CATION EXCHANGE CAPACITY OF LAYER SILICATES AND PALAGONITIZED GLASS IN MAFIC VOLCANIC ROCKS: A COMPARATIVE STUDY OF BULK EXTRACTION AND IN SITU TECHNIQUES

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Abstract—The cation exchange capacities (CEC) and extractable cations in smectite, corrensite and palagonitized glass from hydrothermally-altered pillow lavas and hyaloclastite breccias were measured by both bulk wet chemical and in situ microanalytical techniques. Smectite has CEC's between 60 and 120 meq/100 g, palagonitized glass between 30 and 60 meq/100 g, and corrensite approximately 35 meq/100 g as determined by the in situ CsCl-exchange method. These experiments generally verify that Cs exchanges for those cations that are presumed (from the stoichiometry implied by microprobe analyses) to occupy interlayer sites in sheet silicates. Results of conventional CEC determinations are consistent with those determined by the in situ experiments; the individual microanalytical values for smectite and palagonitized glass bracket the bulk CEC values. The in situ experiments imply that Mg is the major extractable cation in smectite, Ca in corrensite, and both Mg and Ca in the palagonitized glass. We speculate that discrepancies between the equivalents of extractable cations predicted from elemental analysis and the equivalents of Cs sorbed may be due to the presence of charge-balancing protons that are not detected by the microprobe analyses. The sum of equivalents of cations extracted by NH4-acetate is about the same as the CEC determined by both the in situ and the bulk methods. Cation proportions indicated by NH4-acetate extractions from bulk samples are also generally consistent with the in situ results for all elements except Mg, which is a minor leachate of the NH4-acetate extractions in all the samples. To explain this discrepancy, we propose that 1) Mg may occupy structural sites within palagonitized glass, which inhibit its extraction by NH4 or Cs, and/or 2) there is a significant quantity of smectite, unsampled by the electron microprobe analyses, which contains insignificant interlayer Mg.

Key Words—Cation Exchange Capacity, Corrensite, Electron microprobe analysis, Extractable cations, Palagonite, Smectite.

INTRODUCTION

Incipient alteration of mafic volcanic rocks, particularly in hydrothermal environments, entails the palagonitization of glass with concomitant crystallization of layer silicates (primarily smectite) and zeolites. Palagonitization is also an important process in the weathering/saprolitization of mafic volcanic rocks. Geologists traditionally characterize the in situ properties of palagonitic materials such as their textures and mineralogies with light, scanning or transmission electron microscopes (Hay and Iijima 1968; Dimroth and Lichtblau 1979; Jakobsson and Moore 1986; Thorseth et al. 1991; Zhou et al. 1992) and their compositional variations with electron microprobes (e.g., Staudigel and Hart 1983; Furnes 1984; Zhou and Fyfe 1989; Jercinovic et al. 1990; Thorseth et al. 1995). Soil scientists typically measure bulk properties such as size fraction distribution, the structural response to chemical and thermal treatments as determined by X-ray diffraction (XRD) and chemical characteristics such as cation exchange capacity (CEC) and extractable cations (Singer 1974; Golden et al. 1993; Berkgaut et al. 1994). Collectively, these data have documented that profound compositional, mineralogical and textural heterogeneities typically accompany the palagonitization of mafic glasses. The process of palagonitization is thought to affect: 1) the composition of seawater and the oceanic crust (Staudigel and Hart 1983); 2) the spectral properties of planetary surfaces (Golden et al. 1993); 3) the sorption/retention properties of glass-hosted, nuclear-waste repositories (Jercinovic et al. 1990); and 4) the biogeochemical cycling of nutrients in soils developed on volcanic protoliths.

We examined some compositional effects accompanying the palagonitization of mafic volcanoclastic rocks, also known as metabasites, from an exhumed stratigraphic section of a Pliocene aged submarine seamount exposed on La Palma, in the Canary Islands. Published microprobe data on the composition of trioctahedral smectite formed during hydrothermal alteration of these rocks (Schiffman and Staudigel 1995) support the hypothesis that interlayer sites are dominantly filled with Mg. The present study was initiated to test this hypothesis by measuring the cation exchange capacity (CEC) and extractable cations of this smectite with both traditional bulk methods and an in situ method using the electron microprobe (Hillier and Clayton 1992). Since the bulk clay fractions of hyaloclastitic samples contain appreciable palagonitized
glass, we also measured its \textit{in situ} properties. Previous studies (Singer 1974; Bergkaut et al. 1994) have shown that “palagonite” has a relatively high CEC (60 to 100 meq/100 g, as measured on bulk clay fractions), although the relative contribution of exchangeable cations from dominantly amorphous material versus crystalline layer silicates has not been previously explored.

In this paper, the term palagonite is used in reference to a bulk sample of metabasite which contains a mixture of palagonitized glass, authigenic minerals: smectite, corrensite, zeolites, carbonates and Fe-Ti oxides and phosphates, and primary minerals: plagioclase feldspars, clinopyroxene and olivine.

**GEOLOGICAL SETTING**

The Pliocene Seamount Series is a submarine basement complex on La Palma, in the Canary Islands (Staudigel 1981; Staudigel and Schmincke 1984). Samples for this study were collected from surface outcrops along the Barranco de las Angustias, where an approximately 3.5 km thick stratigraphic section, predominantly composed of alkaline, mafic pillow lavas and volcanoclastites, is exposed. The exact locations of the 5 samples examined in this study are shown in Schiffman and Staudigel’s Figure 1 (1995).

Submarine hydrothermal metamorphism of the Seamount Series has resulted in a relatively complete low P-T facies series, with implied thermal gradients of 200 to 300 °C/km, serially encompassing the zeolite, prehnite-pumpellyite and greenschist facies (Schiffman and Staudigel 1994). Alteration within the upper 800 m of the Seamount Series extrusive section, where all but one of the samples examined for this study were collected, is characterized by the presence of palagonite containing, palagonitized glass, smectite, apatite, calcite and zeolites, including analcime and thomsonite-natrolite solid solution. Zeolites and calcite mostly fill veins and vesicles, as well as cement pore space in palagonitized hyaloclastites. Smectite occurs primarily as vesicle linings and as a recrystallization product of palagonite. In the samples examined for this study, clinopyroxenes are fresh, olivines are ubiquitously replaced by smectite and volcanic glass is completely palagonitized. Plagioclase may be fresh or partially zeolitized. Corrensite replaces smectite as the dominant layer silicate mineral at depths from approximately 800 to 1100 m in the extrusive section (Schiffman and Staudigel 1994).

**ANALYTICAL METHODS**

Preparation of clay and silt size fractions for XRD analysis utilized standard procedures (Whittig and Alldardice 1986). Rock fragments ground in a micronizing mill were treated with a buffered (pH 5.0) sodium acetate solution to remove carbonate. The < 2 μm and 2 to 10 μm size fraction were separated by centrifugation in dilute sodium carbonate solution, and the fractionated clays were plated onto porous ceramic tiles maintained under vacuum suction (Kinter and Diamond 1966). Duplicate tiles, saturated with 0.5 M MgCl₂, were prepared for each sample. One clay mount was washed with distilled water, air-dried overnight and then analyzed. It was then saturated with 1 M KCl, dried overnight and analyzed. Finally it was heated at 550 °C for 1 h prior to analysis. The other mount was solvated with glycerol, dried overnight, and then analyzed. The mounts were analyzed on a Diano 8000 X-ray diffractometer operated at 50 kV and 15 mA, producing CuKα radiation, with a graphite monochromator. The samples were routinely scanned between 2 and 30 °2θ at 2 °2θ/min.

Backscattered electron (BSE) imaging and mineral compositional analyses were performed on doubly polished, carbon-coated, thin sections using a Cameca SX-50 electron microprobe. Quantitative, wavelength dispersive, analyses of smectite, corrensite and palagonitized glass were performed at 15 keV and 5 to 10 nA beam current using a rastered, defocused beam with an approximately 10 μm diameter. The following silicate, oxide and chloride standards were used in conjunction with conventional ZAF matrix corrections: omphacite (Na), tremolite (Mg), anorthite (Al), tremolite (Si), orthoclase (K), wollastonite (Ca), TiO₂ (Ti), rhodonite (Mn), fayalite (Fe) and CsCl (Cs). The Cs-La line was measured using a PET dispersive crystal. Each analyte line and its corresponding background were measured for 10 s. A chloride working standard (Bilgrami and Howie 1960) was routinely analyzed at the beginning of each session to ensure accuracy.

The \textit{in situ} CEC’s of layer silicates and palagonite were determined using the “Cs-staining” method outlined by Hillier and Clayton (1992). After removing the carbon coating, a solution of 1 M CsCl was applied by eyedropper to the surface of polished thin sections. After 3 h, thin sections were thoroughly rinsed and then soaked in distilled water for an additional 4 h. The latter was necessary to ensure that there were no residual precipitates of CsCl, which are easily detected by BSE examination. After air-drying, thin sections were carbon-coated again and re-analyzed, using CsCl as a calibration standard. As explained in Hillier and Clayton (1992), for each analysis:

\[
\text{in situ CEC (meq/100 g)} = \left( \frac{1000 \times \text{wt\% Cs}_2\text{O}}{282/2} \right) \]

Although Hillier and Clayton (1992) suggested that the CsCl solution should be applied overnight prior to rinsing, we found that 3 h was adequate for the La Palma samples. Cs-exchange was as complete for layer silicates and palagonitized glass on newly polished surfaces created after the outer 10 to 15 microns of a previously CsCl-saturated sample was removed.
Table 1. Lithology, mineralogy, and cation exchange characteristics of La Palma metabasites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lithology</th>
<th>Mineralogy</th>
<th>In situ layer silicate mineral†</th>
<th>In situ palagonitized glass‡</th>
<th>Excess salt method§</th>
<th>Sum of bulk exchangeable cations¶</th>
<th>% carbonate††</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lp743f</td>
<td>Interpillow hyaloclastite matrix</td>
<td>sm + pa (1:3)</td>
<td>(120 (12)</td>
<td>(61 (12)</td>
<td>77</td>
<td>48</td>
<td>0.15</td>
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<tr>
<td>Lp747a</td>
<td>Pillow basalt interior</td>
<td>sm</td>
<td>60 (6)</td>
<td>none</td>
<td>50</td>
<td>56</td>
<td>1.10</td>
</tr>
<tr>
<td>Lp754k</td>
<td>Interpillow hyaloclastite matrix</td>
<td>sm + pa (1:1)</td>
<td>69 (7)</td>
<td>33 (14)</td>
<td>55</td>
<td>95</td>
<td>0.38</td>
</tr>
<tr>
<td>Lp758b</td>
<td>Pillow basalt interior</td>
<td>co</td>
<td>35 (10)</td>
<td>none</td>
<td>52</td>
<td>35#</td>
<td>12.81</td>
</tr>
<tr>
<td>Lp762h</td>
<td>Hyaloclastite pillow breccia</td>
<td>sm + pa (3:1)</td>
<td>85 (6)</td>
<td>44 (14)</td>
<td>79</td>
<td>62</td>
<td>0.67</td>
</tr>
</tbody>
</table>

† Mineralogy determined by combination of XRD of <2 micron and 2 to 10 micron fractions and microprobe analysis. Key: sm = smectite; pa = palagonitized glass; co = corrensite; ( ) = ratio of smectite to palagonitized glass estimated by petrography.
‡ CEC determined by microprobe analyses of CsCl-saturated material. Mean value of the number of spot analyses given within parentheses.
§ CEC determined by excess salt method on <2 micron size fraction.
¶ Sum of Ca, K, Na and Mg cations extracted with 1 M l-1/4 acetate at pH 7.0 on <2 mm fraction, adjusted for dissolution of CaCO3.
# The high carbonate content in this sample precludes the adjustment for extractable Ca due to dissolution of CaCO3.
†† CO2 measured manometrically after reaction with 2 M HCL for 30 min.

Conventional CEC was determined using the “excess salt” method (Jackson 1979). Clay size fractions (< 2 μm) were saturated with 1 M CaCl2 and then equilibrated with 0.01 M CaCl2. The Ca was replaced by 1 M MgCl2, and measured by atomic absorption. The CEC value presented in Table 1 is the mean of 2 or 3 replications that have a spread of generally less than 10%.

Extractable cations were measured on ground, bulk material (of the < 2 mm size fraction) leached with 1 M NH4-acetate at pH 7.0. The Ca2+ and Mg2+ were measured by atomic absorption; K+ and Na+ were measured by flame photometry. The CaCO3 content of the < 2 mm size fraction was measured by manometric determination of evolved CO2 (Soil Survey Staff 1992) after reaction with 2 M HCL for 30 min.

RESULTS

XRD

In a paragenetic study of the hydrothermal layer silicates from the La Palma Seamount Series, Schiffman and Staudigel (1995) reported XRD data on the clay size fractions of the 5 samples used in the present study. Results on these 5 samples are summarized in Table 1. All contain a single layer silicate mineral. Four of the 5 samples contain triocahedral smectite and the fifth (LP 758B, from deeper in the stratigraphic section) contains corrensite. Although 3 of the 5 samples, LP 743f, 754k and LP 762h, are hyaloclastites and contain significant quantities of palagonitized glass, the samples also all contain abundant, well-crystallized smectite. Strong diffraction peaks from the smectite preclude the positive identification of palagonitized glass by XRD studies (Singer 1974; Zhou et al. 1992). The XRD patterns of the silt size (2 to 10 μm) fractions indicate that the silts contain layer silicates identical to those from the clay fraction.

BSE Petrography/X-ray Dot Mapping

The BSE micrographs and X-ray dot maps depicting the textural and compositional relationships of palagonitized glass and layer silicates are presented in Figures 1 through 4. Petrographic studies of palagonitized glasses have traditionally employed plane polarized light techniques, which image absorption colors that reflect corresponding compositional variations. The BSE technique, which has not been widely applied to the study of palagonite, produces images of gray-level variations, which reflect compositional variations, but can also be readily correlated with X-ray dot maps of the same area (Figures 2–4).

In the 3 hyaloclastites (LP743f, LP754k and LP762h), palagonitized glass accounts for over 50% of the sample volume. Figure 1 depicts some typical textural relationships in these hyaloclastites. Clasts are composed of palagonitized glass that is often concentrically zoned, either around amygdules filled by smectite and zeolites (Figure 1a, upper right) or the margins of the fragments themselves (Figure 1b). Locally, it is difficult to ascertain whether smectite aggregates are amygdaloidal, or if they recrystallized from palagonitized glass (Figure 1a, lower left).

Micrographs of CsLa X-ray dot maps collected from the CsCl-treated polished thin sections provide powerful qualitative information on the relative CEC of the various mineral components of the hyaloclastites. Figure 2 depicts corresponding BSE and Cs X-ray images of sample LP762h. These images were taken from a thin edge of the polished samples along which the synthetic glass of the slide substrate is partially
exposed between amygdules filled with smectite or zeolites, which are rimmed by palagonitized basaltic glass. In the BSE micrograph (Figure 2a), smectite exhibits the brightest tone; whereas the synthetic glass and zeolite exhibit the darkest tones and the palagonite is intermediate in gray level. The corresponding X-ray dot map shows that the smectite exhibits the greatest concentration of Cs and thus the highest CEC. The density of Cs X-rays in the palagonitized glass and therefore its CEC is notably lower. As expected, the synthetic glass and the zeolite did not accumulate Cs from the CsCl treatment. Figure 3 shows a similar pair of micrographs from sample LP754K. The BSE micrograph (Figure 3a) depicts an elongate amygdule filled with smectite, zeolite and apatite. The corresponding X-ray map shows that only the smectite and the palagonitized glass that encloses the amygdule have accumulated Cs from the CsCl treatment. In the holocrystalline samples, which do not contain palagonitized glass, smectite is the only mineral that exhibits CEC. Figure 4 shows a pair of micrographs from the interior of a basaltic pillow (sample LP 747a). Primary phases seen in the BSE image (Figure 4a) include plagioclase, clinopyroxene and Fe-Ti oxide; secondary phases include smectite and zeolite. Of all the crystalline phases, only smectite exhibits Cs-enrichment (Figure 4b).

**Electron Microprobe Analyses**

Representative quantitative analyses of smectite, corrensite and palagonitized glass are presented in Table 2. Compositional data are shown for the layer silicates and palagonite in both the pre- and post-CsCl treated states. Note that the pre- and post-CsCl pairs for each sample are not necessarily from the same locality in each polished mount.

Smectite from the La Palma sample suite is trioctahedral with Fe:Mg generally less than 0.5. In a study of the La Palma smectite, Schiffman and Staudigel (1995) noted that the sum of Al(VI) + Fe + Mn + Ti + Mg exceeded 6.0 for many of the microprobe spot analyses recalculated on a 22 O basis. For this reason, Schiffman and Staudigel (1995) hypothesized that significant Mg, up to 0.8 cations/22 O, may occupy an interlayer site, as opposed to octahedral sites in this smectite.
Results of re-analysis of these samples after CsCl-saturation generally corroborate this hypothesis. After treatment, microprobe analyses indicate that the "excess" Mg, that is, beyond that which can be accommodated in 6 octahedral sites/22 O, decreased proportionally with the measured uptake of Cs, compared to before- and after-treatment analyses shown in Table 2. The CsCl-saturation also stripped the smectites of Na, K and most Ca. Although CsCl-saturation did not quantitatively remove all the "excess" Mg in the La Palma smectites, there is an obvious inverse correlation between the remaining "excess" Mg and the Cs fixed in the interlayer sites (Figure 5a). The Cs-concentrations in the La Palma smectite, which range from approximately 5 to nearly 16 wt% as Cs₂O (Table 2), correspond to CEC's between 60 and 120 meq/100 g (Table 1). The in situ measured CEC's of smectite from the three hyaloclastitic samples are all greater than the CEC of the smectite from the holocrystalline pillow basalt sample (LP747a, Table 1).

La Palma corrensite, a regular interstratification of tri-octahedral smectite and chlorite, is compositionally similar to smectite, especially in Fe:Mg (Schiffman and Staudigel 1995). However, the corrensite contains negligible "excess" Mg; Ca is the dominant interlayer cation (Table 2). Microprobe analyses of the corrensite after CsCl-treatment indicate that Ca is not quantitatively removed, although the remaining Ca exhibits a pronounced inverse correlation with Cs (Figure 5b). The mean CEC for the La Palma corrensite (35 meq/100 g in sample LP758b, Table 1) is lower than that of any measured for smectite, but the CEC of the smectite component of the corrensite is within the range of CEC for the other smectites within samples.

Although the CsCl-saturation experiments on smectite and corrensite yielded systematic correlations between Cs uptake and, respectively, Mg and Ca depletion, the results of in situ experiments on palagonitized glass are more equivocal. Since palagonite exhibits a broad composition range, which may vary greatly over distances of a few microns (Figure 6a–6d), it is difficult to relocate the exact sample volume for analysis after the CsCl treatment. However, aside from this difficulty, microprobe analyses clearly indicate that La
Palma palagonitized glass has a finite and, within a
given sample, consistent CEC, ranging from approxi-
mately 30 to 60 meq/100 g (Tables 1 and 2).

Conventional CEC and Extractable Cation Analyses

Data from the 5 samples are presented in Table 1
and Table 3. Conventional CEC values for the < 2 μm
size fractions are between 50 and 80 meq/100 g. Total
extractable cation values for the < 2 μm fraction from
these same samples, corrected where possible for ex-
tractable Ca due to CaCO₃ dissolution, range from ap-
proximately 50 to 95 meq/100 g. In 4 of the 5 samples,
CaCO₃ constitutes less than approximately 1 wt% of
the bulk sample. In the corrensite-bearing pillow basalt
interior (sample LP758b), the percentage of CaCO₃ is
too great (almost 13 wt%, Table 1) to allow an esti-
mation of the extractable Ca from exchange sites ver-
sus solid-phase CaCO₃. In all of the samples, Ca is the
dominant extractable cation (32 to 73 meq/100 g; Ta-
ble 3), followed by Mg (3 to 13 meq/100 g), Na (0.5
to 10 meq/100 g) and K (0.4 to 1.5 meq/100 g).

DISCUSSION

CEC of Layer Silicates and Palagonitized Glass

The La Palma smectite generally has a high layer
charge (Table 2, 0.8 to 2.0; Schiffman and Staudigel
1995), which approaches that of vermiculite. Nonethe-
less, these clays uniformly exhibit systematic smectite-
like behavior in XRD analysis; they expand to 17 to
18 Å on glycerol solvation and collapse to 10 Å upon
heating to 550 °C.

A comparison of CEC values determined by the in situ
CsCl saturation technique, versus those deter-
mined by the conventional excess salt method is pre-
sented in Table 1. These 2 values can be compared
directly for the holocrystalline pillow basalt samples,
which do not contain palagonitized glass and in which
layer silicates are the only materials that have extract-
able cation sites. Cation exchange by zeolites is prob-
ably not significant because zeolites do not occur to
any significant extent in the clay fractions based upon
XRD, and because cation exchange for Ca²⁺ and Cs⁺
is minimal for analcime (Baldr and Whittig 1968).
For the smectite-bearing pillow basalt (747a), the
mean in situ value (60 meq/100 g) agrees well with
the conventionally-determined value (50 meq/100 g).
For the corrensite-bearing pillow basalt (758b), the
mean in situ value (35 meq/100 g) is nearly 30% less
than the conventionally-determined value (52 meq/100 g).
One possible explanation for this discrepancy can
be seen in the data presented (Figure 5b). Electron
microprobe analyses presented in Table 2, as well as
by Schiffman and Staudigel (1995), indicate that for
the La Palma corrensite, Ca is the dominant interlayer
cation. But, the CsCl-treatments apparently did not re-
sult in complete Ca/Cs exchange. The most extensive-
ly exchanged corrensite still retains approximately
0.09 Cs/25 O (Figure 5b). Thus, the in situ data are
conservative estimations of the corrensite CEC.

In the 3 samples that contain layer silicates as well
as palagonitized glass, the direct comparison of in situ
and conventional CEC results is not appropriate be-
cause the conventional CEC measures multiple ex-
changing components, whereas the in situ method is
more discrete. However, the conventional CEC data,
which reflect the mean CEC of the < 2 μm size frac-
tion, should be bracketed by the in situ CEC values of
smectite and palagonitized glass within that same sam-
ple (Table 1). Similarly, by mass balance, the 3 CEC
values for each sample can be used to calculate an
approximate mass ratio of smectite to palagonitized
glass. Thus, in sample LP762h, the conventionally
determined CEC value of 79 meq/100 g (Table 1) tran-
lates to a nearly 3:1 ratio of smectite/palagonite. Con-
versely, in sample LP743f, the conventionally deter-
mined value of 77 meq/100 g translates to a nearly 1:
3 ratio of smectite/palagonite. These ratios are corroborated by petrographic observations on the
smectite/palagonitized glass within each of these sam-
pies (Table 1).

The range of CEC of palagonitized glass we deter-
mined by the in situ method (30 to 60 meq/100 g) is
generally lower than that determined by conventional
methods reported in previous studies (for example,
Singer (1974) and Berkgaut et al. (1994) reported 60
to 100 meq/100 g). However, the conventional mea-
surements reported in the literature were done on bulk
“palagonite,” which typically contains layer silicates
of a presumably higher CEC than the palagonitized
glass itself. Thus, conventional CEC measurements
of “palagonite” clay fractions may over-estimate the
CEC of the palagonitized glass itself.

Extractable Cations

A comparison of total extractable cations as deter-
mimed 1) by leaching bulk samples with NH₄-acetate;
and 2) estimated indirectly by electron microprobe
analyses is presented in Table 3. This table presents
three sets of values for extractable cation data on each
element of interest: Ca, Mg, Na and K. Values listed
in the first column of each elemental set (in units of
meg/100 g) are those from NH₄-acetate extraction. In
the second column, these data have been converted
into units of charge per formula unit based on an av-
erage formula weight of 825 g for smectite and 950 g
for corrensite. Re-calculated in this form, these values
can be directly compared with the range in charge
for each cation (third column of each set) determined
from structural formulae obtained from electron microprobe
analyses of the non-CsCl-saturated layer silicates.

With one major exception, Mg, there is generally uni-
form agreement of the values determined by NH₄-ac-
etate extraction and microprobe analyses. These results
Table 2. Electron microprobe analyses, recalculated structural formulae and estimated cation exchange capacities of smectite, corrensite and palagonitized glass from La Palma metabasites.

<table>
<thead>
<tr>
<th></th>
<th>Smectite (22 O)</th>
<th>Corrensite (25 O)</th>
<th>Palagonitized glass (22 O)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>LP743F pre-CsCl</td>
<td>LP743F post-CsCl</td>
<td>LP754k pre-CsCl</td>
</tr>
<tr>
<td>SiO2</td>
<td>38.45</td>
<td>37.05</td>
<td>41.02</td>
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<tr>
<td>Al2O3</td>
<td>12.68</td>
<td>11.95</td>
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<tr>
<td>FeO</td>
<td>19.18</td>
<td>12.89</td>
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<td>MgO</td>
<td>16.15</td>
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<td>MnO</td>
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<td>TiO2</td>
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<tr>
<td>Cs2O</td>
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<tr>
<td>Total Si</td>
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<td>0.54</td>
</tr>
<tr>
<td>Ca</td>
<td>0.19</td>
<td>0.03</td>
<td>0.21</td>
</tr>
<tr>
<td>Na</td>
<td>0.03</td>
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</tr>
<tr>
<td>K</td>
<td>0.11</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cs</td>
<td>0.00</td>
<td>1.13</td>
<td>0.00</td>
</tr>
<tr>
<td>Sum IL</td>
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<td>1.17</td>
<td>0.81</td>
</tr>
<tr>
<td>IL charge</td>
<td>1.70</td>
<td>1.20</td>
<td>1.56</td>
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</table>

imply that the layer silicates are the main source of extractable cations in these samples, and/or that during treatment of bulk samples with NH₄-acetate, the palagonitized glass is contributing extractable cations congruently with that implied by the proportions of interlayer cations, especially Ca, Na and K, from the layer silicates.

However, there is an order of magnitude less Mg extracted by NH₄-acetate than expected from the electron microprobe analyses of smectite (Table 3). This is the case in all the smectite-bearing samples, even LP743f, for which the in situ CEC data indicate that Cs has completely exchanged with Mg and thus implying that Mg should be readily extractable by NH₄-acetate treatment. In other samples, which show less complete Cs/Mg exchange in smectite (Figure 5a), it is possible that some of the "excess" Mg may not occupy exchangeable/extractable hydrated, interlayer sites in the smectite. Rather, these Mg cations could occur in brucite-like layers, which would indicate the development of minor chlorite interstratification with smectite (Bailey 1982). Small amounts, that is, <10%, of chlorite interlayering are not precluded by the results of XRD analysis (apparently clean smectite) for the La Palma samples (Schiffman and Friedleifsson 1991), although the amount of interlayered brucite required to explain the discrepancy between the Mg data sets in Table 3 would certainly be reflected in systematic differences in the XRD behavior of these clays. Non-crystalline remnants within the smectite would probably cause at least some XRD peak broadening, but we did not evaluate this effect.

Since the cations extracted by NH₄-acetate treatment are a combination of those contributed by layer silicates as well as the palagonitized glass, it is possible that the high Mg/Ca extractable cation ratios implied by the smectite structural formulae (Tables 2 and 3) could be offset by an antithetically low Mg/Ca for the palagonitized glass. In Table 2, the palagonitized glass analyses have been arbitrarily recalculated on a 22 O basis—the same used for smectite structural formulae. Previous workers (Jercinovic et al. 1990; Zhou et al. 1992) have argued that palagonitized glass has a proto-smectite-like structure containing crystallites of both di- and tri-octahedral 2:1 layer silicates. The recalculated analyses in Table 2 are consistent with these findings: the sum of octahedral Al + Fe + Ti + Mn + Mg in the La Palma palagonitized glass is generally between 4.7 and 6.4 cations/22 O. If these recalculated palagonitized glass analyses have any further structural analogy with smectite, it might be predicted that more Ca than Mg would be extracted in the La Palma
palagonitized glass, since most of the recalculated palagonitized glass analyses in Table 2 contain over 1 Ca/22 O and none contain “excess” Mg (for a trioctahedral-like structure). However, the NH₄-acetate extraction data, even for the most palagonite-rich sample, that is, LP 743f, which contains roughly a 3:1 ratio of palagonite:smectite, do not support this: the amount of extractable Ca is roughly that predicted from smectite structural formulae alone. The observed lack of correlation between the NH₄-acetate extraction and in situ Ca:Mg ratios may be a result of the former technique, although BaCl₂ extractions on these same bulk samples did not produce significantly different results (Southard 1995, unpublished data). Specifically, the extraction techniques may preferentially leach Ca with respect to Mg if the latter cations are not fully in exchangeable sites. We propose that Mg may occupy remnant network-modifying sites within the tectosilicate-like structure of the original (now palagonitized) basaltic glass, and thus be preferentially resistant to both NH₄-acetate and Cs extraction techniques. Alternatively, the high Mg charge as indicated by the microprobe analyses of smectite (Table 3) in all the La Palma samples may not be representative of the entire population of smectite in these samples. That is, smectite which does not occur in coarse aggregates (for example, that coating grain boundaries and thus volumetrically significant) and which was not analyzed, might have an insignificant amount of interlayer Mg with respect to Ca.

The results of the in situ CEC analyses on the palagonitized glass in sample LP754K do offer some clues regarding which elements are actually being extracted when Cs is exchanged into this material. Figure 6 shows concentration profiles of 4 elements determined from microprobe analyses before and after CsCl-saturation. The concentration profiles begin (to the left) and terminate (to the right) within the 2 rounded smectite aggregates labeled “SM” in Figure 1a. The palagonitized glass is markedly zoned in composition. The smectite aggregates are encircled by ap-

---

Table 2. Extended.

<table>
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<tr>
<th>Palagonitized glass (22 O)</th>
<th>LP754k pre-CsCl</th>
<th>LP754k post-CsCl</th>
<th>LP754k post-CsCl</th>
<th>LP754k post-CsCl</th>
<th>LP762h post-CsCl</th>
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<td>1.63</td>
<td>2.98</td>
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<tr>
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<td>2.88</td>
<td>0.16</td>
<td>0.01</td>
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<tr>
<td>Mg</td>
<td>0.10</td>
<td>0.05</td>
<td>0.18</td>
<td>0.21</td>
<td>0.32</td>
<td>0.32</td>
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<td>3.98</td>
<td>0.00</td>
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<tr>
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<td>88.76</td>
<td>92.80</td>
<td>93.98</td>
<td>89.64</td>
<td>89.26</td>
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</tbody>
</table>

Figure 5. Results of in situ CEC experiments by CsCl-treatment. A) Cs versus “excess” Mg [that remaining after the 6 octahedral sites/22 O have been filled with Al(Ⅵ), Ti, Mn and Fe] in smectite; B) Cs versus Ca in corrensite (25 O basis).
Figure 6. Results of electron microprobe elemental traverses depicting compositional variations for A) SiO$_2$; B) MgO; C) CaO; and D) TiO$_2$ in hyaloclastite sample LP754k. The traverse, from lower left to upper right, begins and ends within the 2, labeled smectite aggregates seen in Figure 1A, and crosses 2 types of palagonitized glass: high-Ti (PA1) and low-Ti (PA2). Key: Filled circles = pre-CsCl-saturation results; open squares = results after CsCl-saturation; and filled squares = negligible compositional change occurred after CsCl-saturation.
proximately 100 mm thick bands of isotropic, Ca- and Ti-rich palagonitized glass ("PA 1" in Figure 1a and "palagonitized glass 1" in Figure 6), which themselves are enclosed within slightly birefringent palagonitized glass ("PA 2" in Figure 1a and "palagonitized glass 2" in Figure 6), whose composition more closely approximates basaltic (compare third and fifth palagonitized glass analyses in Table 2).

Both varieties of palagonitized glass described above have approximately the same CEC (that is, 30 to 35 meq/100 g as measured by the in situ method (Table 1); although it is unclear which cations are displaced by Cs. From the compositional data on both types of palagonitized glass shown in Figure 6, only Mg exhibits a consistent pattern of depletion in the post-versus pre-CsCl treated state. Specifically, MgO is depleted (relative to its abundance in the pre-treated palagonitized glass) in 11 of the 14 analyses within the traverse shown in Figure 6. Although these depletions are as large as 2 to 3 wt% MgO, that is, within the central portion of the palagonitized glass 2 zone (Figure 6), most of the observed depletions are less than 1 wt%. The CaO is depleted in 6 of the 7 analyses from the type 1 palagonitized glass, in amounts up to 4 wt%, but from only 2 of the 7 analyses in the type 2 palagonitized glass. No other element (including K₂O, Na₂O, Al₂O₃ and FeO, which are not shown on Figure 6) is depleted, relative to its pre-treated abundance, in more than 8 of the 14 analyses.

Can the measured MgO and CaO depletions account for the 30 to 35 meq/100 g CEC as indicated by the in situ CEC results? A loss of 0.5 wt% MgO in palagonitized glass, typical of the results from the in situ exchange experiments, is equivalent to approximately 0.1 Mg/22 O; a loss of 1.25 wt% CaO is equivalent to approximately 0.2 Ca/22 O (Table 2). The measured in situ CEC's of 30 to 35 meq/100 g, which are apparently constant for both types of the palagonitized glasses, correspond to contents of between 0.2 to 0.4 equivalents of Cs/22 O (Table 2). Therefore, exchangeable Mg and/or Ca generally cannot account for the entire measured in situ CEC of the palagonitized glass. One possibility that should be further investigated, is that the negative structural charge of the palagonitized glass is partially neutralized by H protons, which may readily exchange with network modifying cations during the onset of silicate glass dissolution (Petit et al. 1990), and which are not detectable by electron microprobe analysis.

CONCLUSIONS

1) Electron microprobe analyses suggest that the La Palma smectite has appreciable interlayer Mg and are corroborated by the results of in situ CEC measurements.

2) The in situ experiments on 3 hyaloclastite samples indicate that palagonitized glass has a lower CEC (30 to 35 meq/100 g) than smectite (65 to 120 meq/100 g). The CEC's of the <2 μm size fractions in these hyaloclastites, as obtained by the conventional excess salt method, are bracketed by the in situ measured CEC's of layer silicates and palagonitized glass.

3) Exchangeable cations, for example, Mg in smectite and Ca in corrensite, are not completely replaced by Cs during the in situ experiments, indicating that the in situ method may yield conservative estimates of the CEC's for the layer silicates. Further, some of the Mg allocated to interlayer positions may actually occupy brucite-like octahedral positions that are not exchangeable by Cs. The apparent lack of stoichiometric exchange of Cs for interlayer cations may also be due to the presence of exchangeable protons that are not measured by the microanalytic techniques.

4) The sums of cations extracted by NH₄-acetate on bulk samples are generally similar to the CEC determined by both the excess salt and in situ methods. Except for Mg, the proportions of NH₄-extractable cations are similar to those predicted from the stoichi-
ometry of layer silicates. The in situ experiments on palagonitized glass indicate that some Mg and Ca may exchange for Cs, although the NH$_4$-acetate extractions do not corroborate this. This discrepancy may be attributable to Mg and Ca, which occupy remnant network-modifying sites within the tectosilicate-like structure of the original (now palagonitized) basaltic glass, and thus are resistant to extraction with NH$_4$-acetate. Alternatively, the (high) extractable Mg-content of the smectite as implied by electron microprobe analyses may not be representative of all of the smectite in these samples.

ACKNOWLEDGMENTS

Schiffman's work on layer silicate mineralogy has been supported by NSF grant EAR-9203743, Southard's by Hatch project CA-D*-LAW-4525-H. Thanks to H. Staudigel and J. Gee for their help with field work in La Palma and subsequent petrographic study of these metabasites, and to S. Munn for her help with lab work. Thanks to S. Hillier for telling P. Schiffman about the in situ CEC method. Reviews by S. Hillier and W. Lynn improved the clarity and content of this manuscript.

REFERENCES


(Received 13 October 1995; accepted 20 December 1995; Ms. 2699)