into pelagic barite in microenvironments, along with their associated isotope fractionation Δ^{138}Ba values (‰). The first pathway consists of two steps: initial biological uptake of Ba, followed by remineralization (organic-matter-associated Ba) that leads to the formation of pelagic barite in microenvironments. The second pathway involves the direct enrichment of seawater Ba to form pelagic barite in microenvironments. Assuming both pathways contribute equally (50%:50%) to pelagic barite formation, as suggested by Ganeshram et al. (2003), the overall pelagic barite isotope fractionation factor ranges from −0.39 to −0.56‰. This range aligns with the observed values (−0.4 to −0.5‰) in field pelagic barite and may help explain the discrepancy between Ba isotope fractionation factors in pelagic barite and those observed in laboratory-precipitated barite.

Although the exact controls of biological uptake Ba isotope fractionation factors are not clear, the variation in *T. weissflogii* $\Delta^{138}Ba_{bio\text{-}sw}$ values appears independent of growth rates, as shown by comparisons with the cell quota Ba/P in both sets of culture experiments (Fig. 5). Some studies have similarly found that isotope fractionation factors are not influenced by phytoplankton growth rates when the elements are primarily involved in building frustules and shells, such as Si isotopes in diatoms (de La Rocha et al., 1997) and Ca isotopes in coccolithophores (Langer et al., 2007). Given that Ba uptake is likely due to passive leakage of Ba ions into the cell via transporters similar to these elements (Sternberg et al., 2005), it is not unreasonable to see that Ba isotope fractionation in *T. weissflogii* is not strongly driven by growth rates.

Despite all observed Ba isotope fractionation $\Delta^{138}Ba_{bio\text{-}sw}$ values for *T. weissflogii* being negative, there is a slight trend of increasing $\Delta^{138}Ba_{bio\text{-}sw}$ values with higher Ba concentrations in the culture medium (Fig. 5a). Previous studies in diatoms culturing experiments with varying Zn availability have shown that EDTA can have a huge effect on Zn isotopes by binding isotopically heavier Zn, leaving the bioavailable Zn pool isotopically lighter, and thus leading to lighter Zn isotope fractionation in diatoms under low [Zn] conditions (Ban et al., 2002; John et al., 2007; Köbberich and Vance, 2019). Although the effect of EDTA on Ba isotopes is unknown, the formation constant of Ba-EDTA complex (log K_f = 7.88) is much smaller the Zn-EDTA complex (log K_f = 16.5) (Harris and Lucy, 2016). In addition, the variation of culture medium [Ba] is only 5-fold in this study, which is much smaller than the ones in the Zn experiments (up to 10,000-fold). Thus, EDTA is unlikely to cause a large difference in bioavailable Ba and isotope fractionation in this study.

The mismatch between Ba isotope fractionation Δ^{138}Ba values in pelagic barite ($\Delta^{138}Ba_{bar\text{-}sw}$ = -0.4 to −0.5 ‰, Horner et al., 2017; Cao et al., 2020) and laboratory precipitated barite ($\Delta^{138}Ba_{bar\text{-}solution}$ = -0.32 ‰, von Allmen et al., 2010) present a challenging question in the marine Ba isotope system. Ganeshram et al. (2003) found that the respiration of organic matter can contribute at least 50 % of Ba in pelagic barite despite only 2–4 % of respired Ba being involved in this process, highlighting the role of organic-matter-associated Ba in pelagic barite formation. Horner et al. (2015) and Horner and Crockford (2021) proposed that organic-matter-associated Ba may induce a negative isotope fractionation relative to seawater, explaining why pelagic barite has a more negative isotope fractionation factor than lab-precipitate barite. The biological uptake $\Delta^{138}Ba_{bio\text{-}sw}$ values from cultured diatoms in this study provide the first evidence to test the hypothesis. Following the models proposed by Horner et al. (2015), Fig. 6 illustrates two pathways for Ba enrichment in microenvironments and their corresponding isotope fractionation $\Delta^{138}Ba_{bar\text{-}sw}$ in the conversion of dissolved seawater Ba into pelagic barite. One pathway involves a two-steps process, where biologically taken-up Ba being is first remineralized in microenvironments before barite precipitation. The other involves alternative processes that allow seawater Ba to be directly preconcentrated in these environments.

In comparison, the measured $\Delta^{138}Ba_{bio\text{-}sw}$ values (−0.14 to −0.47 ‰) in cultured *T. weissflogii* are generally less negative than the values observed for pelagic barite in field studies ($\Delta^{138}Ba_{bar\text{-}sw}$ = -0.4 to −0.5 ‰; Horner et al., 2017; Cao et al., 2020), with one exception (−0.47 ‰). This suggests that biologically assimilated Ba is unlikely to be the sole contributor (100 %) to pelagic barite formation, aligning well with the observations of Ganeshram et al. (2003) and others discussed in Section 4.2. Under the biological pathway (Fig. 6), the pelagic barite Ba isotope fractionation $\Delta^{138}Ba_{bio\text{-}bar\text{-}sw}$ value is the sum of two steps: $\Delta^{138}Ba_{bio\text{-}sw}$ (−0.14 to −0.47 ‰) + $\Delta^{138}Ba_{bar\text{-}solution}$ (−0.32 ‰) = -0.46 to −0.79 ‰. Assuming that 50 % of pelagic barite Ba originates from the biological pathway ($\Delta^{138}Ba_{bar\text{-}bio\text{-}sw}$) and the other 50 % from the direct seawater enrichment pathway ($\Delta^{138}Ba_{dir\text{-}bar\text{-}sw}$ = $\Delta^{138}Ba_{bar\text{-}solution}$) (Ganeshram et al., 2003), the overall pelagic barite Ba isotope fractionation factor is estimated to range from −0.39 to −0.56 ‰, which agrees well with the values (−0.4 to −0.5 ‰) observed in field studies (Horner et al., 2017; Cao et al., 2020). This implies that pelagic barite Ba isotope records may reflect not only changes in seawater Ba isotopes or the depths at which barite forms but also factors influencing the proportion of different Ba sources and pathways in pelagic barite. These factors are likely associated with microenvironment conditions, such as organic respiration rate and barite saturation.

Although it has been demonstrated that the contribution of biologically assimilated Ba to barite formation and Ba export production is small (Fig. 4; Section 4.2), the exact mechanism by which Ba is incorporated into organic matter requires further study. Martinez-Ruiz et al. (2018) have investigated the role of microbial processes in pelagic barite formation during the degradation of organic matter, where phosphate groups in the EPS of bacterial biofilms facilitate Ba enrichment and barite nucleation. Other processes, such as adsorption onto Fe and Mn oxides and abiotic precipitation in localized supersaturated microzones, may also play significant roles in Ba enrichment within pelagic microenvironments (Dehairs et al., 1980; Monnin et al., 1999; Ganeshram et al., 2003; Sternberg et al., 2005). Future studies on the sources and pathways of Ba and their isotope fractionation associated with different enrichment processes may help us better understand the transfer of Ba in microenvironments and improve our understanding of the oceanic Ba isotopic budget.

5. Conclusions

In this study, culture experiments demonstrated the variations of Ba cell quota in the marine diatom *Thalassiosira weissflogii* under different concentrations of [Ba] in the culture medium. Biological Ba uptake shows a positive relationship with the [Ba] in the culture medium and a negative relationship with its specific growth rates. We propose that the efficiency of transporters of other group II elements (mainly Ca) on cell membrane is the cause deciding the accidental cellular uptake of Ba. Linking marine Ba and C cycles, the Ba/C ratios of cultured *T. weissflogii*

have been explored for the first time, and exhibit values down to 43,500 times lower than those observed in sinking particles from field studies. Rapid organic C degradation alone cannot fully explain this discrepancy, suggesting that an additional Ba supply is necessary to sustain the downward particulate Ba flux associated with export production.

Ba isotope compositions in cultured *T. weissflogii* indicate a preferential uptake of lighter Ba isotopes compared to the culture medium. The isotopic fractionation $\Delta^{138}Ba_{bio\text{-}sw}$ values range from −0.14 ‰ to −0.47 ‰, independent of growth rates. The Ba isotope results from cultured diatoms provide the first evidence explaining the mismatch between Ba isotope fractionation factors in pelagic barite and laboratory-precipitated barite. Initial isotope fractionation from seawater through biological uptake can result in a more negative isotope fractionation factor in pelagic barite than those observed in laboratory-precipitated barite. However, based on the results of Ba/C ratios in cultured diatoms and sediment traps, biological uptake is unlikely to be the sole or primary source of Ba for pelagic barite formation. To improve our understanding of Ba isotopes in pelagic barite and its applications in paleoceanography, future studies should investigate additional Ba sources to explain Ba enrichment and constrain isotope fractionation during pelagic barite formation in marine environments.

CRediT authorship contribution statement

Yu-Te Hsieh: Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **Po-Kai Yang:** Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Tung-Yuan Ho:** Writing – review & editing, Supervision, Methodology, Investigation, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We thank Ling-Wei Tseng, Mei-Chen Lu, Ya-Lan Chou, and Bin-Yu Zeng for their assistance with the culturing experiments. We also thank Chih-Chiang Hsieh and Chia-Jung Lu for their help with ICP-MS analysis. We appreciate the discussions with Wen-Hsuan Liao and Pei-Chi Ho. We thank the associate editor, Susan Little for handling the manuscript. We are grateful to the two reviewers, Yibo Lin and Tristan Horner, for their constructive comments and suggestions, which have helped improve this manuscript. The field and related experimental studies were supported by Taiwan NSTC grants 113-2611-M-002-021, 113-2611-M-002-001, 112-2611-M-002-004, and 111-2611-M-002-007.

Appendix A. Supplementary material

The Supplementary Material includes information on (A) trace element concentrations in the natural seawater used for the culturing experiment; (B) nutrient and trace element concentrations in the culture medium; (C) the calculation of specific growth rates; and (D) the Ba isotope mixing model for the culture medium. Supplementary material to this article can be found online at https://doi.org/10.1016/j.gca.2025.03.006.

Data availability

Data are available through Mendeley Data at https://doi.org/10.17632/bw9r5hmjrd.1.

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