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Research paper

Boron isotopic fractionation in aqueous boric acid solutions over synthetic minerals: Effect of layer and surface charge on fractionation factor

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ABSTRACT

Boron isotopic fractionation in boric acid solutions during adsorption on synthetic manganese oxides (birnessite "**B**" and cryptomelane "**C**") and Mg–Al-layered double hydroxide "**LDH**" was investigated. The materials were characterized by elemental analyses, powder X-ray diffraction, FTIR spectra, BET surface area and zeta potential measurements. Batch experiments were conducted without changing the solution pH to correlate the boron sorption properties of the adsorbents with isotopic fractionation in the associated boric acid solutions. The results showed that boron isotopic composition of the contact solution is heavily dependent on the selective adsorption of $B(OH)_3$ or $B(OH)_4^-$ species due to the charge properties of the minerals. With **B** and **C**, possessing negatively charged surfaces, $^{10}B(OH)_4^-$ was preferentially fractionated in the solution due to the transfer of the Lewis acidic $^{11}B(OH)_3$ species while with **LDH** selective adsoption of $^{10}B(OH)_4^-$ by positive layers was favorable resulting in the enrichment of the heavier isotope in the solution.

1. Introduction

Boron has two naturally occurring isotopes, ^{10}B (19.9%) and ^{11}B (80.1%). Isotopic composition of boron containing wastewater is important to provide information about seawater/groundwater contamination and distinction in different geochemical environments. Boric acid and borates are widely used in industrial applications (Garrett, 1998; Hosmane, 2012) and thus fractionation of boron isotopes helps enrichment of the desired isotope for specialty applications such as the use of ^{10}B as neutron absorber, radiation shield and neutron detector in nuclear reactors.

Most of the boron in water is present as undissociated boric acid. Boric acid is a weak acid and partitioning between aqueous boric acid and the borate ion depends on solution pH (Eq. (1)) (Bassett, 1980). At low concentrations and at $pH < 7$, only the mononuclear $B(OH)_3$ species exist. With increasing pH, polyborate anions are formed which hydrolyze at high pH ($pH > 10$) and produce the monoborate anion $B(OH)_4^-$. The isotopic fractionation of boron dominantly occurs between the trigonal and tetrahedral configurations (Eq. (2)) and is pH dependent (Hemming and Hanson, 1992; Simon and Smith, 2000). The equilibrium constant of reaction 2 is larger than unity which means that ^{11}B is preferentially fractionated into $B(OH)_3$ species in solution whereas ^{10}B is into $B(OH)_4^-$ (Oi, 2000; Pagani et al., 2005; Zeebe, 2005; Klochko et al., 2006).

$$B(OH)_{3(aq)} + H_2O_{(l)} \Leftrightarrow B(OH)_4{}^-{}_{(aq)} + H^+{}_{(aq)} \quad -\log K = 9.24 \tag{1}$$

$$^{10}B(OH)_{3(aq)} + {}^{11}B(OH)_4{}^-{}_{(aq)} \rightarrow {}^{11}B(OH)_{3(aq)} + {}^{10}B(OH)_4{}^-{}_{(aq)} \tag{2}$$

In geochemical and environmental systems, the role of minerals is also important in this fractionation process in addition to pH. Over the last two decades the interaction of boron with clays (Palmer et al., 1987; Sanchez-Valle et al., 2005), oxides (Lemarchand et al., 2007), hydroxides (Xiao et al., 2011) and carbonates (Hemming et al., 1995; Sanyal et al., 2000; Xiao et al., 2006) has been shown to significantly fractionate boron isotopes. The fractionation is believed to proceed through a sorption or exchange mechanism due to the differences in coordination and bonding environments specific to the substrate when aqueous boric acid is adsorbed on these minerals. There is evidence that the lighter isotope is preferentially adsorbed on the solid surface while ^{11}B is enriched in the aqueous phase (Spivack and Edmond, 1987; Wunder et al., 2005; Lemarchand et al., 2005; Sanchez-Valle et al., 2005).

Isotopic fractionation of boron in terms of mineral–water interactions has been reported by examining the sorption onto iron and manganese oxides (Lemarchand et al., 2007) and during brucite ($Mg(OH)_2$) deposition from boron containing artificial solutions (Xiao et al., 2011),

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as a function of pH. In this study, we prepared synthetic analogs of manganese oxide minerals: *i.* birnessite "B" (a layered material with negatively charged sheets) and *ii.* cryptomelane "C" (tunnel structure with negatively charged surfaces) (Post, 1999) and also the topochemically transformed form of the brucite mineral: Mg–Al-layered double hydroxide "LDH" (a synthetic anionic clay with positively charged sheets) (Rives, 2001). We performed batch experiments to correlate the boron sorption properties of these samples with isotopic fractionation in the associated boric acid solutions as a function of the layer and surface charge, without changing the solution pH. Although boron adsorption and intercalation with LDH's have been extensively studied (Ay et al., 2011; Theiss et al., 2013; Qiu et al., 2014), boron isotopic fractionation with LDH's and polymorphic manganese oxides has not yet been reported to the best of the authors' knowledge.

2. Materials and methods

2.1. Material preparation and characterization

The following reagent grade chemicals were used as received: $KMnO_4$ (Merck), KOH (Merck), $MnSO_4 \cdot H_2O$ (Merck), $Mg(NO_3)_2 \cdot 6H_2O$ (Sigma), $Al(NO_3)_3 \cdot 9H_2O$ (Carlo Erba), NaOH (Merck).

2.1.1. Birnessite

Birnessite was synthesized by a reflux method. 35 mL of 5 M KOH solution was slowly added to a solution containing 6.3 mmol of $KMnO_4$ in 25 mL of deionized water with vigorous stirring. The resulting solution was refluxed at 90 °C for 12 h under continuous stirring. The precipitated solid (**B**) was filtered, washed with deionized water and finally dried at 100 °C for 24 h.

2.1.2. Cryptomelane

Cryptomelane was prepared according to Espinal et al. (2012) but in a modified way. 3.96 g (23.4 mmol) of $MnSO_4 \cdot H_2O$ was dissolved in 20 mL of deionized water containing 2 mL concentrated nitric acid. To this solution, a $KMnO_4$ solution (16.5 mmol in 50 mL deionized water) was slowly added. The resulting solution was kept under reflux at 100 °C for 24 h. The precipitated solid (**C**) was filtered, washed with deionized water and finally dried at 100 °C for 24 h.

2.1.3. Mg–Al-Layered double hydroxide

The synthesis of the LDH was carried out under nitrogen atmosphere and the solutions were prepared with deionized water refluxed under nitrogen for 4 h to remove the dissolved CO_2.

The sample (**LDH**) was prepared by the co-precipitation method according to the procedure reported by Ay et al. (2011). $Mg(NO_3)_2 \cdot 6H_2O$ (70 mmol) and $Al(NO_3)_2 \cdot 9H_2O$ (140 mmol) were dissolved in 50 mL deionized water at room temperature. 240 mL 2 M KOH solution was added dropwise into this solution (pH: 9.5–10) containing the metal salts. The slurry was stirred under a nitrogen atmosphere at 90 °C for 4 h. Additionally the resulting slurry was stirred at room temperature for 1 day and then aged for 1 day. The product was separated by centrifugation, washed several times and dried in a vacuum desiccator.

2.1.4. Instruments and characterization

Element analysis for metal ions was performed using an Agilent 7500a ICP-MS spectrometer. The water content was determined by thermogravimetry on a Shimadzu DTG-60-H thermal analysis system at a heating rate of 10 °C/min under nitrogen flow. Powder X-ray diffraction patterns (XRD) were recorded using a Rigaku D/MAX-2200 diffractometer equipped with graphite-filtered Cu Kα radiation ($\lambda = 1.54056$ Å) from 3 to 70° (2θ) at a scanning rate of 4°min^{-1}. Fourier transform infrared spectra (FTIR) were recorded in the range 4000–400 cm^{-1} on a Nicolet 6700 instrument using the KBr pellet technique. The morphology and dimension of the synthesized products were observed with a FEI quanta 200 FEG scanning electron microscope (SEM). Zeta potential measurement was carried out using a MALVERN NanoZS90, without any pH adjustment. The specific surface areas (BET) were determined with a Monosorb Model/Quantochrome Instrument. Analysis was made with N_2 gas as adsorbent after degassing the samples at 70 °C for 4 h. Surface areas and pore sizes were calculated by the Barrett, Joyner and Halenda (BJH) method.

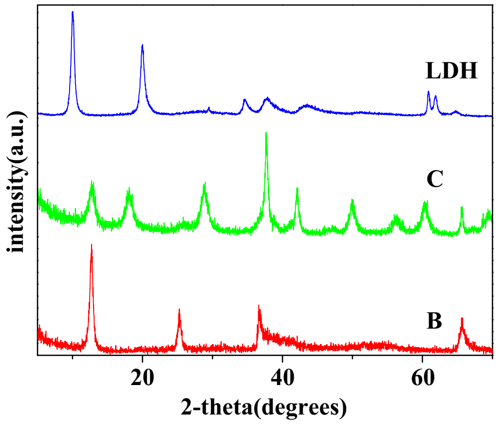

Fig. 1. Powder XRD patterns of **B**, **C** and **LDH**.

2.2. Boron adsorption experiments and isotopic analyses

Batch experiments were conducted by interacting fixed amounts of synthetic mineral samples with standard boric acid solutions and following the changes in the solution boron concentrations and $^{11}B/^{10}B$ ratios.

Typically, 0.3 g of the mineral sample (**B** or **C**) was added to 20 mL 30 mM H_3BO_3 and equilibrated with 10 mL of 20 mM $CaCl_2$ solution to maintain the ionic strength. pH was adjusted to 8.5 by adding KOH solution. The mixtures were stirred for 2 h, 6 h, 12 h, 24 h, 48 h, 72 h and 1 week at room temperature. At the end of each run, the suspensions were centrifuged (2000 rpm, 5 min) and aliquots of clear supernatants were taken and filtered to be analyzed for boron concentration and isotopic composition. This procedure was repeated with **LDH** but using 25 mL of 89 mM of H_3BO_3 solution diluted with 5 mL of water. With lower boric acid concentrations, it was not possible to follow up the isotopic variations in the supernatant solutions due to the complete sorption of boron species by LDH.

Boron contents in the supernatants were determined by the carminic acid method (Weicher, 1963). The arithmetic mean of three measurements for each point is shown in the graphs in Fig. 2 with standard error bars.

The isotopic compositions of boron in the supernatant solutions were measured by Perkin Elmer ELAN 9000 ICP-MS instrument. The reference used in this study was boric acid supplied by Etibor Inc. Repeated analyses of the standard boric acid solution gave an averaged $^{11}B/^{10}B$ ratio of 4.3476 ± 0.00082. For sample solutions, the arithmetic mean of four replicates was taken as the isotopic ratio. Reproducibility

Table 1
Chemical compositions and some properties of the minerals used in fractionation experiments.

Sample	Formula	BET (m^2/g)	Pore size (Å)	ζ pot. (mV)
B	$K_{0.3}MnO_2 \cdot 1.8H_2O$	125	1.9	−47.8
C	$K_{0.1}MnO_2 \cdot 0.5H_2O$	405	5.1	−14.7
LDH	$[Mg_{0.58}Al_{0.42}(OH)_2](NO_3)_{0.42} \cdot 0.6H_2O$	104	5.5	+20.9