Clays and Clay Minerals, Vol. 62, No. 3, 224–234, 2014.

METHODS FOR *IN SITU* SIMS MICROANALYSIS OF BORON AND ITS ISOTOPES IN PALAGONITE

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Abstract—Boron has been shown to be a useful trace element in clay-mineralization reactions, raising the possibility that B studies may provide a means to investigate environmental controls on palagonitization. The objective of the present study was to address calibration, matrix effects, and B exchangeability issues such that meaningful secondary ion mass spectrometry (SIMS) microanalysis of B in thin sections of palagonite will be feasible. Silver Hill illite (IMt-1) was found to be a suitable calibration reference material, based on compositional similarity, relatively high B content, and ease of mounting on thin-section samples for SIMS microanalysis. Matrix effects of borated sideromelane and illite were compared and found to be similar, confirming previous studies which showed no matrix effects for B among minerals. Boron substitutes for Si in tetrahedral sites and also can be adsorbed in exchangeable sites of 2:1 clay minerals. Similarly, B can be found in tetrahedral and exchangeable sites within palagonite, which consists of both layered and amorphous volumes. In order to measure tetrahedral B content and isotopic ratio in the palagonite, exchangeable B was removed by soaking sample thin sections in a 1 M NH_4Cl solution until exchangeable cation concentrations were constant. Treated samples showed decreases in B content and isotopic ratio with exchange. Extraction of exchangeable B permits the direct measurement of tetrahedral B content and isotopic ratio. The exchange technique devised and tested here should have broad applicability to thin-section microanalysis of B in clay and clay-like materials where cation exchange can be used for surface-analytical techniques. The present study represents an initial attempt to address sample-preparation, calibration, and potential matrix-effects problems for analyses by SIMS. Further refinements may improve the accuracy of the measurements, but the results presented here indicate that meaningful measurements are possible.

Key Words—B content, B exchangeability, B isotopes, Boron, Palagonitization, Sideromelane, SIMS, Thin Section.

INTRODUCTION

Sideromelane (basalt glass) is a thermodynamically unstable material which, in aqueous, low-temperature environments, can undergo a geochemical alteration process known as "palagonitization" (Fisher and Schmincke, 1984). Palagonitization is a hydrolytic alteration process during which sideromelane is dissolved and hydrated by water, forming palagonitized sideromelane (referred to hereafter as palagonite). Concurrent with dissolution and hydration of sideromelane is the precipitation (to varying extents) of authigenic minerals, mainly smectites and zeolites (Stroncik and Schmincke, 2001; Walton and Schiffman, 2003; Pauly *et al.*, 2011); see Figure 1. Palagonitization is a globally significant process, with broad geological implications for volcano-edifice stability (Schiffman *et al.*, 2006), nuclear-waste storage (Zielinski, 1980; Jercinovic *et al.*, 1990; Crovisier *et al.*, 2003), and Martian crustal evolution (Bishop *et al.*, 2002). The factors controlling palagonitization are still not well understood, however.

Palagonite is regarded as the initial sideromelane replacement product during hydrolytic alteration, the ultimate fate of palagonite being conversion to smectite (Stroncik and Schmincke, 2001; Pauly *et al.*, 2011). Many early workers (Hay and Iijima, 1968a; Singer, 1974; Eggleton and Keller, 1982; Zhou and Fyfe, 1989) suggested that palagonite has a smectite-like structure. Palagonite appears to be amorphous to poorly crystalline when examined using X-ray diffraction on hand-separated palagonites (Stroncik and Schmincke, 2001). High-resolution transmission electron microscopy (HRTEM) images of a palagonite sample (Drief and Schiffman, 2004) show the existence of both amorphous material and poorly crystalline sheeted material with variable layer stackings (Figure 2). Currently, palagonite is considered to be a metastable proto-smectite replacement product of sideromelane (Pauly *et al.*, 2011).

Palagonite is commonly observed rimming sideromelane fragments in hyaloclastites (Figure 1). These palagonitized rinds are friable and generally <100 μm thick; isolating palagonite completely from fresh sideromelane is extremely difficult, therefore. An advantage of using *in situ* micro-analytical methods to study palagonite is the ability to analyze palagonite and co-existing fresh sideromelane in its textural/petrologic

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DOI: 10.1346/CCMN.2014.0620306

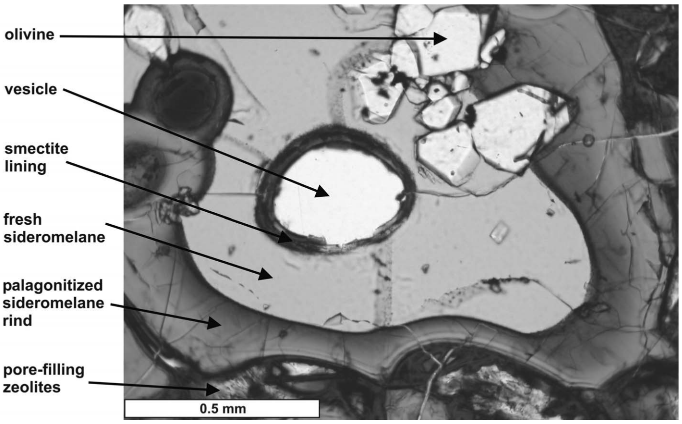

Figure 1. Thin-section photomicrograph (plane-polarized light) of sample R0777-17.4, palagonitized hyaloclastite from the Hawaii Scientific Drilling Project (Mauna Kea volcano, SE flank). A single vesiculated sideromelane fragment is shown. Palagonitization has created a dark altered rind (palagonite) around the lighter fresh sideromelane, a smectite lining within the clear vesicle, and pore-filling zeolites as shown.

context. Electron probe microanalysis (EPMA) has been used for many years to characterize the *in situ* major-element composition of palagonite (Stroncik and Schmincke, 2001; Pauly *et al.*, 2011 and references therein). Laser-ablation inductively coupled plasma mass spectroscopy (LA-ICP-MS) has been used to determine the *in situ* trace-element composition of palagonite samples (Walton *et al.*, 2005; Walton and Schiffman, 2003; Pauly *et al.*, 2011). With these studies as a foundation, a logical next step would be to carry out an *in situ* trace-element study in order to evaluate the geochemical-process controls on palagonitization.

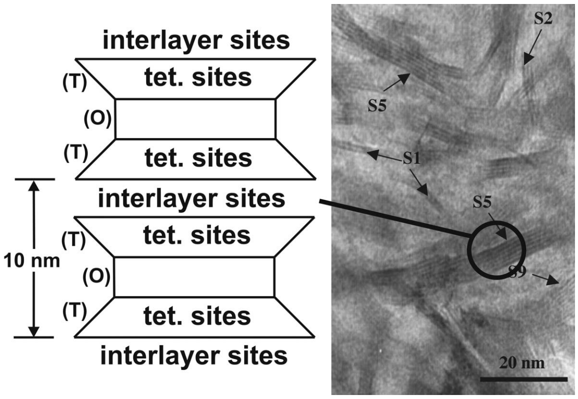

Figure 2. HRTEM lattice-fringe image of the palagonitized portion of sample R0777-17.4 (see Figure 1). Layered intervals, showing different layer stackings (*e.g.* S2 = two layers of 1 nm each), are visible, consistent with previous workers' suggestions that palagonite resembles smectite (see text). Amorphous intervals are also distinguishable. Bubble and schematic enlargement (this study) show tetrahedral (tet.) and interlayer sites for B occupancy within the smectite-like areas (image after Drief and Schiffman, 2004). Interlayer sites dominate cation exchange in smectite-groups minerals, but exchange may also occur at sites (*e.g.* edge sites) in addition to interlayer sites.

Elements having stable isotopes that fractionate during geochemical processes have been used successfully as tracers of geochemical processes (Hoefs, 2004; Lerman and Clauer, 2007). By definition, $\delta^{11}B$ (‰) = $((^{11}B/^{10}B_{sample})/(^{11}B/^{10}B_{standard})-1) \times 1000$; the standard used in most studies is NIST-SRM 951 boric acid (Palmer and Swihart, 1996). Substantial ^{11}B enrichment in seawater ($\delta^{11}B$ ~+40‰; Hoefs, 2004) relative to sideromelane ($\delta^{11}B$ −10 to 0‰; Hoefs, 2004) has been attributed to isotopic fractionation that occurs as ^{10}B is incorporated by clay minerals during low-temperature alteration of oceanic crust (Hemming and Hanson, 1992). The B isotopic system is not affected by changes in oxidation state, and it has a known dependence on fluid composition and temperature (Williams *et al.*, 2012). These factors suggest that B may be useful as a trace element for studying palagonite-water fractionation during palagonitization.

Boron has two stable isotopes, ^{10}B (~19%) and ^{11}B (~81%). Isotope systematics (Palmer and Swihart, 1996) indicate that ^{11}B is concentrated into trigonal coordination sites, and ^{10}B is concentrated into tetrahedrally coordinated sites. The relative distribution of $B(OH)_4^-$ and $B(OH)_3$ in aqueous solutions is controlled by pH (Hemming and Hanson, 1992), with $B(OH)_3$ dominant at pH <8 (Palmer and Swihart, 1996) at 25ºC. The tetrahedral sheet of clay minerals will thus incorporate ^{10}B preferentially in the tetrahedral sites (Palmer and Swihart, 1996, and references therein), unless the fluid has a high pH at which tetrahedral borate anion dominates the fluid phase. This raises the possibilities that, similar to clay minerals such as smectite, B can substitute into tetrahedral sites within the layered intervals, and that B isotopic fractionation between palagonite and water can occur during palagonitization.

Secondary ion mass spectrometry (SIMS) has been shown to be useful for routine B microanalyses (content and isotopic ratio) of minerals and glasses (Hervig, 1996). The analysis of palagonite by SIMS has not been attempted previously, although SIMS has been used successfully to analyze B in clay minerals (Williams *et al.*, 2012 and references therein). These recent studies are of particular relevance to the present study due to the apparent similarities described above between palagonite and smectite (Figure 2). As a prerequisite to performing similar studies of palagonitization, in the present study methods were tested for conducting reproducible *in situ* SIMS microanalyses of B and its isotopes in polished thin sections of palagonite.

Expandable clay minerals such as smectite normally have a negative charge on their basal siloxane surface due to cation substitutions in the silicate framework. In a simple model, the basal siloxane surface attracts cations, which occupy the sites labeled ‘interlayer sites’ in Figure 2; some cation exchange at other sites is also possible. However, Brindley and Brown (1980) found that neutral as well as negatively charged species are held in the interlayers of illite-smectite, raising the possibility that both of the dominant aqueous B species (neutral $B(OH)_3$ as well as negatively charged $B(OH)_4^-$) could be held in interlayer sites. Based on infrared spectroscopy work (Moore and Reynolds, 1991; Sposito *et al.*, 1991), cations attracted to the basal siloxane surfaces are hydrated, so neutral $B(OH)_3$ may be introduced and incorporated with the water. Because B trapped in exchangeable sites may not be in equilibrium with B in the silicate framework (Williams *et al.*, 2007), the isotopic composition of tetrahedrally bound B (substituted for Si) and exchangeable B must be separated (Williams and Hervig, 2006). According to Zhang *et al.* (1998) and Williams and Hervig (2005) adsorbed B could can be removed from exchangeable sites of bulk smectite separates using a concentrated 1 M NH_4Cl solution. Using major-element composition as analyzed by EPMA, Schiffman and Southard (1996) showed that cations can be exchanged in thin-section samples of both smectite and palagonite using a CsCl solution. As part of the present study, an experiment was performed on palagonite thin sections to determine if adsorbed B can be removed from exchangeable sites of the sample using NH_4Cl solution.

ANALYTICAL METHODS

SIMS

Analytical conditions. In situ B content and $\delta^{11}B$ were analyzed using a Cameca ims 3f SIMS at the Arizona State University SIMS Facility (Hervig, 1996; http://sims.asu.edu). Each analysis used an O^- primary beam current of 3−5 nA. The analyses were done in spot mode for high spatial resolution (10 μm craters), and the sample was pre-sputtered for 5 min to remove any remaining surface contaminants and achieve stable secondary ion signals. The primary beam voltage was −12.5 kV with a sample voltage of −4500 V for a total impact energy of ~17 keV. The SIMS was operated at a mass resolving power (MRP) of ~1200 (MRP = mass/Δmass at 10% peak width), sufficient to separate the $^{10}BH^+$ species from $^{11}B^+$, and ions with ~20±20 eV initial kinetic energy were allowed into the mass spectrometer. Energy filtering (secondary ions with 75±20 eV initial kinetic energy) was used for B-content analyses (Hervig, 1996). Measurements were made on the major B isotope ^{11}B, which is four times more abundant than the minor isotope ^{10}B, and normalized to ^{30}Si, a minor isotope of Si, selected to keep the ions detected on the same electron multiplier used to count the ^{11}B. Boron content was determined using a well established calibration curve (Williams *et al.*, 2012) based on analyses of various minerals and glasses (NIST standards) with certified B contents. The B-content analyses were run for long enough (10−15 min) to acquire sufficient counts for errors to be <10%. The actual time depended on the amount of B in each sample. The analytical errors were compared with predicted errors (from counting statistics) and if the analytical error was more than twice the predicted error, the analysis was evaluated for potential charging or other instrumental instability. Analyses that did not agree closely with the predicted errors were disregarded, but such analyses were useful as warning signs of an instrumental setup problem (charging) or aging electron multiplier.

After analysis of the B content, analyses of $^{11}B/^{10}B$ ratio were made in the same analytical crater. Energy filtering was not used for B-isotope ratio analysis, but rather entrance and exit slits were adjusted to the appropriate MRP. The isotope-ratio analyses must be far more precise than trace-element analyses. Here users normally count for 2 s on ^{11}B and 8 s on the less abundant ^{10}B. For this study 100 cycles were measured, but where B contents were small the number of cycles was increased to improve statistics. The total analysis time for each sample depended on the number of cycles. Again the standard error (standard deviation from the average/square-root 100, where 100 measurements were made) was compared to the predicted error based on total number of ion counts, to determine the statistical significance of results.

Reference material for calibration. Ideally the reference material would be mineralogically identical to the unknown sample, so that matrix effects on SIMS analyses of both materials would also be identical. Because of the natural variability of palagonite, however, like clay minerals, defining and characterizing a reference material composed of palagonite is not possible. Phases with similar chemistry to palagonite (smectite and illite) were tested as potential reference materials. An advantage of using a clay mineral as a reference material is that a drop of a dilute clay mineral suspension can be applied directly onto polished thin sections, where it then orients clay particles flat as it dries, a requirement for SIMS analysis. The on-sample location of the reference material allows the instrumental mass fractionation (IMF) to be determined readily between analyses of the unknown materials without having to exchange samples and disturb the vacuum. This 'bracketing' of reference material analyses between unknown analyses is critical for assessing instrumental stability during analytical sessions.

Natural illite and smectite were evaluated as potential reference materials. SWy-1 smectite (Crook County, Wyoming, from the Source Clays Repository of The Clay Minerals Society) was tested but was not selected as a reference material for this study because of the possibility of large analytical errors due to its relatively small B content. Illite IMt-1 (Silver Hill, Montana, also from the Source Clays Repository) was tested and selected for use. IMt-1 has a relatively large B content (240±20 ppm; Williams *et al.*, 2001), with B located in the silicate tetrahedral sites, similar to palagonite (Figure 2), and it has also been analyzed previously (Williams *et al.*, 2001) for isotopic composition using both positive and negative thermal-ion mass spectrometry (TIMS).

Matrix effects. Because the proposed reference material (IMt-1) does not have identical chemistry to the palagonites of interest, the difference between measured B isotope ratios for IMt-1 and a synthetically borated basalt glass, estimated to represent the initial composition of the material subsequently palagonitized, was examined closely. A borated basalt with 2300 ppm B (BB-1), was synthesized using glassy basalt from the Juan de Fuca ridge (sample TT-152 of Hervig *et al.*, 2002) and NIST-SRM 951 boric acid; synthesis details were given by Hervig *et al.* (2002). Because BB-1 was doped with 2300 ppm NIST standard boric acid (SRM 951), its isotopic composition is 0‰ by definition. No significant change of the B content in BB-1 was noted (Hervig *et al.*, 2002) during melt-aqueous solution fractionation experimental runs at 950−1100ºC and 110−170 MPa; no change in isotopic composition of BB-1 during initial preparation was expected, therefore. The B content and δ^{11}B of IMt-1 has been analyzed using both TIMS and SIMS and has given consistent isotopic ratios over the past 15 years (Williams *et al.*, 2012). Boron isotopic ratios are reported relative to NIST 951 boric acid, and the IMt-1 internal reference was used to determine the instrumental mass fractionation (IMF) during each analytical session. Three SIMS analyses of IMt-1 were followed by five analyses of BB-1 and three further analyses of IMt-1 during a single SIMS session (Table 1). The SIMS analyses were compared to the average of five TIMS analyses of IMt-1 (bulk δ^{11}B = −9.1±0.6‰, determined independently by TIMS; Williams *et al.*, 2001).

The SIMS instrumental fractionation (α_{inst}) was calculated by taking the ratio of the ^{11}B/^{10}B measured by SIMS of the reference material (IMt-1) divided by the ^{11}B/^{10}B ratio measured by TIMS. The SIMS measurement on BB-1 was then corrected by dividing the raw isotope ratio by α_{inst}. The δ value was then calculated using standard notation relative to the accepted standard for B which is NIST SRM 951 boric acid with a certified ^{11}B/^{10}B ratio of 4.0437 (Catanzaro *et al.*, 1970):

$$\text{Raw } (^{11}\text{B}/^{10}\text{B}) / \alpha_{\text{inst}} = \text{corrected ratio}$$
$$\delta^{11}\text{B‰} = ((\text{corrected ratio}/4.0437)^{-1}) \times 1000$$

The IMF based on independent analyses of IMt-1 averaged −40.7±0.4‰ (1σ S.E. of six analyses) over the analytical session (Table 1). If no matrix effects for analysis of the illite *vs.* glass were found, the same IMF (or α_{inst} correction) should give the correct isotopic ratios for both materials. Five analyses of BB-1, corrected by the α_{inst} determined using IMt-1 are listed in Table 1. The average value is −0.9±0.6‰ (1σ), which is within error of 0‰ (δ^{11}B of NIST 951 boric acid standard) and suggests that any matrix effects are at the sub-permil level. This finding is consistent with other studies. No matrix effects for B measurements by SIMS were found (Hervig *et al.*, 2002) when analyzing basalt and rhyolite glasses, metamorphic minerals, and diagenetic materials. No appreciable matrix effects between rhyolite and basalt were noted either (Rosner *et al.*, 2008). Boron isotopic analyses of various clay minerals were compared with different mineral standards and NIST standards and no matrix effects for B were found (Williams *et al.*, 2001). In addition, the instrumental drift over the analytical session was also found to be at sub-permil levels (Table 1).

Electron probe microanalysis (EPMA)

The *in situ* major-element composition of palagonite was determined using a Cameca SX-100 electron microprobe at the University of California, Davis. A conductive C-coating ~250 Å thick was applied to the samples prior to analysis. The electron-beam settings were 15 KeV accelerating voltage with 2 nA regulated current, and the beam was rastered over a 5 μm × 5 μm area. Peaks and backgrounds were typically counted for 10 s. Net intensities relative to oxide and silicate calibration standards were converted to concentrations using standard ZAF correction techniques (Schiffman and Roeske, 2002). Accuracy was evaluated by analyzing working reference standards as unknowns under the same analytical conditions.

Samples

In order to assess palagonite B composition variability, eight samples of palagonitized hyaloclastite representing three palagonitization environments (submarine volcaniclastic, seafloor volcanic, and marine phreatomagmatic) were selected for this study. These

Table 1. $\delta^{11}B$ analyses of borated basalt glass (BB-1) by SIMS using IMt-1 as the reference material. BB-1 analyses were pre- and post-bracketed with IMt-1 analyses to monitor and calculate average instrumental mass fractionation (IMF) during BB-1 analyses.

	SIMS measurements					Calculated Values	
Sample	$^{11}B/^{10}B$	S.E. (ratio)	raw $\delta^{11}B$ (‰)	S.E. (‰)	$\alpha_{\text{inst.}}$	corrected $^{11}B/^{10}B$	corrected $\delta^{11}B$ (‰)
IMt-1	3.8453	0.0029	−49.1	0.8	0.9597	4.0069	−9.1
	3.8435	0.0026	−49.5	0.7	0.9592	4.0069	−9.1
	3.8398	0.0030	−50.4	0.8	0.9583	4.0069	−9.1
Average	3.8429		−49.7		0.9591	4.0069	
Std. Dev.	0.0028		0.7		0.0007		
BB-1	3.8722	0.0013	−42.4	0.3		4.0377	−1.5
	3.8772	0.0015	−41.2	0.4		4.0430	−0.2
	3.8751	0.0013	−41.7	0.3		4.0408	−0.7
	3.8733	0.0016	−42.1	0.4		4.0389	−1.2
	3.8790	0.0015	−40.7	0.4		4.0448	+0.3
Average	3.8754						−0.9
Std. Dev.	0.0028						0.6
IMt-1	3.8479	0.0028	−48.4	0.7	0.9603	4.0069	−9.1
	3.8396	0.0022	−50.5	0.6	0.9582	4.0069	−9.1
	3.8389	0.0027	−50.6	0.7	0.9581	4.0069	−9.1
Average	3.8421				0.9589		
Std. Dev.	0.0050				0.0012		
IMt-1: Session							
Average	3.8432		−49.8		0.9590		
Std. Dev.	0.0037		0.9		0.0009		

S.E. = standard error

$\alpha_{\text{inst.}}$ = SIMS $^{11}B/^{10}B$ / TIMS $^{11}B/^{10}B$

Corrected $^{11}B/^{10}B$ = measured ratio / $\alpha_{\text{inst.}}$

Bulk $\delta^{11}B$ measured using TIMS (positive and negative; $n = 5$) (Williams *et al.*, 2001):

$^{11}B/^{10}B$	S.E. (ratio)	$\delta^{11}B$ (‰)	S.E. (‰)
4.0069	0.0024	−9.1	0.6

samples were described by Pauly *et al.* (2011). Boron is a ubiquitous contaminant in nature, common in water and airborne particles and it can easily contaminate lab samples, therefore. A major issue with any trace-B analytical study is the prevention of B contamination during sample handling. Great care was taken, therefore, during this experiment, to avoid sample contact with B-bearing lab materials such as borosilicate glass lab ware, unfiltered water, and dust.

One-inch (25.4 mm) diameter, 100 μm-thick, polished sections of each sample were prepared. A ~30 nm gold coating was applied to each sample, and then the B content and $\delta^{11}B$ were analyzed using SIMS as described above at selected spots within palagonitized areas on all eight samples. Exact analysis-spot locations were recorded photographically. Two of the eight samples, with relatively wide palagonitized rims, were chosen for cation-exchange experiments allowing evaluation of the potential for quantitative removal of exchangeable B from thin-sectioned palagonite. Both samples were analyzed for major-element composition using EPMA as close as possible to the previously recorded analytical craters. The C coat required for EPMA was removed by polishing. The samples were then rinsed with nominally B-free distilled, de-ionized water that had been filtered through an Amberlite resin column (Tonarini *et al.*, 1997), then washed with 0.1 M mannitol, a polyhydric alcohol which has been shown to bind and remove adsorbed B contaminants from exterior mineral surfaces (Hingston, 1964; Tonarini *et al.*, 1997; Williams *et al.*, 2001). Both samples were then soaked in a 1 M NH_4Cl exchange solution (prepared using B-free distilled, de-ionized water and 99.7% pure NH_4Cl) for 20 h. The samples were then re-analyzed using EPMA at the same spots (relocated as precisely as possible using back scattered electron images) as had been analyzed previously. These steps were repeated as necessary until a steady-state elemental composition of major exchangeable cations (Na, K, and Ca) was reached. Because neither of the major aqueous B species is a cation, the total soak duration required for complete Na, K, and Ca exchange was assumed to be greater than or equal to the total soak time required for complete B exchange. The other six samples were then soaked in 1 M NH_4Cl for the determined soak duration.

Table 2. Effect of soaking polished thin sections on palagonite major-element composition (EPMA measurements). The averages of four analyses prior to soaking and after three successive 20-h exposures to NH_4Cl solutions are shown for two different samples. The purpose of this process was to remove B from the palagonite exchangeable sites. These data are summarized in Figure 3.

Sample	Cum. soak Time (h)	SiO_2	Al_2O_3	TiO_2	FeO	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	Total
		Wt.% oxide										
R0777-17.4	0	42.13	7.94	4.69	14.56	0.09	1.87	9.47	0.88	0.58	0.11	82.35
R0777-17.4	20	47.70	8.64	5.49	16.95	0.06	2.14	4.91	0.03	0.05	0.10	86.10
R0777-17.4	40	48.90	8.33	5.48	17.09	0.19	2.14	4.25	0.06	0.04	0.06	86.62
R0777-17.4	60	48.31	8.66	5.43	16.64	0.12	2.25	4.00	0.05	0.02	0.12	85.61
S708-9	0	38.81	8.51	4.04	16.72	0.10	2.75	5.10	2.35	1.19	0.10	79.76
S708-9	20	42.66	9.40	4.24	18.05	0.10	2.73	3.97	0.23	0.09	0.07	81.64
S708-9	40	44.09	9.51	4.32	18.74	0.12	2.65	3.60	0.06	0.03	0.06	83.30
S708-9	60	44.63	9.64	4.16	18.83	0.13	2.50	3.62	0.14	0.09	0.07	83.90

All eight samples were then rinsed and washed as above. IMt-1 was re-applied to the samples as a B reference material, the sections were re-coated with ~30 nm of gold, and palagonitized areas of the samples were then re-analyzed for B content and $\delta^{11}B$ using SIMS at the same spots as had been analyzed previously.

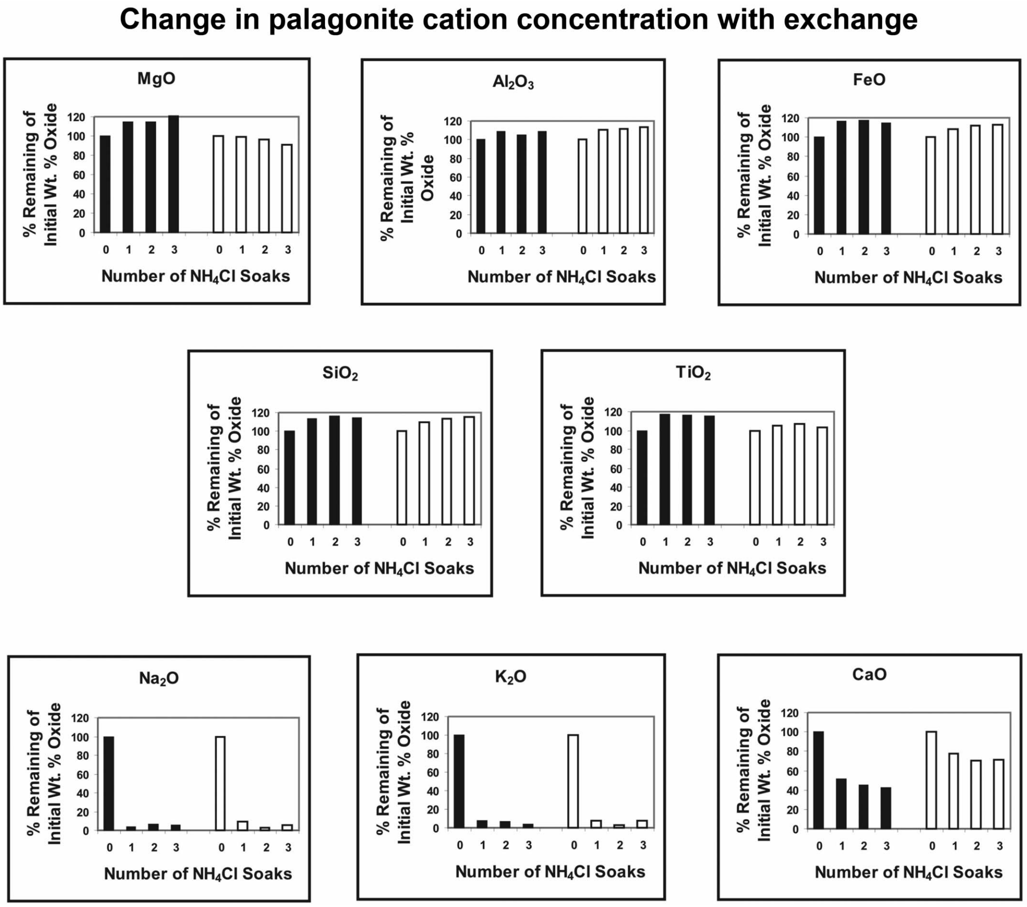

Figure 3. Percentage of original cation concentration remaining after exchange with 1 M NH_4Cl solution. Shaded bars are for sample R0777-17.4; non-shaded bars are for sample S708-9. Soak 0 values are pre-exchange (100%), shown for reference. The duration of each soak was 20 h. Al, Fe, Si, and Ti do not appear to have exchanged. Na and K concentration decreased relatively rapidly to essentially steady state with the first soak. Ca concentration decreased more slowly, reaching steady state with two soaks.

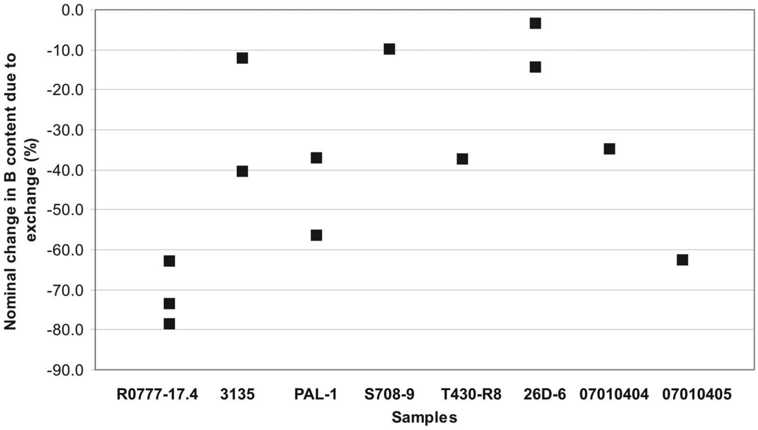

Figure 4. Nominal percentage change in B content (bulk minus tetrahedral) due to cation exchange for eight palagonite samples (the measured pre-and post-exchange B-content measurements are accurate within ±10%; see Table 3). The B content decreased for all samples; the percentage decrease was very variable over the sample set.

RESULTS

Major-element analyses (EPMA) for the two samples subjected to three 20-h soaks in 1 M NH_4Cl are summarized in Table 2 and changes in major exchange-cation chemistry with increasing exposure time is illustrated in Figure 3. The concentrations of framework cations were unchanged with NH_4Cl soak, as was Ti, demonstrating that no dissolution of glass occurred during the cation-exchange treatments. Concentrations of cations expected to occupy exchangeable sites (Na, K, Ca) decreased with increasing NH_4Cl treatment time. The Na and K concentrations declined dramatically and reached steady state during the first 20 h of treatment (essentially no change with the subsequent soaks); Ca concentration declined more slowly, reaching steady state during the second 20-h soak (essentially no change with the third 20 h treatment).

The measured pre- and post-exchange B content and δ^{11}B values are listed in Table 3. The B-content values decreased with NH_4Cl soak for all eight palagonite thin-section samples in the present study. The measured decrease in B content ranged from 3.1 to 78.1% of the original value (Figure 4). The δ^{11}B values also decreased with NH_4Cl treatment for all eight polished sections. The measured decrease in δ^{11}B values ranged from 1.9 to 27.9‰ (Figure 5).

DISCUSSION

Exchange-soak duration

The unchanged concentrations of Mg, Al, Fe, Si, and Ti with NH_4Cl exchange treatment (Table 2, Figure 3) confirm that these cations were all structurally bound and that no dissolution of the glass occurred. The significant decrease in the concentration of Na, K, and Ca indicate that these cations were held weakly in exchangeable sites of the palagonite. Neutral boric acid and negative borate anion, the two dominant aqueous B species, were similarly removed by the exchange solution (Table 3). The rapid decline in Na and K

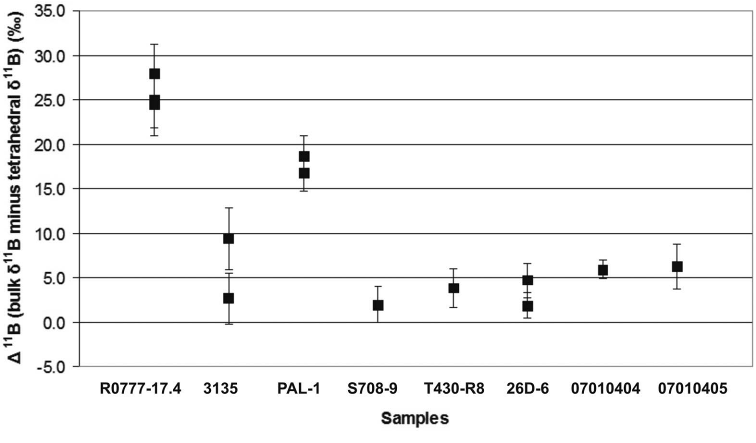

Figure 5. Change in δ^{11}B (bulk minus tetrahedral) due to cation exchange for eight palagonite samples (see Table 3). δ^{11}B decreased for all samples; the magnitude of the decrease was very variable over the sample set.

Table 3. Measured palagonite B content and $\delta^{11}B$ for the eight samples in the present study. Calculated changes in B content and $\delta^{11}B$ due to the cation exchange procedure are summarized in Figures 4 and 5, respectively.

Sample	Analysis	Measured Pre-exchange B content (ppm)	Measured Pre-exchange B content error, ±	Measured Post-exchange B content (ppm)	Measured Bulk B content minus Post-exchange B content error, ±	Calculated Bulk B content minus Tetrahedral B content (ppm)	Calculated Tetrahedral B content Error, ± (ppm)	Measured Pre-exchange $\delta^{11}B$ (‰)	Measured Pre-exchange S.E. (‰)	Measured Post-exchange $\delta^{11}B$ (‰)	Measured Post-exchange S.E. (‰)	Calculated $\Delta^{11}B$ (‰)	Calculated $\Delta^{11}B$ Error, ± (‰)
R0777-17.4	a	56	10%	15	10%	41	7.1	+17.3	1.1	-7.8	2.2	25.1	3.2
	b	40	10%	15	10%	25	5.5	+24.6	1.1	-3.3	2.2	27.9	3.3
	c	64	10%	14	10%	50	7.8	+20.4	1.1	-4.1	2.5	24.5	3.5
3135	a	17	10%	15	10%	2	3.2	+19.9	1.5	+10.5	2.0	9.4	3.5
	b	20	10%	12	10%	8	3.2	+16.6	1.2	+13.9	1.6	2.7	2.8
PAL-1	a	82	10%	36	10%	46	11.8	+35.6	1.0	+18.8	1.0	16.8	2.0
	b	71	10%	45	10%	26	11.6	+31.8	1.2	+13.1	1.1	18.7	2.3
S708-9	a	83	10%	75	10%	8	15.8	+36.1	0.9	+34.1	1.1	2.0	2.0
T430-R8	a	81	10%	51	10%	30	13.2	+9.7	0.9	+5.8	1.3	3.9	2.2
26D-6	a	255	10%	219	10%	36	47.4	-2.4	0.6	-4.3	0.9	1.9	1.5
	b	196	10%	190	10%	6	38.6	+7.6	0.9	+2.9	1.1	4.7	2.0
07010404	a	586	10%	384	10%	202	97	–0.9	0.6	-6.9	0.6	5.9	1.1
07010405	a	61	10%	23	10%	38	8.4	+5.7	1.0	-0.6	1.5	6.3	2.5

S.E. = Standard error

$\Delta^{11}B$: pre-exchange $\delta^{11}B$ (bulk $\delta^{11}B$) minus post-exchange $\delta^{11}B$ (tetrahedral $\delta^{11}B$)

concentrations with NH_4Cl exchange is consistent with relatively weak bonding in exchangeable sites due to the hydrated radius/charge ratio of these cations. Because the decreasing Ca concentration did not reach steady state until some point during the second 20-h exchange treatment, in order to be conservative, the soak duration in 1 M NH_4Cl assumed to be required for complete B exchange in the upper ~2.3 μm (Potts, 1987) of exposed surface, was 60 h. This method for exchangeable B extraction should be applicable to thin-section samples of sheet silicates and other clay-like minerals.

Significance of pre- and post-exchange B measurements

Determination of pre-exchange (bulk) and post-exchange (tetrahedral) B content and isotopic ratio allows the exchangeable B content and isotope ratios to be calculated by mass balance. In particular, the exchangeable B may not be in equilibrium with the B in the tetrahedral sheet, and this B may have a large influence on the bulk $\delta^{11}B$ analysis (Figure 5). The $\delta^{11}B$ of B in the tetrahedral sites of the palagonite ($\delta^{11}B_{tet}$) depends on temperature and the relative abundances of the two aqueous B species $^{10}B(OH)_4^-$ and $^{11}B(OH)_3$, which in turn depend on pH (Hemming and Hanson, 1992). Assuming a temperature, therefore, allows the composition of the fluid associated with palagonitization to be inferred from $\delta^{11}B_{tet}$ using the calibrated B-isotope fractionation equation for conditions of low pH (Williams *et al.*, 2007). This fractionation does not apply to high-pH conditions where $B(OH)_4^-$ dominates the fluid. Exchangeable B isotopic ratios ($\delta^{11}B_{ex}$) potentially give an indication of the most recent fluid composition, although $\delta^{11}B_{ex}$ values do not necessarily reflect $\delta^{11}B$ values of water in equilibrium with the silicate but rather fluids introduced after the initial stages of illitization (Williams *et al.*, 2007). Such isotopic differences may also be useful for the interpretation of changes in the B-isotope composition of palagonites and associated fluids over time due to changing environmental conditions (*e.g.* influx of meteoric or hydrothermal fluids into a previously seawater-dominated system) during palagonitization.

The wide variability in B content and $\delta^{11}B$ values (Table 3) suggests that future research could determine the significance of the variations, and how they are attributable to palagonitization conditions such as fluid composition, temperature, *etc*. For example, although samples R0777-17.4, PAL-1, 3135, and S708-9 are all from submarine volcaniclastic settings (Pauly *et al.*, 2011), $\delta^{11}B_{tet}$ values for these samples vary by nearly 40‰, suggesting that local chemical variables, more than temperature, affected palagonitization.

Evaluation of methods developed

The B-exchange and SIMS calibration methods for characterization of B content and isotopic composition of palagonite samples presented here provide a basis for analysis so long as care is taken to show that matrix effects are not a concern. Matrix effects have been noted between glass and minerals (Chaussidon and Jambon, 1994), and these methods may not be appropriate for palagonites formed from glasses not compositionally similar to the BB-1 glass used in this study. Because palagonite is no longer a glass and not yet a clay mineral, well established methods for measuring B isotopes in glass and clay minerals can serve only as guidance. This manuscript documents the first attempt at such measurements and will hopefully stimulate future work to improve and refine these methods.

CONCLUSIONS

(1) Use of IMt-1 (Silver Hill illite, <2 μm fraction) from the Source Clays Repository as a reference material allowed accurate SIMS analyses for B and its isotopes in both basaltic glass, the precursor of palagonite, and palagonitized intervals of eight samples. The B content and isotopic ratios measured in palagonite using IMt-1 as the reference material have a precision of <10% and ±2.5‰, respectively.

(2) Concentrations of Na, K, and Ca (occupying exchangeable sites) in two thin-section samples of palagonite decreased significantly after exchange with a 1 M NH_4Cl solution, indicating that these cations exchanged with NH_4^+. Of the three cation concentrations monitored using EPMA, Ca decreased most slowly, and reached steady state during the second 20-h soak.

(3) SIMS measurements of bulk B content, tetrahedral B content, bulk $\delta^{11}B$, and tetrahedral $\delta^{11}B$ showed that the B content and $\delta^{11}B$ of palagonite changed significantly after 60 h of exchange with NH_4Cl for all eight thin sections of palagonite, indicating that exchangeable B had been extracted. This method for extraction of exchangeable B should be applicable to thick or thin sections of sheet silicates and other clay-like materials, allowing calculation of exchangeable B content and $\delta^{11}B_{ex}$ using mass balance.

(4) The present study addressed calibration, matrix effects, and the removal of exchangeable B not equilibrated with the tetrahedral sites in palagonite. These sample-preparation procedures may now be applied to *in situ* SIMS microanalysis of B content and isotopic ratio in thin-section samples of palagonite by SIMS. Caution must be taken, however, to ensure that the composition of the palagonitized glass is similar to that of the reference material, as shown for the BB-1 glass used here to demonstrate that there are no matrix effects. Some compositional variations have been reported to cause matrix effects on B measurements, especially where large variations in Fe and Mg contents exist (Chaussidon and Jambon, 1994). The present study does not prove unambiguously the absence of matrix effects for all palagonites, but for the samples studied, significant trends which are greater than such possible

analytical artifacts were found. The matrix composition must be evaluated when measuring glasses. The present study demonstrated, however, that with attention to such details, meaningful measurements of the B composition of palagonite are possible.

ACKNOWLEDGMENTS

Dave Clague, Alicé Davis, Michelle Coombs, Mike Garcia, Don Thomas, and Jose Honnorez are thanked for providing some of the samples used in this study. Sveinn Jakobsson and Hjalti Franzson supported sample-collection fieldwork. This research was supported by NSF-EAR grant 0125666 as well as by the NSF-supported SIMS Facility and the Center for Solid State Science at Arizona State University. Klaus Franzreb is also thanked for providing technical support on the Cameca 3f SIMS. Two Editors in Chief (J.W. Stucki and M.A. Velbel) and three anonymous reviewers helped to improve the manuscript with thoughtful comments which are much appreciated.

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(*Received 12 February 2011; revised 6 June 2014; Ms. 633; AE: J.W. Stucki*)