Boron isotope geochemistry during diagenesis. Part I. Experimental determination of fractionation during illitization of smectite

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Abstract—Experiments were performed to measure the isotopic fractionation of boron between illite/smectite (I/S) clay minerals and water as a function of temperature (300° and 350°C) and degree of illitization. Corresponding changes in the oxygen isotopes were monitored as an indication of the approach to equilibrium. The kinetics of the B-isotope exchange follows the mineralogical restructuring of smectite as it recrystallizes to illite. An initial decline in Δ11B(I/S) occurs when the I/S is randomly ordered (RO). The Δ11B(I/S) values reach a plateau during R1 ordering of the I/S, representing a metastable condition. The greatest change in Δ11B(I/S) is observed during long-range (R3) ordering of the I/S when neoformation occurs.

Values of Δ11B(I/S) measured on the equilibrium reaction products were used to construct a B-isotope fractionation curve. There is a linear correlation among data from these experiments and 1100°C basaltic melt-fluid fractionation experiments (Hervig and Moore, 2000) that can be extrapolated to include adsorption experiments at 25°C (Palmer et al., 1987). Unlike other stable isotopic systems (e.g., oxygen) there is no mineral-specific fractionation of B-isotopes, but rather a coordination dependence of the fractionation. Under diagenetic conditions B is predominantly in trigonal coordination in fluids but substitutes in tetrahedral sites of silicates. The preference of 11B for tetrahedral bonds is the major fractionating factor of B in silicates.

1. INTRODUCTION

Clay minerals are abundant and highly reactive minerals in clastic sedimentary basins. They adsorb boron on surface sites at low temperatures (<120°C) (You et al., 1996) and substitute boron for tetrahedral silicon during diagenesis (Spivack et al., 1987). Boron is most abundant in the sedimentary clay minerals illite/smectite (I/S) (Harder, 1970), which contain orders of magnitude more boron than other common diagenetic minerals (e.g., quartz, carbonates, and feldspar). Boron is a highly mobile element, preferring aqueous phases to that of most minerals (Levinson, 1980). Thus, by understanding how the aqueous boron is incorporated into typical clay minerals, important insights may be gained to the fluid and chemical dynamics of a sedimentary basin. To use this geochemical tool, one must be able to interpret the boron isotopic composition of paleofluids that were present in a basin at the time of clay mineral diagenesis. Late-stage or deep diagenesis of clay minerals (Eberl, 1993) coincides with the time/temperatures associated with organic maturation processes that lead to the expulsion and accumulation of hydrocarbons. The presence of anomalously high B-contents of many oil field brines (Collins, 1975) leads us to investigate whether there is an expulsion of organically bound-B that can be used to trace hydrocarbon migration paths (Williams et al., in press). Thus, we examined the potential for the common authigenic clay mineral, illite, to incorporate boron and record isotopic ratios acquired during crystallization. Lacking definitive information on the fractionation between aqueous-B and B substituted for Si in tetrahedral sites of illite, this research began with the simple goal of measuring the isotopic changes in boron during illitization of smectite.

The experiments address two fundamental questions. First, how is boron incorporated into tetrahedral sites of authigenic illite? Is it a gradual increase with burial, like the increase in illite layers in I/S, or does it occur in stages associated with the restructuring (ordering) of the I/S? Second, what is the equilibrium fractionation of 11B/10B between the tetrahedral layers of the silicate and the fluids as a function of temperature? It is important to distinguish between adsorbed-B on the surfaces of the clay, and “fixed-B” that substitutes for Si. The adsorption of B on clay surfaces has been extensively studied (Schwarcz et al., 1969; Keren and Mezumen, 1981; Palmer et al., 1987), but because it can be easily exchanged (Bassett, 1977), it is not useful in determining paleofluid chemistries. Fixed-B is more useful for interpreting paleofluids because it exchanges with pore fluid-B only when Si-O bonds are broken. Furthermore, Si is released from the clay mineral during this exchange and may be a potential source for quartz cements (Hower et al., 1976). This exchange reaction could, therefore, provide an important diagenetic marker if a significant change in Δ11B could be linked to the release of Si.

Oxygen isotope changes during the illitization of smectite should also be linked to the fixed-B isotope exchange. Concurrent changes in Δ11B and Δ18O of I/S were examined in the experiments performed. The reaction of smectite to illite was conducted at 300 and 350°C; therefore, the kinetics were fast compared with a basin undergoing burial. However, after 4 to 5 months, the oxygen isotope fractionation between the I/S and water approximated that predicted for the experiment temperatures (Savin and Lee, 1988), indicating nearly 100% isotopic re-equilibration (Whitney and Northrup, 1988). It is assumed that the results of these experiments also establish isotopic
equilibrium for boron, because B cannot exchange without a change in $\delta^{11}$O.

2. EXPERIMENTAL SETUP

Smectite was reacted to illite by following the experimental method used by Whitney and Northrup (1988) for measuring the O-isotope changes coincident with illitization. The starting material was a smectite standard (SWy-1), which was size fractionated to select the $<2\mu m$ fraction, and K-saturated (Moore and Reynolds, 1989). Trace amounts of quartz and muscovite were included in this size fraction, which along with the added K, promote the reaction of smectite to illite (Whitney and Northrup, 1988) at 300°C and 350°C, 100 MPa (1 kbar) pressure. A 1:1 ratio of mineral to water (by weight) was used (200 mg solid: 200 $m^3$ liquid). The aqueous solution contained the boron isotope standard NBS SRM 951 boric acid at an initial pH of 6.8. The samples were sealed in 5-cm long, 5-mm OD Au capsules. The capsules were placed in a hydrothermal bomb closed with a Bridgeman seal, using deionized water as the pressurizing medium (Fig. 1). Temperature was measured by using an inconel-sheathed chromel/alumel thermocouple inside the pressure vessel, placed in the center of the long axis of the capsules. This allowed minimal uncertainties in temperature estimated at $<5°C$. Pressure was measured by using Bourdon-tube gauges and was monitored within $\pm 5$ MPa. The siliciclastic reaction buffers the pH (Hutcheon et al., 1993) during the experiment to low values (pH $\approx 6$ after quench); thus, the predominant aqueous boron species is trigonal B(OH)$_3$. This is also true for most oil field waters in deep sedimentary basins, although there is the possibility of formation of some polynuclear B-species when B concentrations are high (Bassett, 1977).

Three experiments were performed to test the effect of B-concentration and temperature on B-substitution in illite. Experiment 1, run at 350°C, used a low aqueous B-concentration (20 ppm). These conditions limited the amount of B available for fixation in the mineral to two times the original B-content. This was intended to simulate conditions observed in the Gulf of Mexico sedimentary basin where B-contents of I/S essentially doubles during progressive illitization (Perry, 1972). Experiments 2 and 3 used high concentrations of aqueous-B (1000 ppm) so that the B supply would not be limited. These two experiments differed only in temperature (and run time), with experiment 2 at 350°C and experiment 3 at 300°C.

3. MATERIALS AND METHODS

3.1. Sample Extraction and Preparation

The experiments at 350°C (experiments 1 and 2) ran for 120 days, with samples collected at intervals to monitor the reaction progress. The 300°C experiment (experiment 3) ran an extra month in an attempt to reach equilibrium conditions. Duplicate capsules were run in the first experiment to determine the reproducibility of results. The experiment was quenched on sampling days, and the capsules were opened under vacuum on an extraction line. The aqueous contents were collected in a U-tube cold trap. Only samples that yielded 100% recovery of fluid ($\approx 200 \mu L$ fluid) were analyzed for O-isotope ratios. Conventional analyses of O-isotopes (by Mountain Mass Spectrometry Inc.) required $\approx 150 \mu L$ of solution.

Measurement of the aqueous-B content and $\delta^{11}$B of waters from the experiment capsules was not possible because of fractionation of the B during quench and vacuum line extraction. Aqueous-B is adsorbed to the clay minerals during the experiment quench to room temperatures. Furthermore, Xiao et al. (1997) showed that a significant portion of B does not volatilize during evaporation. During extraction of the Au capsules, the solution is vaporized at $\approx 70°C$ in a 10$^{-4}$ torr vacuum and condensed in a liquid nitrogen cold trap. Because B is not quantitatively transferred into the volatile phase, some of the aqueous-B is left on the clay mineral and Au capsule surfaces. This was tested by carefully washing the clay minerals and interior of the Au capsule and analyzing the B-content. This was intended to simulate conditions observed in the Gulf of Mexico sedimentary basin where B-contents of I/S essentially doubles during progressive illitization (Perry, 1972). Experiments 2 and 3 used high concentrations of aqueous-B (1000 ppm) so that the B supply would not be limited. These two experiments differed only in temperature (and run time), with experiment 2 at 350°C and experiment 3 at 300°C.

The solid reaction product and Au capsule were rinsed in “B-free” water to remove adsorbed-B. The “B-free” water is deionized water that has been filtered through a column of amberlite resin to remove traces of B. ICP analyses of this water showed no detectable levels of B with a detection limit of 4 ppb. The solid was additionally washed 2 h in mannitol solution (Ishikawa and Nakamura, 1990; Xiao et al., 1997) to enhance removal of the adsorbed-B. The mannitol solution also contained no detectable levels of B. The samples were then rinsed three times in B-free water. The solution was kept for ICP analysis of the B-content. The solid sample was then split into two aliquots. About 100 mg was mounted as oriented clay slides for X-ray diffraction (XRD). A small drop of the clay slurry was dried onto a B-free 1-inch round glass slide for isotope analysis. The clay standard (1Mt-I illite) was added to each mount so that sample changes were not required between analyses of sample and standard. The air-dried clay mounts were Au-coated for analysis by secondary ion mass spectrometry (SIMS).

3.2. X-Ray Diffraction

The solid experimental run products were ethylene-glycolated and examined by XRD to monitor the decrease in expandability of the mixed-layered I/S as illitization occurred. The characterization of mixed-layered clay minerals is described in Moore and Reynolds (1989). The analyses were performed by using Siemens D500 and D5000 spectrophotometers with CuK$\alpha$ radiation. The D5000 instrument was set up with a position sensitive detector (PSD) for more rapid analysis of small quantities of material. Comparison of the results from each diffractometer indicates that the peaks are positioned correctly,
but the relative intensities using PSD may be unreliable on oriented mounts (Batchelder and Cressy, 1998). Because the goal was to monitor shifts in the major peak positions for the I/S, the intensity did not affect our interpretation. The percent illite in ethylene-glycol I/S was estimated by using the \(\Delta 2\theta\) between the 001/002 and 002/003 peaks of I/S (Moore and Reynolds, 1989, p. 251). Nearest neighbor (R1) ordering (ISIS) is indicated by a strong reflection at \(\sim 6.5^\circ 2\theta\) whereas a reflection near \(5^\circ 2\theta\) indicates random (R0) interstratification. When this peak shifts to \(>7^\circ 2\theta\) for a long-range (R3) ordering (ISII) is indicated.

### 3.3. Secondary Ion Mass Spectrometry

SIMS measurements of B-isotopes do not yield the high-precision results of thermal ionization mass spectrometry (TIMS; Swihart, 1996), but the analyses can be performed directly on the solid products without digestion and the possibility of inducing isotope fractionation during ion exchange. The SIMS analyses ( Cameca IMS 3f) used a primary beam of O\(^{-}\) defocused to \(\sim 50 \mu m\) in diameter. By defocusing the beam, the sample was sputtered more uniformly with time yielding a more stable secondary ion current. The depth of the analytical crater after 30 min of ion bombardment was <5 microns. The general method for analysis of B-isotope ratios in silicates by SIMS can be found in Hervig (1996) and Chauvin et al. (1997). Modifications to allow analyses of B-isotopes in clay minerals are described below.

### 3.4. Boron Isotope Analysis of Clay Minerals

Boron isotope ratios are reported in delta notation as:

\[
\delta^{11}B = \left(\frac{\left(^{11}B/^{10}B\right)_{\text{sample}} - 1}{\left(^{11}B/^{10}B\right)_{\text{standard}}}\right) \times 10^3
\]

where the standard is NBS SRM 951, boric acid, with a \(^{11}B/^{10}B\) ratio of 4.0437. The IMF is instrumental mass fractionation determined by measuring a mineral standard on which the \(^{11}B/^{10}B\) is known. B-isotope analyses were calibrated by measuring clay mineral standards IMt-1 (Silver Hill Illite) and SWy-1 (Wyoming smectite) that had been characterized by bulk thermal ionization mass spectrometry (TIMS). The clay standards were rinsed three times in B-free water and centrifuged to select the <2-μm fraction. Aliquots of this standard were analyzed by the method of Tonarini et al. (1997) by using alkali carbonate fusion and ion-exchange separation for boron purification, and PTIMS using Cs\(_2\)BO\(_2\) (analyses performed at Rice University by W. P. Leeman). Three replicate analyses of the IMt-1 illite averaged \(-8.66 \pm 0.23\%\). Another aliquot was analyzed by NTIMS (analyses performed at University of Calgary) with two replicates averaging \(-9.86 \pm 0.65\%\). An average \(\delta^{11}B\) value of \(-\%) was used for the IMt-1 illite. The difference between the measured ratio by SIMS and the TIMS value determines the instrumental mass fractionation (IMF) factor. The SWy-1 smectite contained too little B for analysis by PTIMS but was analyzed by NTIMS giving a \(\delta^{11}B\) value of \(\sim 3 \pm 1\%\). SIMS analyses reproduced this value during several analytical sessions by using the same IMF value determined for the illite. This confirms the observation of Chauvin et al. (1997) who found no significant matrix effect of various minerals on B-isotope analyses.

During our clay analysis sessions over 3 years, the IMF has varied between \(-30\) and \(-52\%\) (i.e., the raw \(^{11}B/^{10}B\) ratio is \(\sim 5\%\) lighter than the TIMS values), depending on the instrumental set up. During each SIMS analytical session, the \(^{11}B/^{10}B\) ratio was measured on IMt-1 standard before and after sample analyses. The IMF remains constant (within error) during each analytical session, allowing the correction for \(^{11}B\) relative to NBS SRM 951 with errors generally \(\sim 1\%\) (1σ). The Cameca IMS 3f at ASU has produced isotope ratio measurements that match well with other SIMS laboratories (Gnaser and Hutcheon, 1986; Belshaw et al., 1995; Smith and Yardley, 1996; Chauvin et al., 1997).

The primary current used for analyses was determined by the intensity of the \(^{10}B\) (minor isotope) secondary ion signal. To achieve a precision of \(<2\%\), the primary current was increased until there was stable emission of \(\sim 500\) counts per second (cps) on \(^{10}B\). Generally, this required 3 to 5 nA of primary current. The analyses were set up to count for 20 s on mass 10 and 5 s on mass 11 for 49 cycles. To eliminate \(^{11}BH\) interference with \(^{10}B\) counts, the entrance slits were closed down until the two peaks could be separated (Fig. 2). The magnetic field was adjusted to collect counts from the center of the \(^{10}B\) peak, and this was checked every 10 cycles to correct for any drift that might occur. These conditions resulted in integrated signals for \(^{11}B\) and \(^{10}B\) of \(\geq 5 \times 10^5\) counts, indicating an error based on counting statistics of \(\leq 2\%\). The actual errors determined by the standard error of 49 measurements of \(^{11}B/^{10}B\) in each analysis are equal to, or greater than, the predicted errors. Analyses that produced errors greater than two times the predicted error were eliminated. This condition usually indicates a problem such as sample charging, low counts due to sample aberrations (e.g., not flat, or that the primary ion beam has drifted out of alignment).

An analysis of B-isotope ratios in clay minerals by SIMS is burdened by two major problems. First, B occurs in two sites of clay minerals, surface-adsorbed and tetrahedral-layer sites, and the isotopic ratios of the B in each site is different (Spivack et al., 1987; Palmer et al., 1987). Second, the clay size fraction is by definition <2 μm in diameter, and often the authigenic crystals are even smaller (<0.2 μm), so a SIMS analysis samples numerous crystallites during a single analysis. In essence then, these are small-volume bulk analyses that consume <3 ng of material (\(\sim 10^{13}\) atoms of sample). Because the proportion of adsorbed-B and fixed-B in any particular clay mineral cluster may be variable, it is impossible to know how much B in a SIMS analysis of bulk clay is fixed or adsorbed. It is very important, therefore, to remove adsorbed-B from the surface of clay minerals with mannitol before isotope analysis of fixed-B, as was done in our analyses.

The measurement of fixed-B content in the product was determined by SIMS using a calibration curve based on the counts of B (mass 11) relative to Si (mass 30). The calibration curve (Fig. 3) was measured on borosilicate glasses with known B-content by using the same high-mass resolution conditions used for the B-isotope analyses. Boron analyses of the clay standards IMt-1 (illite) and SWy-1 (smectite) were compared with measurements made by ICP-AES on an aliquot digested in HF-HCL. The ICP value for the B-content of IMt-1 was \(240 \pm 20\) ppm, and the SWy-1 contained \(12 \pm 2\) ppm B. Individual SIMS point analyses of B in the clay standards, using the calibration curve, agreed within 5 to 10%.

Notably, the Si content of the I/S in experimental run products is variable by \(\pm 10\%\), but the I/S cannot be separated from detrital quartz in the <2 μm size fraction. The calculated B-content of these samples varies by \(<5\%\) because of this uncertainty but may actually underestimate the B-content of the product slightly.

### 3.5. Oxygen Isotope Analysis of Clay Minerals

SIMS was also used to analyze O-isotope ratios of the solid run products. The analytical setup is significantly different and more com-
showed that the effect of adsorbed water on the overall O-isotope ratio measurement. Nonetheless, on the depending on mineral orientation, which could cause a variable isotope (between the layers). Figure 6 shows a difference in sputtering rates al., 1997). Sputtering rates were measured on a large muscovite crystal orientation on the secondary ion sputtering rate and IMF (e.g., Eiler et measurements. There is still some question about the effect of mineral charge compensation. A primary beam of Cs\(^+\) is used instead of O\(^+\). Use of a positive primary beam adds significant charge buildup to a silicate sample (insulator) that results in unstable secondary ion signals unless it is neutralized by use of an electron gun. A normal incidence electron gun was used to compensate the charge during oxygen isotope analysis of the clays.

Extreme energy filtering was used to eliminate molecular interferences (Hervig et al., 1992). Several tests were made to determine how to calibrate different clay minerals. First, standards of kaolinite (KGa-1), smectite (SWy-1), and illite (IMt-1) were analyzed by conventional O-isotope methods (analyses performed at University of Western Ontario by Fred Longstaffe) so that they could be used as SIMS standards. The instrumental mass fractionations (in the SIMS) for the illite and smectite standards were not significantly different, perhaps because of their common two-layer structure. Raw oxygen isotope ratios on these two phases by SIMS were 65% lighter than nominal values (IMF = -65‰). This calibration varied little over multiple analytical sessions. The one-layer kaolinite standard produces less instrumental fractionation with a reproducible average of -53‰ (Fig. 4).

To test the effect of oxygen from adsorbed interlayer water on the overall O-isotope composition of smectite, an aliquot of SWy-1 was soaked in \(^{18}\)O-enriched water (Fig. 5) and then analyzed. The test showed that the effect of adsorbed water on the overall O-isotope ratio is small. The isotopic composition should be affected by no more than \(\approx 0.25\)‰, which is far less than the analytical precision of the SIMS measurements. There is still some question about the effect of mineral orientation on the secondary ion sputtering rate and IMF (e.g., Eiler et al., 1997). Sputtering rates were measured on a large muscovite crystal oriented to sputter parallel to the c-axis (flat surface) or perpendicular (between the layers). Figure 6 shows a difference in sputtering rates depending on mineral orientation, which could cause a variable isotope ratio measurement. Nonetheless, on the \(<2\) μm scale, analyses encompass many differently oriented clay crystallites so there is an averaging of this effect. For example, analyses of pore-filling kaolinite books in a thin section from North Sea reservoirs show O-isotope variations \(<4\)‰ (Fig. 7), which could reflect actual changes in the water chemistry as pore fluids evolved (Williams et al., 1997; Williams and Hervig, 1997). Furthermore, clay mineral standards mounted separately with each sample analyzed have shown consistent results over 3 yr.

3.6. Thermal Ionization Mass Spectrometry

A thermal ionization mass spectrometer was used to detect negative ions for B-isotope ratio analysis. Negative thermal ionization mass spectrometry (NTIMS) is a common technique for analysis of solutions with very small amounts of B (Heumann and Zeininger, 1985; Vengosh et al., 1989; Klotzli, 1992) because the ionization efficiency for negative ions is greater than for positive ions. Analyses can be made on samples containing as little as 10 ng of B (Hemming and Hanson, 1994). The aqueous samples are loaded on a rhenium filament that has been outgassed to remove surface impurities. Generally, 1 to 3 μL of solution was used along with 3 μL of a Ba(OH)\(_2\) solution (10 μg Ba) as an emission activator. The filament is heated in vacuum \((\approx 2 \times 10^{-7} \text{ torr})\) by a current of \(\approx 1800 \text{ mA}\). A stable emission current is generated at temperatures of 850 to 900°C.

The spectrometer is set up to measure B\(_2\)O\(_3\) emitted from the filament using a single Faraday cup collector. The masses measured are 42 (\(^{10}\)B\(^{16}\)O\(_2\)) and 43 (\(^{11}\)B\(^{16}\)O\(_2\)). Interference from \(^{17}\)O (Klotzli, 1992) is negligible because the abundance of \(^{17}\)O is far less than the analytical errors (\(\pm 2\)‰). The masses were alternately sampled in 10 cycles per block. At least 10 blocks of data are averaged to obtain an isotope ratio. Analyses yield errors on the order of 1 to 2‰. Measurements of the boron isotope standard NBS SRM 951 yielded a \(^{11}\)B/\(^{10}\)B ratio of 4.0337 \(\pm 0.0041\). Analyses of seawater collected from the Pacific Ocean yield a \(^{8}\)B value of +39.8‰, which is in excellent agreement with that measured by others (Hemming and Hanson, 1994).

4. RESULTS

4.1. Mineralogical

The mineralogical changes that occurred during the reaction are indicated by XRD spectra of the experimental run products.
Figure 8 shows the results from experiment 1, which represent the mineralogical changes observed in all three experiments. The spectra show the extent of illitization and other minor products formed (quartz and chlorite) as the reaction progressed. During the first week of the experiment, the smectite reacts to \( \approx 50\% \) illite (Fig. 8). R1 ordering begins at least by day 10 as indicated by the appearance of a peak near 13 Å \((\approx 6^\circ 2\theta)\). Figure 9 shows the variation in illitization progress for each experiment. Experiment 1, with low B-content, shows a gradual illitization similar to that reported by Whitney and Northrup (1988). After 30 days of reaction, the I/S is 70% illite, and it approaches 80% illite after 120 days. Experiment 2, with higher B in solution, takes twice as long (2 months) to reach 70% illite. It reaches a plateau at \( \approx 60\% \) illite during the first 36 days, with a more sudden change to 75% illite at 60 days. All three experiments show a significant shift in the 13 Å peak to 12 Å between 30 and 60 days, indicating a long-range ordering sequence. This R3 ordering indicates that each smectite layer is surrounded by three illite layers (Srodon, 1980). Experiment 3, at 300°C, never progresses beyond \( \approx 70\% \) illitization even after 150 days of reaction time. In fact, there is only a small increase in the illitization after the first week of reaction at 300°C. The higher temperature experiments (experiments 1 and 2) produced an 80/20 R3 ordered I/S after 120 days. A small peak appears at 3.5 Å after 60 days (Fig. 8), indicating a small amount of chlorite produced. This is more obvious in the spectra from day 90 and day 120 when the chlorite 7 Å peak appears. Production of chlorite was also observed in the illitization experiments of Whitney and Northrup (1988). The trace quantities of chlorite produced are not volumetrically important enough to influence the isotope ratio measurements, which average information from multiple (up to 59) individual analyses. Finally, the increasing intensity of the quartz peak at 26.6° \( 2\theta \) after 60 days (Fig. 8) suggests that increasing amounts of Si are produced during long-range (R3) ordering associated with recrystallization of the I/S.

### 4.2. Isotope Exchange

#### 4.2.1. Oxygen

The O-isotope changes in the solid and liquid reaction products are shown as a function of time in Figure 10. Changes in the oxygen isotope ratio are most dramatic during the first 20 days of the experiment, and then equilibrium is approached gradually over the duration of the experiments. A decreased rate of change in the O-isotope re-equilibration occurs as R1 ordering of the I/S begins. The oxygen isotope composition of the I/S and water asymptotically approaches equilibrium \( \Delta \) values (2–3‰; Savin and Lee, 1988) after 60 days, during R3 ordering. The gradual change observed in \( \delta^{18} \)O of the water during R3 ordering is not recognizable in the clays due to the large errors \((\pm 2\%)\) associated with clay analyses. Nonetheless, the final \( \Delta \) between the \( \delta^{18} \)O of the I/S and \( \delta^{18} \)O of the water is \( \approx 3 \pm 2\% \); therefore, it appears that the end products of the experiment have nearly reached equilibrium with respect to
oxygen. Equilibrium is indicated (according to 100% O-isotope resetting) after 120 days at 350°C and 150 days at 300°C. Therefore, only the final isotope ratio measured for fixed-B in the I/S can be used to calculate the equilibrium fractionation between the water and illitic clay minerals.

4.2.2. Boron

Changes in the B-content (Fig. 11) and isotopic ratios (Fig. 12) of solid run products occur as the illitization reaction progresses. Table 1 summarizes the analytical results for boron.

![X-ray diffraction spectra of solid reaction products from experiment 1. The mineralogical changes show increased ordering and illitization of smectite with time. Numbers above peaks indicate d-spacing (Å). Other products include chlorite (chl) and quartz (qtz) during R3 ordering.](image)
in the solid run products. Temperature and aqueous B-content were different for each experiment, resulting in variable reaction paths. There are notable differences in the quantity of B incorporated into I/S during the reaction. The starting smectite (SWy-1) contained 12 ppm fixed-B after washing and K-saturation removed adsorbed-B. The $\delta^{11}B$ of the fixed-B in the starting material was $-3 \pm 1\%e$ ($1\sigma$).

Experiment 1, with a low aqueous B-content, showed insignificant changes in the fixed-B content of the clay over the first 30 days of reaction time. After 60 days, however, the fixed-B content doubled, coincident with long-range (R3) ordering of the I/S (Fig. 11). Experiment 2 differed from experiment 1 only in the higher concentration of aqueous-B. The fixed-B content of the I/S increased to nearly 60 ppm during R1 ordering but equilibrated at 50 ppm after R3 ordering. Similarly, the experiment 3 results indicate an initially high fixed-B content of the I/S increasing to $\approx 95$ ppm during R1 ordering, with only 50 ppm fixed-B in the R3 ordered end product.

Changes in the isotopic composition of the fixed-B (Fig. 12) for each experiment show very similar trends. There is a rapid decline in $\delta^{11}B$ from the initial $-3\%e$ $\delta^{11}B$, while the I/S is randomly ordered (R0). The experiments containing abundant aqueous-B (experiments 2 and 3) both show a plateau in $\delta^{11}B$ at $-7 \pm 1\%e$ during R1 ordering. When R3 ordering begins after 60 days of reaction, the isotope ratio of the fixed-B decreases further. Experiment 1 (low aqueous-B) decreased only slightly during R3 ordering, probably because of the limited B supply. The B supply in experiments 2 and 3 was not similarly limited. During R3 ordering of the I/S the $\delta^{11}B$ reached $-12 \pm 0.5\%e$ at 350°C and $-15 \pm 0.9\%e$ at 300°C. The B-isotopic exchange was complete after 120 days at 350°C and 150 days at 300°C, as indicated by O-isotope equilibrium.

Boron in solution was measured by ICP analysis of the B washed from the capsule walls and solid product (using manitol). This fraction of B is essentially representative of what was in solution at experimental temperatures, because the partition coefficient is zero for adsorbed-B above 120°C (You et al., 1996). However, an estimated loss of up to 20% of the original B-content of the capsules (fixed-B + aqueous-B) during vacuum extraction may have induced fractionation. Because of the unreliability of this procedure, the $\delta^{11}B_{\text{water}}$ was determined by mass balance calculations (Table 2). Based on measurements of B-content and $\delta^{11}B$ of the solids and calculating these values for the water by difference, the mass balance calculations determined the ideal fractionation ($\delta^{11}B_{\text{water}} = \delta^{11}B_{\text{mineral}} - \delta^{11}B_{\text{water}}$) at the experimental temperatures. These calculations assume that no B was lost from the Au capsules by diffusion, which is unlikely at the temperatures of the experiments. Analysis of the pressurizing fluid used in the hydrothermal reaction vessel showed 11 ppm B, which would not affect the calculated fractionation factors and is likely from other contaminants (pressurizing water, steel, and/or lubricants used to seal the vessel).

5. DISCUSSION

5.1. Background

Clay minerals generally concentrate the light isotopes of boron over the heavy isotope, which prefers the aqueous phase.
This is contrary to what is observed in most stable isotopic systems. Heavy isotopes form bonds with a lower vibrational frequency than lighter isotopes of the same element and, therefore, should make stronger bonds (Faure, 1986). Thus, the light isotopes are more reactive and are usually concentrated in more volatile phases. In the case of boron, however, the coordination state plays an important role in fractionation (Palmer and Swihart, 1996). In solution, boron occurs predominantly as B(OH)₃ or B(OH)₄⁻, although there may be polynuclear species and organic-B molecules as well (Bassett, 1977; Mackin, 1987). The light isotope, ¹⁰B, prefers tetrahedral coordination, and the heavy isotope ¹¹B prefers trigonal coordination (Palmer and Swihart, 1996).

Spivack et al. (1987) showed that adsorbed-B in marine sediments has an average δ¹⁴B of +15‰, but it accounts for only 10 to 20% of the total-B in the sediment. The rest is “non-desorbable-B,” meaning that portion that was not removed by sonifying in B-free water after three washings. The nondesorbable-B fraction of the marine sediment had δ¹⁴B values ranging from 0 to −10‰ (Spivack et al., 1987). This covers the average range of δ¹⁴B values found in granitic and basaltic source materials (Leeman and Sisson, 1996). Spivack et al. (1987) found no evidence for fixation of B into clay minerals (substitution for Si) during early diagenesis. Therefore, all of the isotopic variations observed in shallow marine sediments are interpreted to result from interactions between pore fluid B and surface adsorbed-B and are consequently pH dependent.

The experimental results presented here address the isotopic behavior of B during late diagenesis when recrystallization of smectite to illite allows B-substitution for Si. In deep sedimentary basins undergoing siliciclastic diagenesis, the pH of pore fluids is buffered to values below 7 (Hutcheon et al., 1993) where B(OH)₃ is the predominant aqueous-B species (Palmer et al., 1987). As a result, ¹¹B prefers the aqueous phase. Illite/smectite undergoes significant recrystallization during diagenesis and provides tetrahedral coordination sites preferred by ¹⁰B (Spivack et al., 1987; Ishikawa and Nakamura, 1990). It is this coordination preference that causes ¹⁰B-enrichment in clay minerals.

Whitney and Northrup (1988) and others (Eberl, 1993; Yates and Rosenberg, 1997) suggested that there may be more than one mechanism of illitization: initially, a layer-by-layer transformation related to charge distribution of layers, and finally a complete dissolution-precipitation, or “neoformation.” Only a partial isotopic equilibration occurs during the early reaction of smectite to illite, but neoformation requires complete breakdown and reassembly, resulting in ordered I/S. It is during this neoformation stage that the isotope ratios are 100% reset.

During early recrystallization of the smectite (~60°C), aqueous-B may be adsorbed onto clay surfaces or incorporated into interlayer sites. Boron is adsorbed to the mineral surface in tetrahedral coordination; therefore, Palmer and Swihart (1996) argued that the largest isotope fractionation occurs during adsorption. The incorporation of surface-adsorbed-B (tetrahedral)
into lattice structure tetrahedral sites should not significantly affect the magnitude of the fractionation (Palmer and Swihart, 1996). However, during the neoformation stage, at temperatures approaching ~120°C, adsorbed-B is negligible (You et al., 1996), so the equilibrium isotopic fractionations measured in experiments at 300 to 350°C represent the fractionation between the aqueous-B (trigonal) and tetrahedral layers of the sheet silicate, not adsorption sites.

5.2. Interpretation

5.2.1. Boron trends

Different kinetic pathways for the incorporation of B into illite are expressed by the variable trends in the fixed-B content of the I/S over time (Fig. 11). The trends observed in the experiments are kinetic effects that might be quite different at the low temperatures of diagenesis. Experiments 2 and 3 differed only in temperature, but each showed a maximum B-content during R1 ordering. Experiment 3 (300°C) incorporated more B initially (~95 ppm) than experiment 2 (~60 ppm at 350°C), perhaps reflecting a temperature dependence of the layer charge distribution that affects the amount of B trapped in the interlayer. The lower temperature reaction might leave the interlayer open longer so that more B could be incorporated before the layer collapse. The fact that there is no significant change in the B-isotope composition during R1 ordering (Fig. 12) suggests that the B incorporated during this period of crystal reordering is not going into the tetrahedral layer. Otherwise, we would expect isotope changes corresponding to the increased B-content of the I/S.

The metastable B-isotope plateau observed during R1 ordering may reveal important insights to the mechanism of illitization. One model for formation of illite from smectite is that Al substitution for Si causes a charge imbalance that is compensated by fixing interlayer ions (primarily K⁺). Because B³⁺ behaves chemically in a manner similar to Al³⁺ but occurs only in tetrahedral coordination in the illite lattice (Palmer and Swihart, 1996), we can use it to better evaluate the timing of the tchermakitic substitution (tetrahedral Al for Si). The nearly invariable δ¹¹B (~7 ± 1‰) observed during R1 ordering indicates that Si–O bonds are not being broken. It is possible that the observed increase in B-content, with unchanging δ¹¹B, represents a period when the interlayer collapses because of a charge imbalance in the octahedral sites. This might trap B (and other ions) in the interlayer producing an R1 ordered I/S that protects interlayer ions from exchange or removal by mannitol.

Boles and Franks (1979) suggested that the illitization reaction requires Al that might be derived from the dissolution of smectite layers (see also Pallastro, 1985). We suggest that the R3 ordering and neoformation of illite crystals reflects a period where Si–O bonds in the tetrahedral layer are breaking, allowing B (and Al) substitution recorded by the progressive change in δ¹¹B toward equilibrium. Complete dissolution of the R1-ordered “illite” would allow a redistribution of B that was

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**Fig. 11. Changes in fixed-B content with time for all experiments. Gray lines denote general trends. Vertical dashed lines show changes in ordering of the I/S.**
previously trapped in the interlayer. During neoformation, the availability of Al from dissolution of smectite could compete with B for the tetrahedral Si sites, accounting for the reduced final B-content of the I/S at equilibrium.

The total amount of B incorporated in the authigenic illite (I/S) in these experiments at equilibrium is approximately five times more than the starting material. In nature the fixed-B content of illites is commonly much higher, on the order of hundreds of ppm (Harder, 1970). Early experiments on B-fixation in illite (Couch and Grim, 1968) showed that B-ion activity increases with salinity of the solution, especially in the presence of CaCl₂ (Shafer and Sieverts, 1941). The dissociation of boric acid: 

\[
B(OH)_3 + 2H_2O \leftrightarrow H_3O^+ + B(OH)_4^{-}
\]

may be enhanced with increased ionic strength of solution (Couch and Grim, 1968).

Another possible limitation to B-uptake in the experiments could be the high aqueous B-concentrations used. Nies and Campbell (1964) showed that at boric acid concentrations above 0.5M (≈5500 ppm B) there is an increase in the population of polynuclear borate ions. If B(OH)₃ is not the dominant aqueous species, then B-uptake by illite may be limited. Nonetheless, the concentration of B in the experiment solution (1000 ppm B) and the concentrations found in oil field brines (100’s -1000’s ppm B) (Collins, 1975) is well below that used by Nies and Campbell (1964). Couch and Grim (1968) found that the major factors contributing to boron fixation were salinity, aqueous B-concentration, and temperature. They suggested that the surface area of the clay mineral may play a role in B-uptake, but they did not establish that equilibrium conditions were achieved in their experiments. At equilibrium, the experiments described here showed no correlation between the amount of fixed-B and the isotopic composition.

5.2.2. Oxygen trends

The O-isotopes (Fig. 10) show a more gradual change between R1 and R3 ordering than the results for B-isotopes. This indicates that B-substitution is not directly linked to each O-bond exchange. This is expected because oxygen is being exchanged with the tetrahedral layer, hydroxyl sites, and with interlayer water as dehydration of the smectite occurs. The oxygen isotope changes do not reflect one unique mechanism of exchange. However, the equilibrium B-exchange is related only to the breaking of tetrahedral Si–O bonds. The heaviest O is released from the tetrahedral layers of the clay during R3 ordering, as B substitutes in new tetrahedral sites. The particular crystallographic position of B in the tetrahedral layer of the illite makes it a unique diagenetic marker.

5.2.3. Boron isotope fractionation

The B-isotope fractionation curve (Fig. 13) was constructed from the results of the illitization experiments described here (300°C, 350°C; 1 kbar), a fluid-silicate melt fractionation measured at 1100°C (Hervig and Moore, 2000) and the fractionation between water and adsorbed-B on clay surfaces at 25°C.
Based on these data, a linear change in fractionation with reciprocal temperature is observed. All of these experiments determined that the isotope fractionation occurs as a result of the coordination change of B from trigonal in the fluid to tetrahedral in the minerals. It is observed that minerals containing B in trigonal sites (i.e., borates and carbonates) would not follow the same fractionation curve (Oi et al., 1991; Hemming and Hanson, 1992).

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### Table 1. Summary of boron analytical results by secondary ion mass spectrometry.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{11}\text{B}$ (ppm)</th>
<th>$^{11}\text{B}$ SE‰</th>
<th>PE‰</th>
<th>IMF</th>
<th>$\delta^{11}\text{B}$</th>
<th>n</th>
<th>B (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 0</td>
<td>3.8254</td>
<td>0.0082</td>
<td>0.8</td>
<td>0.8</td>
<td>-50.9</td>
<td>0.4</td>
<td>7</td>
</tr>
<tr>
<td>Day 5</td>
<td>3.8209</td>
<td>0.0147</td>
<td>1.5</td>
<td>1.3</td>
<td>-51.4</td>
<td>0.4</td>
<td>14</td>
</tr>
<tr>
<td>Day 10</td>
<td>3.8119</td>
<td>0.0257</td>
<td>2.6</td>
<td>2.6</td>
<td>-43.0</td>
<td>0.6</td>
<td>7</td>
</tr>
<tr>
<td>Day 20</td>
<td>3.8170</td>
<td>0.0223</td>
<td>1.7</td>
<td>1.5</td>
<td>-51.4</td>
<td>0.1</td>
<td>6</td>
</tr>
<tr>
<td>Day 30</td>
<td>3.8279</td>
<td>0.0179</td>
<td>1.8</td>
<td>1.6</td>
<td>-46.0</td>
<td>0.5</td>
<td>15</td>
</tr>
<tr>
<td>Day 60</td>
<td>3.7990</td>
<td>0.0150</td>
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<td>1.5</td>
<td>-52.0</td>
<td>0.3</td>
<td>4</td>
</tr>
<tr>
<td>Day 90</td>
<td>3.7974</td>
<td>0.0182</td>
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<td>1.6</td>
<td>-52.0</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>Day 120</td>
<td>3.8187</td>
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<td>1.8</td>
<td>1.4</td>
<td>-48.0</td>
<td>0.5</td>
<td>20</td>
</tr>
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### Table 2. Mass balance for mineral-water B-isotope fractionation at 300 and 350°C.

<table>
<thead>
<tr>
<th>Mass balance calculations for 350°C experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>fixed-B (ppm)</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>water B (ppm)</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>Final</td>
</tr>
<tr>
<td>fixed-B (ppm)</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>water B (ppm)*</td>
</tr>
<tr>
<td>962</td>
</tr>
<tr>
<td>Calculated water</td>
</tr>
<tr>
<td>$\Delta_{\text{mineral-water}}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Mass balance calculations for 300°C experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
</tr>
<tr>
<td>fixed-B (ppm)</td>
</tr>
<tr>
<td>12</td>
</tr>
<tr>
<td>water B (ppm)</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>Final</td>
</tr>
<tr>
<td>fixed-B (ppm)</td>
</tr>
<tr>
<td>45</td>
</tr>
<tr>
<td>water B (ppm)*</td>
</tr>
<tr>
<td>967</td>
</tr>
<tr>
<td>Calculated water</td>
</tr>
<tr>
<td>$\Delta_{\text{mineral-water}}$</td>
</tr>
</tbody>
</table>

*The final water B-content and $\delta^{11}\text{B}$ were determined by difference because there was no loss of B from the sealed Au capsules. See text for further discussion.
Mass balance calculations (Table 2) determined the B-isotope fractionation between I/S and water at 350 and 300°C. During quenching of the experiment and extraction of the fluid from the Au-capsules, B would be adsorbed on the clay surfaces, but this quantity of B is not representative of the conditions at higher temperatures and was removed. Experiment 1 results were not used in these calculations because of the limited B-content of the solution. Detection limitations and analytical errors on such low concentrations led to a propagation of large errors. Nonetheless, experiments 2 and 3 contained an abundance of B in solution so that errors in the measurements of B-content and $\delta^{11}$B did not significantly affect the fractionation factor determined. The B-contents were measured with <5% error. Errors in the B-isotope analyses of the run products were under 1‰, and the B-isotope fractionations were calculated by assuming a closed system. Propagation of errors gave $\approx 1.5$‰ (2σ) for each experimental fractionation determination.

The adsorbed-B fractionation measured by Palmer et al. (1987) for clay minerals at 25°C was used to anchor the fractionation curve at the low temperature end. At this temperature the fixed-B composition does not reflect equilibrium conditions with the aqueous fluid, but it reflects the chemical environment of its source material. Boron is not fixed in the silicon tetrahedra until recrystallization of the I/S occurs at diagenetic temperatures >60°C (Perry, 1972). Nonetheless, the 31.5‰ fractionation measured at 25°C was based on the coordination change of B from trigonal (in solution) to tetrahedral sites on the clay surface and may be a close proxy for the magnitude of fractionation expected for other tetrahedral mineral sites (Palmer and Swihart, 1996). Earlier calculations (Oi et al., 1989) indicated that B-isotope fractionation between trigonal and tetrahedral coordination should be $\approx 20$‰, not 31.5‰. However, further study of natural phases containing B in both coordinations led Oi et al. (1991) to conclude that the fractionation between trigonal and tetrahedral coordination at 25°C was much larger than 20‰, and consistent with Palmer et al. (1987).

The high-temperature (1100°C) fractionation was measured on midocean ridge basaltic glass doped with 2000 ppm B (NBS SRM 951, boric acid) and melted at 100 MPa (1 kbar) pressure over 24 h, with an equal mass of B-free water (Hervig and Moore, 2000). The fractionation between the aqueous fluid and basaltic melt is again related to the coordination change from trigonal to tetrahedral sites in the melt. For other isotopic systems, such as oxygen, the isotope fractionation between fluid and minerals is mineral-specific due to bonding differences associated with variations in different mineral structures. Boron isotope fractionation does not appear to follow this mineral specificity. Under conditions where the dominant aqueous B-species is $\text{B(OH)}_3$, and the mineral sites prefer $\text{B(OH)}_4^-$, the B-isotope fractionation forms a single linear trend with reciprocal temperature, independent of mineral structure. One explanation for this is that the ionic radius of B is much smaller.

![Figure 13. Boron isotope fractionation as a function of reciprocal temperature, compared to oxygen isotope fractionation (from Yeh and Savin, 1977) for I/S.](image-url)
Further experiments are required to refine the B-isotope fractionation curve presented here. However, within the limits of our experimental conditions the fractionation equation is fairly well constrained and can be applied to interpret field data where equilibrium conditions exist (Williams et al., Part II).

6. CONCLUSIONS

The results presented indicate a boron isotope fractionation equation,

$$\Delta_B^{\text{mineral-water}} = -10.12 \left(1000/T(\text{K})\right) + 2.44$$

with a slope that opposes that established for O-isotopes (Yeh and Savin, 1977). Under equilibrium conditions B substitutes for Si in the tetrahedral layers of I/S. Because this requires Si–O bonds to be broken, there is a synchronous change in B for Si in the tetrahedral layers of I/S. Because this requires and Savin, 1977). Under equilibrium conditions B substitutes with a slope that opposes that established for O-isotopes (Yeh and Savin, 1977). Under equilibrium conditions B substitutes for Si in the tetrahedral layers of I/S. Because this requires Si–O bonds to be broken, there is a synchronous change in B for Si in the tetrahedral layers of I/S.

We conclude that the equilibrium fractionation of B-isotopes is primarily a function of temperature and the coordination change from trigonal in aqueous solution to tetrahedral sites in the mineral. Examination of the illitization reaction kinetics reveals multiple tetrahedral coordination sites associated with mixed-layered I/S as the reaction progresses toward equilibrium. At low temperatures (<120°C) surface adsorbed-B is in tetrahedral coordination, causing a large fractionation from trigonal coordination in solution (Palmer and Swihart, 1996). At the temperatures of our experiments (300°, 350°C) adsorption is negligible (You et al., 1996), yet B continues to be incorporated in the clay mineral interlayers where it is held tightly by collapse of the layers during R1 ordering. This B was not removed by washing in mannitol and is therefore not in an exchangeable position. The isotope fractionation associated with the interlayer-B represents a metastable condition. The equilibrium substitution of B for Si in the tetrahedral layers of the I/S does not occur until long-range R3 ordering when Si–O bonds are broken during illite neoformation with simultaneous exchange of tetrahedral oxygen. Substitution of B in the tetrahedral layer of the silicate is temperature dependent (Fig. 13), and the associated fractionation can therefore be used as a geothermometer.

The experiments reported here support a linear fractionation with reciprocal temperature, in accord with data from high-temperature experiments of melt-fluid fractionation (Hervig and Moore, 2000). The linear relationship can be extended to include low temperature (25°C) B-adsorption data (Palmer et al., 1987) because the greatest fractionation results from the coordination change from trigonal to tetrahedral. This relationship allows the application of B-isotopes to understanding fluid sources and migration during burial diagenesis (Williams et al., in press). The study of authigenic illite and muscovite, the most common hosts of B in sedimentary basins, may be critical to understanding important diagenetic events. The neoformation of illite and coincident changes in $^{11}$B at depths related to hydrocarbon generation, make boron a sensitive indicator of pore fluid changes related to organic maturation.

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