Boron isotopic fractionation during incorporation of boron into Mg(OH)₂

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Experiments of boron incorporated into Mg(OH)₂ from magnesium-free synthetic seawater were carried out at various pH values, in order to investigate the adsorption species and the variation of isotopic fractionation of boron on Mg(OH)₂. The results showed that the incorporation of boron into Mg(OH)₂ was very rapid and reached the equilibrium after 4 h. The $[B]_s$ and the partition coefficient K_d between Mg(OH)₂ and final solution decreased with the increasing pH. The maximum values of $[B]_s$ and K_d were much higher than that of boron adsorbed on metal oxide or clay minerals, indicating that the incorporation capability of boron into Mg(OH)₂ was very strong. When the adsorption reached the equilibrium, the $\delta^{11}B_{fsw}$ was lower than $\delta^{11}B_{isw}$. The boron isotopic fractionation $\alpha_{s\text{-}fsw}$ was between 1.0186 and 1.0220 with an average of 1.0203. All these indicated that ^{11}B incorporated into Mg(OH)₂ preferentially due to B(OH)₃ incorporation into Mg(OH)₂ preferentially. The deposition reaction of B(OH)₃ with Mg(OH)₂ was the direct reason for B(OH)₃ incorporation into Mg(OH)₂. During the boron incorporation into Mg(OH)₂, the isotopic fractionation characteristic of boron was decided by the simultaneous existence of adsorption of boron on Mg(OH)₂ and the deposition reaction of H₃BO₃ with Mg(OH)₂. Different from the fact that only $B(OH)_4^-$ species incorporated into bio-carbonate, B(OH)₃ and B(OH)₄ incorporated into Mg(OH)₂ simultaneously, and B(OH)₃ incorporated into it preferentially. The lower pH is, the more incorporated fraction of B(OH)₃ will be. Mg(OH)₂ exists widely in madrepore, which influences the quantitative correspondence of the boron isotopic composition $\delta^{11}B_{carb}$ of corals on the pH of the seawater badly, and brings serious uncertainty to the $\delta^{11}B_{carb}$ as the indicator of the ancient seawater pH.

boron, incorporation, isotopic fractionation, magnesium hydroxide

Bio-carbonates are the main reservoir of boron in seawater. In recent years, topics such as the reconstruction of ancient seawater pH using the isotopic composition of boron in bio-carbonates, the calculation of the past pCO₂, and the influence of these two factors on changes in the ancient climate, have become important issues for the international isotope geochemistry community[1–11], which is called δ^{11}B-pH proxy. One of the main assumptions of the δ^{11}B-pH proxy is that only $B(OH)_4^-$ incorporated into bio-carbonates, with little or no boron isotopic fractionation[2], so the $\delta^{11}B_{carb}$ values in marine

biogenic carbonates potentially recorded the $\delta^{11}B_4$ value of $B(OH)_4^-$ in seawater. A series of inorganic calcite precipitation experiments were carried out in order to determine the dependence of boron isotopic composition of calcite on pH of seawater[12–15]. Their results were consistent with their hypothesis, and supported the fun-

damental assumption that the $B(OH)_4^-$ was the dominant species incorporated into calcite. Palmer et al.[15] found the partition coefficient K_d and isotopic fractionation between solid and solution increased with the increasing pH when boron was adsorbed on ocean clay minerals, indicating that $B(OH)_4^-$ was the dominant adsorbed species. But many recent studies indicated that $B(OH)_4^-$ may not be the only species incorporated into calcite or be adsorbed. Pagani et al.[16] evaluated the boron isotope-pH proxy, and pointed out that $B(OH)_4^-$ may not be the dominant species incorporated into calcite, and $B(OH)_3$ may be also incorporated into calcite. An unusual isotopic fractionation of boron ($\alpha_{s-fsw} > 1$) was found by Xiao et al.[17] from inorganic calcium carbonate precipitation. They concluded that when $Mg(OH)_2$ was deposited at high pH value, $B(OH)_3$ incorporated into carbonates. Lemarchand et al.[18] found that adsorption of boron on Fe and Mn oxides (goethite, birnessite) was also pH-dependent. The boron isotopic fractionation of Fe oxides ranged from $\Delta = -40‰$ at pH<8 to 0‰ at pH > 10. When pH < 8 ^{10}B was enriched in solid and when pH > 10 the fractionation became zero. When pH > 9 reverse fractionation of boron was found, that was ^{10}B enriched at Mn oxides surface. Peak et al.[19] used ATR-FTIR spectroscopy to investigate the mechanism of boric acid ($B(OH)_3$) and borate ($B(OH)_4^-$) adsorption onto hydrous ferric oxide (HFO). Their results confirmed that $B(OH)_3$ may be the main species adsorbed onto HFO. McElligott and Byrne[20] found that $B(OH)_2CO_3^-$ complex can be formed by the reaction of $B(OH)_3$ with HCO_3^-. Tossell[21] used ^{11}B NMR and boron isotopic fractionation to investigate $B(OH)_3$ adsorption onto humic acid. Because $B(OH)_2L^-$ can be formed by reaction of $B(OH)_3$ with humic acid (HL^-), he concluded that boron can be incorporated into calcite by the species of $B(OH)_2CO_3^-$ complex, not by simple anion substitution.

Adsorption of boron on hydrous oxide of Mg was researched widely[22–26]. Petric et al.[22] indicated that boron is co-precipitated and accumulated in MgO during the process of MgO precipitated from seawater. Polat et al.[23] found that the selected materials were very effective in removing boron from water. In addition, boron concentration of calcite and aragonite with high Mg was 5 times more than that without Mg. All these indicated that adsorption capability of boron on Mg was comparatively strong.

Liu et al.[24] and Yuan et al.[25] reported the mechanism of boron adsorption by $Mg(OH)_2$, which suggested that the adsorption was controlled by pH and only the $B(OH)_4^-$ species was adsorbed onto $Mg(OH)_2$ surface. But the influence of $Mg(OH)_2$ on boron isotopic fractionation during adsorption was not researched, so the mechanism of boron adsorbed on $Mg(OH)_2$ was not clear.

Mg is a trace element in the madrepore, and the Mg/Ca ratio in madrepore has been used to research the temperature of the ancient seawater, but the Mg concentration in madrepore is different in different areas and categories[27]. Variable Mg content in scleractinian corals was attributed to adsorption of Mg to crystal surfaces and organic ligands, but Mg also occurs in significant concentrations in corals in mineral phases, such as $Mg(OH)_2$[28]. $Mg(OH)_2$ in living scleractinian coral colonies (*Acropora, Pocillopora, Porites*) in the Great Barrier Reef, Australia, and Florida Keys, United States, was researched in detail by Nothdurft et al.[29], and the $Mg(OH)_2$ was found in the most of the scleractinian corals, which indicated the wide existence of $Mg(OH)_2$ in modern coral reef. The existence of $Mg(OH)_2$ in corals may bring abnormity to the relationship between Mg/Ca and SST[29], and whether this can influence the boron isotopic composition of corals and then leads to the error of the $\delta^{11}B$-pH proxy is what we should concern.

Boron isotopic fractionation experiment during the adsorption of $Mg(OH)_2$ is first researched in this paper. The purpose is to investigate the possible dominant species of boron incorporated into $Mg(OH)_2$ and offer scientific basis to the $\delta^{11}B$-pH proxy.

1 Experiment and method

1.1 Reagents and equipment

1.0 mol/L HCl, 0.5 mol/L NaOH, and 0.5 mol/L $MgCl_2$ were prepared using twice distilled HCl (GR), NaOH (GR), $MgCl_2$ (GR), and boron-free water, respectively. The concentration of the Cs_2CO_3 (99.994% purity) solution used in our study was 12.3 g Cs/L. A suspended graphite solution was prepared using graphite (SP) confected with 80% ethanol and 20% water. For a mannitol concentration of 1.82 g/L, we used GR mannitol confected with boron-free water. The boron-free water was obtained by using 18.2 MΩ milliQ of water exchanged

with an Amberlite IRA 743 boron specific resin. A GV IsoProbe T-single magnetic sector thermal ionization mass spectrometer, UV-2100 type spectrophotometer from Shanghai Unico Ltd. and super clean oven with laminar flow through four KOH-impregnated cellulose fiber filters were used.

Throughout the entire experiment, vessels of Teflon, polyethylene or chert were used in the interest of avoiding boron contamination.
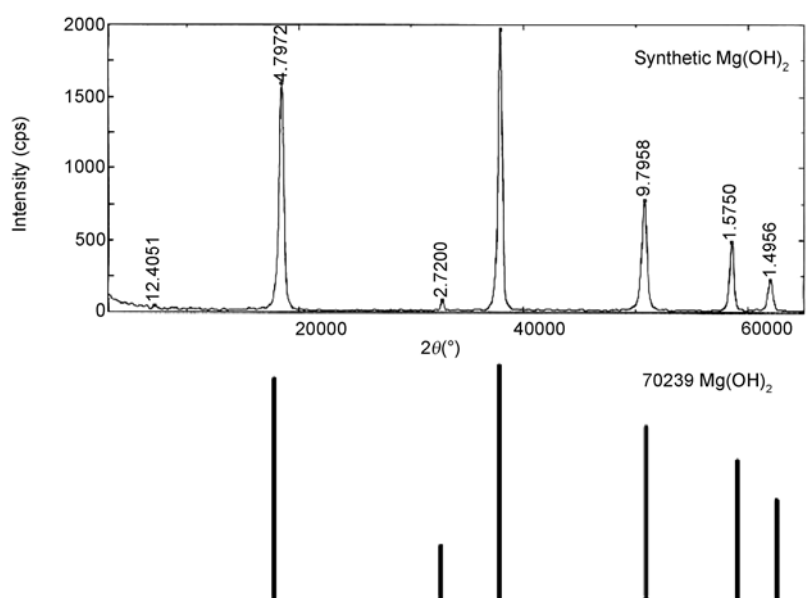
1.2 Preparation of magnesium-free synthetic seawater

Magnesium-free synthetic seawater was synthesized according to Mocledon's method (see http://zhidao.baidu.com/question/26278104.htmL?fr=qrl). The chemical composition of the magnesium-free synthetic seawater is given in Table 1. The measured boron concentration in the synthetic seawater was 45.9 ppm, which was approximately 10 times that of normal seawater (~4.5 ppm), and sufficient for isotopic analysis. The pH value and specific gravity of the synthetic seawater were 3.64 and 1.020, respectively. Using this magnesium-free synthetic seawater can avoid the deposition of $Mg(OH)_2$ when the seawater pH is adjusted.

1.3 Synthesis of $Mg(OH)_2$

The $Mg(OH)_2$ in market is usually used as flame retardant, and the boron concentration is very high. The measured boron concentration of $Mg(OH)_2$ (AR) was 11.6 μg/g, which is 5 % of the smallest adsorption quantity of boron on $Mg(OH)_2$, and can bring significant influence. But the higher purity $Mg(OH)_2$ cannot be bought in market, so it needs to be synthesized in laboratory. There are many ways to synthesize $Mg(OH)_2$ at home and abroad, and the simplest way is used here. The GR $MgCl_2$ passed through boron-specific resin first, and then it reacted with distilled GR $NH_3 \cdot H_2O$. The deposition was separated from parent solution by filtrate, and the $Mg(OH)_2$ deposition was washed with boron-free water until Cl^- was no longer detected. Moreover the deposition was dried at 60°C and placed in air-tight plastic bottles. The total boron blank in the chemical process and filament loading was determined by isotope dilution mass spectrometry (IDMS) to contain 0.5 μg B/g, which was about 0.2% of the smallest adsorption quantity of boron on $Mg(OH)_2$, and can be neglected. The XRD of synthetic $Mg(OH)_2$ is shown in Figure 1. Compared with standard figure 70239 of $Mg(OH)_2$, the

Table 1 Chemical component of magnesium-free synthetic seawater

Chemical component	NaCl	CaCl₂	NaHCO₃	KCl	NaBr	H₃BO₃	Na₂SiO₃	Na₂Si₄O₉	H₃PO₄	Al₂Cl₆	LiNO₃
Concentration (g/L)	26.726	1.153	0.198	0.721	0.058	0.290	0.0024	0.0015	0.002	0.013	0.0013

Figure 1 The synthetic $Mg(OH)_2$ and the standard XRD of 70239 $Mg(OH)_2$.

crystal of it was very perfect, and met the experimental need completely.

1.4 The adsorption experiment of boron on Mg(OH)$_2$

Three experiments were carried out in our study.

(1) The pH influence of solution on adsorption equilibrium time: the adsorption experiments were carried out in a pH-controlled system at a temperature of 25±0.5℃ in a super clean laboratory. About 100 mL of synthetic seawater was first placed inside a plastic bottle of 200 mL. Solutions of NaOH or HCl were slowly added to each beaker of seawater to achieve the following range of pH values: 8.50±0.05, 9.00±0.05, 9.50±0.05, 10.00±0.05, 10.50±0.05, and 11.00±0.05. Then the precise weighted Mg(OH)$_2$ powder of 5.0 g was added into the plastic bottle. Mixed equably, the bottle was vibrated at the vibrator. The experiment was terminated after its reaching different time, and the solution was separated by centrifuge immediately. The boron concentration was conducted with the separated solution.

(2) The equilibrium adsorption experiment at different ratios of solid to solution (R_{s-l}): the pH of synthetic seawater was adjusted to 9.0. According to the ratio requirement of Mg(OH)$_2$ (g) to synthetic seawater (mL) of 1:5, 1:10, 1:20 and 1:30, different ratios of Mg(OH)$_2$ and synthetic seawater were mixed for adsorption experiment, and the succedent process was the same as the above experiment.

(3) The isotopic fractionation experiment of boron: the synthetic seawater of 100 mL with pH values of 8.5, 9.0, 9.5, 10.0, 10.5 and 11.0 was mixed with Mg(OH)$_2$ of 5.0 g, and the experimental temperature was 25±0.5℃. Mixed equably, the bottle was vibrated at the vibrator for 420 min, then the solution and solid was separated by centrifuge. The separated solution and solid were used for boron concentration and isotope analysis.

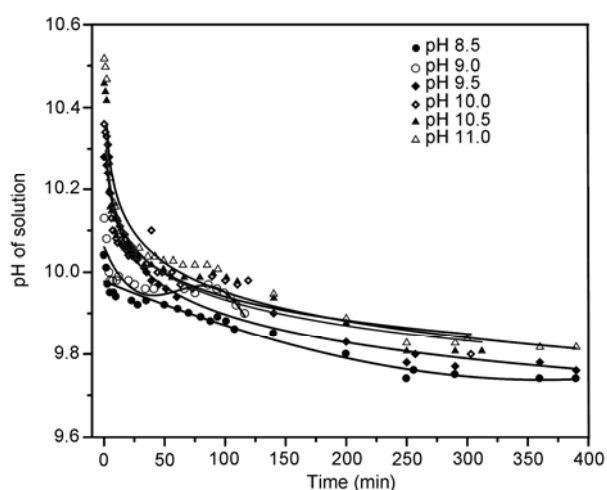## 1.5 The variation of solution pH during the adsorption process

All the pH values of the initial solution were kept invariable in the former adsorption experiments, but the variation of solution pH during the adsorption process was not researched. In our experiment, when Mg(OH)$_2$ was added into synthetic seawater with different pH values, the pH values of the synthetic seawater varied immediately, and became stable after a long time. The stable pH values were different from the adjusted pH values of synthetic seawater, and the variation results are listed in Table 2.

Table 2 Variation of solution pH during the adsorption process of boron

pH$_{ad}$	8.5	9.0	9.5	10.0	10.5	11.0
pH$_0$	10.04	10.13	10.28	10.36	10.46	10.52
pH$_s$	9.75	–	9.77	9.80	9.81	9.83

The detailed variation process of pH is shown in Figure 2. It indicated that, when Mg(OH)$_2$ was added into synthetic seawater with different pH values, the pH values of the synthetic seawater varied immediately. The varied pH values were related with the adjusted pH values, and increased with them. The general tendency was that the varied pH value was close to 10.50, when the adjusted pH values were lower than 10.50, the varied pH would be higher than the adjusted values; when the adjusted pH values were higher than 10.50, the varied pH would be lower than the adjusted values. With the adsorption time increasing all the pH values decreased. The stable pH increased with the adjusted pH values. This may be related with the isoelectric point of Mg(OH)$_2$. The measured pH value of the solution mixed with water of 10 mL and Mg(OH)$_2$ of 1.0 g was 10.58, which was close to the isoelectric point of Mg(OH)$_2$ (10.50[24]). But the reason for decrease of pH values needs to be researched further. When Mg(OH)$_2$ was added into synthetic seawater, the variation of pH was instantaneous, and it cannot be adjusted by adding acid or alkali timely, so the solution pH during the adsorption process cannot be controlled precisely. So only the qualitative discussion of the pH influence of solution

Figure 2 pH variation of solution during the adsorption process of boron.

on boron incorporated into $Mg(OH)_2$ can be discussed in our experiment, but this qualitative discussion should be exact.

1.6 Separation of boron from samples

In preparation for isotopic measurement, boron was extracted from the synthetic seawater and solution using a two-step chromatographic technique[30]. About 0.5 mL of Amberlite IRA 743 boron-specific resin with $80-100$ mesh was placed in a polyethylene column with a diameter of 0.2 cm. The length of the resin bed was 1.5 cm. Some quantity pellucid liquid passed through a column filled with Amberlite IRA 743 resin, and then eluted using approximately 5 mL of 0.1 mol/L HCl at 75℃. An amount of mannitol approximately equimolar to the boron content was added to the eluate, which was then desiccated to near dryness by partial evaporation in a super clean oven with laminar flow at 60℃[31]. The solution was then loaded again into the column filled with a mixed resin composed of 0.5 mL cation-exchange resin (H^+ form) and 0.5 mL anion-exchange resin (ion-exchange II, HCO_3^- form). The boron was eluted by 5 mL of boron-free water. The eluate was evaporated again at 60℃ to produce a solution with a boron concentration of about 1 μg B/μL for isotopic measurement. The total boron blank in chemical process and filament loading was determined by isotope dilution mass spectrometry (IDMS) to contain 46 ng of boron.

1.7 Measurement of boron concentration and isotopic composition

The boron concentrations were determined by the azomethine-H spectrophotometric method. 1 mL of sample solution, 2 mL of buffer solution, and 2 mL of azomethine-H solution were added in that order. After thorough mixing, each intermediate solution was allowed to stand for 120 min. The absorption of the boron-azomethine-H complex was measured at 420 nm using a spectrophotometer. The external precision of the azomethine-H method used here was 2%.

The isotopic compositions of boron in all samples were measured by a GV IsoProbe T single magnetic sector thermal ionization mass spectrometer and the P-TIMS method using $Cs_2BO_2^+$ ions with a graphite loading[32]. 2 μL of graphite slurry was first loaded onto a degassed tantalum filament, and then approximately 1 μL of sample solution containing about $1-2$ μg of boron and an equimolar amount of mannitol were also loaded. This was followed by $1-2$ μL of a Cs_2CO_3 solution containing an equimolar amount of cesium. The loaded material was dried by heating the filament at 1.2 A for 5 min.

The data were collected by switching the magnetic field between the masses 308 ($^{133}Cs_2^{10}B^{16}O_2^+$) and 309 ($^{133}Cs_2^{11}B^{16}O_2^+$), and the intensity ratios ($R_{309/308}$) of the ion beams at masses 308 and 309 were calculated. Calibrated with oxygen isotopes, the $^{11}B/^{10}B$ ratio was calculated as $R_{309/308}-0.00078$. The isotopic composition of boron was expressed as a $\delta^{11}B$ value according to the following formula:

$$\delta^{11}B\ (‰) = [(^{11}B/^{10}B)_{sample}/(^{11}B/^{10}B)_{standard}-1]\times 1000.$$

Here the standard material is NIST SRM 951, the recommended value of which is 4.04362 ± 0.00137[33]. The measured average $^{11}B/^{10}B$ ratio of NIST SRM 951 was 4.05248 ± 0.00272 ($2\sigma_m$, $n = 5$).

2 Results and discussion

2.1 Equilibrium time of boron adsorbed on $Mg(OH)_2$ at different pH values

With the same ratio of solid to solution (1:10 w/v) and different adjusted pH values, 90 samples of 10 mL synthetic seawater were mixed with $Mg(OH)_2$ of 1.0 g, respectively. The adsorption process was the same as in chapter 1.3. The adsorption time of every sample is listed in Table 3. When it reached the adjusted time, $Mg(OH)_2$ and liquid was centrifuged immediately, and the pellucid liquid was used for boron concentration analysis.

The boron concentration in $Mg(OH)_2$ ($[B]_s$) was calculated according to the following formula:

$$[B]_s\,(μg/g)= [([B]_{isw}-[B]_{fsw})\times V_{sw}]\div W_s, \quad (1)$$

where V_{sw} and W_s are the bulk of synthetic seawater and the weight of $Mg(OH)_2$, and $[B]_{isw}$ and $[B]_{fsw,}$ are the boron concentrations of initial seawater and final seawater, respectively.

The partition coefficient K_d between $Mg(OH)_2$ and synthetic seawater is calculated according to the following formula:

$$K_d=[B]_s\div([B]_{fsw}\div 1.020), \quad (2)$$

where the 1.020 is the specific gravity of the synthetic seawater.

The variation of $[B]_{fsw}$ with pH is shown in Figure 3. It indicated that within the former 120 min, boron was

Table 3 Variation of $[B]_{fsw}$ (µg/mL) and K_d with time at different pH_{ad} values

pH_{adj} Time (min)	pH 8.5		pH 9.0		pH 9.5		pH 10.0		pH 10.5		pH 11.0	
	$[B]_{fsw}$	K_d	$[B]_{fsw}$	K_d	$[B]_{fsw}$	K_d	$[B]_{fsw}$	K_d	$[B]_{fsw}$	K_d	$[B]_{fsw}$	K_d
10	9.98	36.8	10.92	32.7	11.17	31. 8	12.84	27.5	11.36	31.0	11.49	30.6
20	7.96	48.7	9.62	38.5	9.72	38.0	10.6	35.9	8.63	44.1	9.76	37.8
30	6.83	58.5	8.33	46.0	8.40	45.6	8.75	43.8	8.38	45.7	8.86	42.9
40	5.92	69.0	6.54	61.4	7.26	54.3	7.53	52.9	6.87	58.0	7.61	51.4
50	5.73	71.6	6.21	65.2	6.78	58.9	6.96	58.5	6.00	67.9	6.60	60. 8
60	4.86	86.2	5.52	74.7	6.25	64. 8	5.86	68.9	6.35	63.6	5.83	70.2
120	2.81	156.6	2.22	200.9	3.11	140.5	3.04	142.3	3.54	122.2	2.98	147.0
180	2.07	216.1	2.31	192.6	2.34	190.0	2.89	152.8	2.65	166.6	2.79	157.8
240	1.47	308.6	2.28	195.3	2.27	196.2	2.58	172.2	2.37	187.5	2.66	166.0
300	1.53	296.1	2.23	199.9	2.42	183.4	2.07	213.6	2.59	170.7	2.59	170.7
360	1.66	272.1	2.14	208.8	2.15	207.7	2.27	195.6	2.41	184.2	2.60	170.0
420	1.84	244.5	2.10	212.9	2.14	208.8	2.21	200.9	2.41	184.2	2.39	185.9
480	1.76	256.0	2.09	214.0	2.16	206.7	2.24	198.9	2.25	198.1	2.30	193.5
540	1.73	260.7	2.12	210.8	2.26	197.1	2.07	214.8	2.35	189.2	2.28	195.3
600	1.56	290.2	2.17	205.7	2.25	198.1	2.40	185.0	2.42	183.4	2.27	196.2
Average[a]	1.70 (0.19)	270 (20)	2.18 (0.08)	209 (5)	2.25 (0.10)	200 (9)	2.34 (0.28)	197 (15)	2.43 (0.13)	185 (8)	2.48 (0.20)	182 (13)

a) The average data calculated using the data between 240 and 600 min, and the number in bracket is the standard deviation.
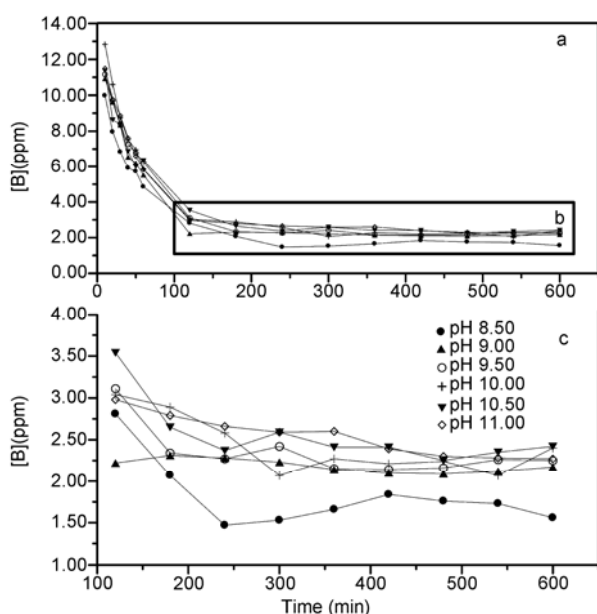
Figure 3 The variation of boron concentration in solution with time. c is the amplificatory figure of b section in a.

adsorbed rapidly by $Mg(OH)_2$, and the boron concentration in solution decreased rapidly. The decreasing speed decreased with pH values increasing, indicating that the capability of boron incorporated into $Mg(OH)_2$ was much stronger at lower pH. When the adsorption time was between 120 and 240 min, the adsorption became slow, indicating that the adsorption tended to be the equilibrium. After 240 min, the boron concentration in solution reached stable stabilization, indicating that the adsorption reached the equilibrium. The pH influence of

solution on the equilibrium time was inconspicuous. It is shown clearly from Figure 3 that the $[B]_{fsw}$ increased with the adjusted pH values. The stable boron concentration in solution was 1.70±0.19 (pH 8.5), 2.18±0.08 (pH 9.0), 2.25±0.10 (pH 9.5), 2.34±0.28 (pH 10.0), 2.43±0.13 (pH 10.5) and 2.48±0.20 (pH 11.0), respectively. This indicated that the adsorption capability of boron on $Mg(OH)_2$ decreased with the increase of adjusted pH values. Both of the initial and final pH of solution increased with the adjusted pH values (Figure 2), so the conclusion that the boron concentration in solution increased with pH was certain.

The equilibrium time of boron adsorbed by different minerals was different. Keren and Mezuman[34] found that the adsorption reached the equilibrium in 2 h when boron was adsorbed by montmorillonite or kaolin. When boron was adsorbed by illite, it reached the equilibrium in 24 h. When the experiment of boron adsorbed on ocean clay minerals was carried out by Palmer and Spivack[15], 72 h was taken as the equilibrium time. Fuente and Muñoz[35] found that, the equilibrium time was related with boron concentration, and it was longer with the lower boron concentration when boron was adsorbed by magnesia. In our study, adsorption can reach the equilibrium in 4 h, which was different from the above studies. This indicated that the adsorbed capability of boron on $Mg(OH)_2$ was much stronger, this was also shown on the partition coefficient K_d between solid and solution.

2.2 Equilibrium time of boron adsorbed on Mg(OH)$_2$ at different ratios of solid to solution R_{s-1}

Keeping the pH stable, the variations of $[B]_{fsw}$ and K_d with time at different R_{s-1} are listed in Table 4 and shown in Figure 4. The result showed that the variation of $[B]_{fsw}$ with time was basically the same. The former 120 min was the rapid decreasing stage and the period of 120 to 240 min was the slow decreasing stage and then after 240 min, the $[B]_{fsw}$ was basically stable, indicating that the adsorption reached the equilibrium. This variation was the same as that of different pH values and the same R_{s-1}. The $[B]_{fsw}$ decreased with the increasing R_{s-1}. When the R_{s-1} increased from 1:30 to 1:5, the average $[B]_{fsw}$ decreased from 7.09 μg/mL to 0.735 μg/mL, indicating that the adsorbed fraction of boron on Mg(OH)$_2$ increased. Compared with Mg(OH)$_2$ of 1.0000 g, the total boron concentration decreased with the R_{s-1} increasing, so the $[B]_s$ decreased from 1166 μg/g to 226 μg/g (Figure 3). This was different from the result of Keren and Mezuman[34]. In their experiment, the boron quantity was invariable, so the variation of boron concentration in solid increased with the R_{s-1} increasing due to the increased boron concentration in solution.

2.3 Boron concentration and partition coefficient K_d between Mg(OH)$_2$ and final solution

At different adjusted pH values (pH$_{ad}$) and ratios of solid to solution (R_{s-1}), the boron concentration in final solution, solid and K_d between them are shown in Figure 5.

It showed that, after the equilibrium, the $[B]_s$ de-

creased with the adjusted pH$_{ad}$. When the adjusted pH$_{ad}$ increased from 8.5 to 11.0, the $[B]_s$ decreased from 443 μg/g to 435 μg/g. No adsorption peak appeared. This was because, for the solution with the adjusted pH value of 8.5, the true adsorbed pH value was between 9.75 and 10.04, and this was not the strongest adsorption phase. It is shown from Figure 5b that the $[B]_s$ was related with the R_{s-1}. When the pH value of solution was invariable, the $[B]_s$ increased with the R_{s-1} decreasing. When the R_{s-1} was 1:30, the $[B]_s$ was 1166 μg/g, which was higher than the former data.

When boron was adsorbed onto the surfaces of oxides of aluminum and iron, at low pH values, the adsorbed boron increased as pH increased, and reached the maximum at pH 7−8. Then it decreased at higher pH values. The maximum adsorption by alumina, amorphous iron oxide and magnetite were 73.4 ppm, 487 ppm, and 19.9 ppm, respectively[36]. When boron was adsorbed by kaolin, montmorillonite or illite, at low pH values, the adsorption increased as pH increased, and the maximum values appeared at pH 8−10. At higher pH values, the adsorption decreased, and the maximum amounts by kaolin and montmorillonite were 9.92 ppm and 33.7 ppm, respectively[37].

The maximum of boron adsorbed onto complex aluminum oxide compounds and Na-montmorillonite appeared at pH 6−9 and pH 9.2, with the values of 1082 ppm and 31.4 ppm, respectively[38]. All of these results indicated that the boron adsorption onto Mg(OH)$_2$ was
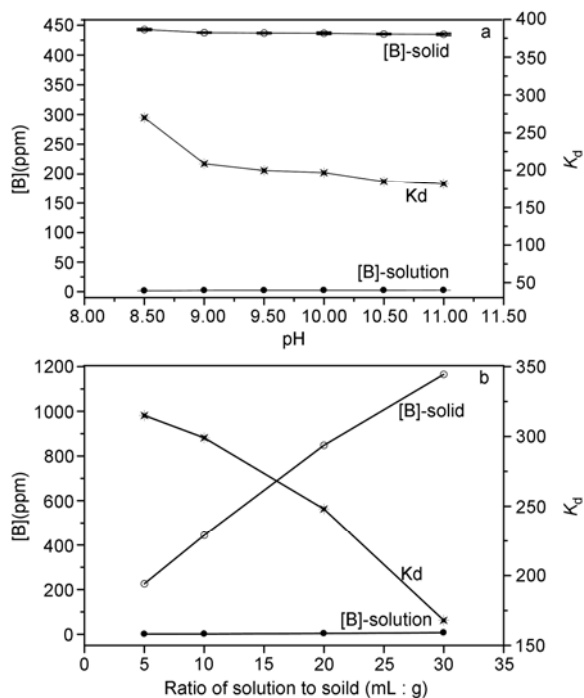
Table 4 Variation of $[B]_{fsw}$ (μg/mL), $[B]_s$ (μg/g) and K_d with time at pH 9.0

Time (min)	R_{s-1} (w/v)											
	1:5			1:10			1:20			1:30		
	$[B]_{fsw}$	$[B]_s$	K_d	$[B]_{fsw}$	$[B]_s$	K_d	$[B]_{fsw}$	$[B]_s$	K_d	$[B]_{fsw}$	$[B]_s$	K_d
20	2.72	216.1	80.93	7.43	385.1	52.9	19.70	524.8	27.2	26.26	590.5	22.9
40	1.93	220.0	116.3	4.71	412.3	89.3	15.34	611.9	40.7	23.45	674.7	29.3
60	1.57	221.8	144.3	4.37	415.6	96.9	12.31	672.5	55.7	19.02	807.6	43.3
120	1.16	223.9	197.6	2.12	438.2	211.2	7.11	776.5	111.4	12.85	992.6	78.8
180	0.76	225.9	302.5	1.78	441.6	252.4	3.49	849.0	248.1	9.96	1079	110.5
240	0.73	226.1	318.0	1.68	442.6	268.4	3.99	838.9	214.3	7.38	1157	159.8
300	0.72	226.1	321.3	1.50	444.4	302.1	3.58	847.2	241.4	7.42	1156	159.0
360	0.70	226.2	327.3	1.57	443.7	287.6	3.51	848.6	246.8	7.24	1161	163.6
420	0.71	226.3	337.0	1.48	445.6	330.0	3.80	842.9	226.4	7.19	1176	178.1
480	0.80	225.7	285.7	1.54	444.0	294.3	3.81	842.5	225.4	7.13	1164	166.5
540	0.78	225.8	294.6	1.53	444.1	295.8	3.01	858.6	290.7	6.68	1178	179.8
600	0.72	226.1	318.8	1.44	445.0	314.8	2.99	859.0	293.3	7.04	1167	169.0
Average[a]	0.735 (43)	226.0(0.2)	315.0 (18)	1.521 (97)	444.0 (1)	299.0 (19)	3.53 (39)	848 (8)	248 (32)	7.09 (29)	1166	168.0 (8)

a) The average data between 240 and 600 min.
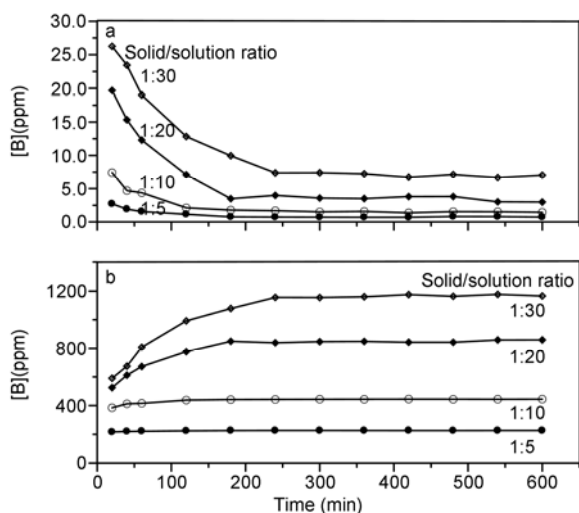
Figure 4 Comparison of adsorption equilibrium time of boron with different ratios of solid to solution ($R_{s\text{-}l}$). a, Variation of boron concentration in final solution with time; b, variation of boron concentration in solid with time.

Figure 5 Variation of boron concentration in final solution, solid and K_d with the adjusted pH values of solution (a) and ratio of solid to solution (b).

much stronger than onto oxides and clay minerals, but was basically the same as that of complex aluminum oxide. The variations of the partition coefficient K_d with pH in our research decreased with the increase of pH_{ad} values of solution or decrease of $R_{s\text{-}l}$ (Figure 5). The maximum K_d did not appear, while it may appear at pH < 8.5. But when the pH_{ad} was 8.5 and 9.0, the K_d was 270 and 315, respectively, higher than those of oxides and humic acids. When boron was adsorbed by metallic oxides, the adsorbed amount of boron increased as pH increased from 8.5 to 9.0, and the highest value appeared at pH 9. The maximum K_d of goethite and birnessite was 40 and 35, respectively. After that, boron adsorption decreased[18]. When boron was absorbed by humic acid, the maximum K_d (40) appeared at pH 9.5—10[39]. The K_d values of goethite, hematite and amorphous iron oxide were 11, 6.4, and 170, respectively[36]. All of these results indicated that the adsorption of boron onto $Mg(OH)_2$ was much stronger than onto metallic oxides and humic acid.

2.4 Isotopic fractionation of boron during the incorporation into $Mg(OH)_2$

When the adsorption of boron reached the equilibrium, isotopic compositions of boron in final solution ($\delta^{11}B_{fsw}$) with different pH_{ad} values are listed in Table 5. The isotopic fractionation factors ($\alpha_{s\text{-}fsw}$) of boron between $Mg(OH)_2$ and final seawater were calculated according to the following formula[15]:

$$\alpha_{s\text{-}fsw} = [1/(\delta^{11}B_{fsw} + 1000)]\times[(\delta^{11}B_{isw} + 1000) - F(\delta^{11}B_{fsw}+1000)]/(1-F), \qquad (3)$$

where $\delta^{11}B_{isw}$ and $\delta^{11}B_{fsw}$ are the isotopic compositions of boron in initial seawater and final seawater, respectively; F is the ratio of the boron concentration in the initial synthetic seawater and in the equilibrium synthetic seawater. The $\delta^{11}B_{isw}$ with different adjusted pH_{ad} values are −7.00‰±0.07‰. The $\delta^{11}B_{fsw}$ are between −19.2‰ and −17.8‰, with an average of −18.5‰, which were enriched in the light isotope compared to the initial seawater ($\delta^{11}B_{isw}$). The calculated $\alpha_{s\text{-}fsw}$ accord-

Table 5 Isotopic compositions of boron ($\delta^{11}B_s$ and $\delta^{11}B_{fsw}$) in $Mg(OH)_2$ and the final seawater and the isotopic fractionation factors of boron ($\alpha_{s\text{-}fsw}$) between $Mg(OH)_2$ and the final seawater

| pH_{ad}	8.5	9.0	9.5	10.0	10.5	11.0
$[B]_{isw}$ ($\mu g \cdot mL^{-1}$)	44.40	44.34	44.21	43.74	43.09	41.97
$[B]_{fsw}$ ($\mu g \cdot mL^{-1}$)	17.11	17.95	18.37	18.74	19.09	19.23
$\delta^{11}B_{fsw}$ (‰)	−18.9±0.5	−17.9±0.3	−17.8±0.3	−19.2±0.2	−19.0±0.3	−18.1±0.2
$\delta^{11}B_s$ (‰)	0.5	0.4	0.7	2.2	2.6	2.4
$\alpha_{s\text{-}fsw}$	1.0198	1.0186	1.0188	1.0218	1.0220	1.0209

ing to formula (3) were between 1.0186 and 1.0220, with an average of 1.0203. The calculated $\delta^{11}B_s$ according to $\delta^{11}B_{fsw}$ and $\alpha_{s\text{-}fsw}$ were between 0.4‰ and 2.6‰, with an average of 1.5‰, which are higher than $\delta^{11}B_{isw}$ ($-7.00‰ \pm 0.07‰$). This was absolutely contrary to the deposition of ocean bio-carbonate[1–10], indicating that the mechanism of boron isotopic fractionation between them was absolutely different. Because the pH values of solution varied during adsorption and the true pH values were not the adjusted pH_{ad} values, the true pH values during adsorption were uncertain and the quantificational discussion between $\alpha_{s\text{-}fsw}$ and pH of solution was impossible.

2.5 A model of boron incorporation into Mg(OH)₂

The characteristics of boron adsorption onto metallic oxides and clay minerals can be described by a phenomenological equation[38]. It is supposed that when $B(OH)_3$, $B(OH)_4^-$, and OH^- coexist in solution, they can be adsorbed by $Mg(OH)_2$, metallic oxides and clay minerals. The affinity coefficients (K_{B3}, K_{B4}, and K_{OH}) are 194, 1745 and 25803 L/mol for $B(OH)_3$, $B(OH)_4^-$ and OH^-, respectively[38]. They compete for the same adsorption site on a solid. At a pH value less than 7, $B(OH)_3$ would be dominant. Because K_{B3} is very low for clay minerals, the boron adsorption would be relatively minor. At pH values lower than 7, the concentration of $B(OH)_4^-$ and OH^- would be very low. Although they have a relatively stronger affinity to clay, their contribution to the total boron adsorption is still very small. When pH value increases to 9, the $B(OH)_4^-$ concentration increases rapidly. The concentration of OH^- is still lower than that of $B(OH)_4^-$, and thus the adsorbed boron would increase rapidly. If pH value was to increase even further, OH^- concentration would increase, and the boron contribution would decrease due to the competition for adsorption site. The adjusted pH values in our study were between 8.5 and 11.0, but the true pH values may be between 9.7 and 10.6. So the variation characteristic of boron concentration in solid with solution pH was unknown, and there was no way to investigate whether or not the adsorption of boron on $Mg(OH)_2$ accords with the above model. But the possibility that $B(OH)_4^-$ species was incorporated into $Mg(OH)_2$ cannot be excluded here and the isotopic fractionation characteristics of boron, the maximum adsorption and K_d values during adsorption can not be explained by this model. When boron is adsorbed by oxides or clay minerals, the adsorption abil-

ity of $B(OH)_4^-$ is much stronger than that of $B(OH)_3$; the preferential adsorption of $B(OH)_4^-$ causes the enrichment of ^{10}B in the $Mg(OH)_2$[15,18]. But that of ^{11}B in $Mg(OH)_2$ indicates that $B(OH)_3$ was preferentially incorporated into $Mg(OH)_2$. This may be caused by a chemical reaction. Methods of eliminating boron from waste water have been summarized by Rodionov et al.[40]. When limewater was added into boron solution, $CaO \cdot B_2O_3 \cdot nH_2O$ deposited. This reaction is described by the following equation:

$$2H_3BO_3 + Ca(OH)_2 + aq \rightarrow CaO \cdot B_2O_3 \cdot nH_2O + aq$$
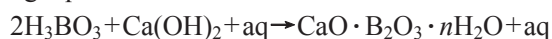
During the adsorption of $Mg(OH)_2$, a similar reaction may occur. $MgO \cdot B_2O_3 \cdot nH_2O$ may be deposited, but its amount relative to $Mg(OH)_2$ may be very small. The above reaction cannot occur for $B(OH)_4^-$, so the B_3 fraction of $Mg(OH)_2$ can exceed that of the solution due to the preferential incorporation of H_3BO_3 into $Mg(OH)_2$, and causes the ^{11}B to be enriched in $Mg(OH)_2$.

During the incorporation of boron into $Mg(OH)_2$, the deposition reaction can also be reflected by K_d and the variation of $[B]_{fsw}$ with solution pH. The $[B]_{fsw}$ increased with the pH_{ad} (Figure 3), indicating the incorporated boron decreased with the increase of pH_{ad}. This was because the fraction of H_3BO_3 in solution decreased with the increasing pH, and decreased the boron incorporated into $Mg(OH)_2$. Figure 3 shows that the K_d decreased with the pH_{ad}, and the maximum K_d was 1166, which is much higher than those of metal oxides or clay minerals. All of this indicated that the process of boron incorporated into $Mg(OH)_2$ was not only an adsorption process, but the deposition reaction may be important.

During the adsorption of $Mg(OH)_2$, the simultaneous occurrence of boron adsorption onto $Mg(OH)_2$ and the deposition reaction of H_3BO_3 with $Mg(OH)_2$ decide the isotopic fractionation characteristic of boron.

2.6 The influence to the $\delta^{11}B$-pH proxy

When the boron isotopic composition of corals is used as the indicator of seawater pH, one of the important hypotheses is that only $B(OH)_4^-$ is incorporated into marine bio-carbonates, causing ^{10}B incorporating into bio-carbonates preferentially. But the existence of $Mg(OH)_2$ in modern corals is wide[29]. Our research showed that, when boron was incorporated into $Mg(OH)_2$, the ^{11}B was enriched in $Mg(OH)_2$. The existence of $Mg(OH)_2$ must bring serious uncertainty to the $\delta^{11}B$-pH proxy. The existence of $Mg(OH)_2$ in corals

may have resulted from increased pH and low CO_2 in an extreme microenvironment, so it is the indicator of extreme microenvironment. At the same time, the exceptional high $\delta^{11}B$ in corals may reflect the existence of high pH microenvironment in oceans, and may not have a relevant relation to the ocean pH of the bulk environment[29]. The boron isotopic compositions of corals ($\delta^{11}B$) in Japan and the Great Barrier Reef, Australia, were between 28‰ and 32‰[41], and whether this is relate to the existence of $Mg(OH)_2$ needs further research.

3 Conclusions

(1) The incorporation of boron into $Mg(OH)_2$ was very rapid and after 4 h it can reach the equilibrium. The $[B]_s$ and the partition coefficient K_d between $Mg(OH)_2$ and final solution decreased with the increasing pH. The maximum of $[B]_s$ and K_d were much higher than that on metal oxide or clay minerals, indicating that the incorporation capability of boron on $Mg(OH)_2$ was much stronger.

(2) When the adsorption reached the equilibrium, the $\delta^{11}B_s$ was higher than $\delta^{11}B_{isw}$; the boron isotopic fractionation $\alpha_{\text{s-fsw}}$ between $Mg(OH)_2$ and final solution was between 1.0186 and 1.0220, with an average of 1.0203. All these indicated that ^{11}B was incorporated into $Mg(OH)_2$ preferentially, caused by $B(OH)_3$ preferential incorporation into $Mg(OH)_2$.

(3) During adsorption of $Mg(OH)_2$, the adsorption of boron on $Mg(OH)_2$ and the deposition reaction of H_3BO_3 with $Mg(OH)_2$ occurred simultaneously, and the latter was the main process. Both of the above processes decided the boron isotopic fractionation between $Mg(OH)_2$ and the final solution.

(4) The existence of $Mg(OH)_2$ in corals can change the boron isotopic fractionation of corals greatly. Under this circumstance, the $\delta^{11}B$ of corals has no quantitative relation to the seawater pH, so the $\delta^{11}B$ of corals will not necessarily reflect ambient seawater pH.

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