THE ROLE OF RANDOMLY MIXED-LAYERED CHLORITE/SMECTITE IN THE TRANSFORMATION OF SMECTITE TO CHLORITE

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Abstract—Vesicular and groundmass phyllosilicates in a hydrothermally altered basalt from the Point Sal ophiolite, California, have been studied using transmission electron microscopy (TEM). Pore-filling phyllosilicates are texturally characterized as having coherent, relatively thick and defect-free crystals of chlorite (14 Å) with occasional 24-Å periodicities. Groundmass phyllosilicates are texturally characterized as 1) randomly oriented crystals up to 200 Å in width and 2) larger, more coherent crystals up to 1000 Å in width. Small crystallites contain predominantly 14-Å layers with some 24-Å units. Large crystals show randomly interlayered chlorite/smectite (C/S), with approximately 50% chlorite on average. Adjacent smectite-like layers are not uncommon in the groundmass phyllosilicates. Electron microprobe analyses show that Fe/Mg ratios of both groundmass and vesicular phyllosilicates are fairly constant.

Termination of brucite-like interlayers has been identified in some of the TEM images. The transformation mechanisms represented by these layer terminations are 1) growth of a brucite-like interlayer within smectite interlayer regions and 2) the dissolution and reprecipitation of elements to form chlorite layers. Both mechanisms require an increase in volume as smectite transforms to chlorite.

The data, combined with that from previously published reports, suggest that randomly interlayered C/S is a metastable phase formed in microenvironments with low water/rock ratios. Chlorite forms in microenvironments in the same sample dominated by higher water/rock ratios. The relatively constant number of Mg's in the structure (Mg#) of both structures indicates that in both microenvironments the bulk rock composition has influence over the composition of phyllosilicates.

Key Words—Chlorite, Corrensite, Hydrothermal Metamorphism, Random Interlayered Chlorite/Smectite, Smectite, Transmission Electron Microscopy.

INTRODUCTION

Smectite and chlorite are ubiquitous products of the diagenesis and low-temperature metamorphism of intermediate to mafic volcanic rocks and volcanogenic sediments. Although much has been learned about the transition from smectite to chlorite, the complex structural and compositional changes that accompany the transformation have not been completely deciphered. Previous work suggests that the transformation of smectite to chlorite occurs in response to an increase in temperature, with progressively higher proportions of chlorite forming as temperature rises (Hoffman and Hower 1979; Horton 1985; Bettison and Schiffman 1988). The range in proportion of expandable layers varies for different occurrences of these mixed-layered phyllosilicates. More recently, the role of fluid composition, porosity and water/rock ratio in determining the stability of phases in any given sequence of rocks has been recognized (Shau and Peacor 1992; Schiffman and Staudigel 1995).

The gradual or continuous transformation of smectite to chlorite, as accommodated through randomly interlayered S/C (with various percentages of expandable layers) and regularly interlayered C/S (corrensite), has been reported from metabasalts (Bettison and Schiffman 1988; Bevins et al. 1991) and sediments (Helmhold and van der Kamp 1984; Chang et al. 1986). However, a discontinuous decrease in smectite proportion, whereby smectite (with less than 20% chlorite), corrensite and chlorite (with less than 10% smectite) occur with increasing temperature, has been reported from diagenetic and hydrothermal environments (Inoue et al. 1984; Inoue 1987; Inoue and Utada 1991; Schiffman and Staudigel 1995).

Presumably, the differences in the transformation process are reflected in the geologic controls of the specific environment (Alt et al. 1986). Schiffman and Staudigel (1995) most recently point to the pervasive alteration of La Palma volcanics as evidence of high water/rock ratios and suggest that the discontinuous transformation of smectite to corrensite to chlorite is favored under these conditions.

The treatment of corrensite as a thermodynamically defined phase has been supported by phase relations and structural models arising from detailed chemical and X-ray diffraction (XRD) analyses (Inoue and Utada 1991; Beaufort and Meunier 1994) and TEM/AEM (atomic emission microscopy) (Shau et al. 1990). The stabilization of corrensite occurs through significant modification of tetrahedral layers (Shau et al. 1990; Meunier et al. 1991; Beaufort and Meunier 1994). Shau et al. (1990) and Beaufort and Meunier (1994)
show that the corrensite structure cannot be viewed as chlorite- and smectite-like stacks, despite the fact that corrensite often has a composition intermediate between the two. With the acceptance of corrensite as a phase, the existence of random smectite-chlorite interlayering has been called into question. Robertson (1989) and Shau et al. (1990) have suggested that XRD patterns interpreted as randomly interstratified C/S or S/C may be more correctly modelled as interlayered chlorite/corrensite or smectite/corrensite (Shau et al. 1990). However, the occurrence of $R = 0$ interlayered S/C has been documented in metamorphosed basalts (Bettison-Varga et al. 1991; Shau and Peacor 1992).

Shau and Peacor (1992) and Schiffman and Staedigel (1995) argue that randomly interlayered C/S occurs as a result of incomplete recrystallization during low fluid/rock alteration. Their work suggests that the permeability structure of metabasalts may in fact provide a significant control over the structure and composition of the interlayered mafic phylllosilicates. In this study, detailed high-resolution TEM (HRTEM) examination of a metabasalt from the Point Sal ophiolite, California, has been undertaken in order to investigate the nature of mafic phylllosilicates in groundmass and vesicle-filling occurrences. This work demonstrates the presence of randomly interlayered C/S under conditions of pervasive alteration and interprets these observations in terms of potential transformation processes in hydrothermally altered rocks.

**PREVIOUS WORK**

The Point Sal remnant of the Jurassic Coast Range ophiolite is located in central California. The geology of the ophiolite has been described by Hopson et al. (1975) and consists of the standard sequence of pillow lavas, sheeted dike or sill complex, a plutonic member and harzburgite. This ophiolite sequence exhibits the effects of submarine hydrothermal alteration, as described by Schiffman et al. (1986).

XRD and microprobe analyses of the mafic phylllosilicates in the lava and dike units are reported by Bettison and Schiffman (1988). Smectite, randomly interlayered C/S with both smectite and chlorite present in amounts >50%, corrensite, chlorite and celadonite occur in the ophiolite. The proportion of expandable layers decreases in the mixed-layered phases with increase in depth in the ophiolite pseudostratigraphy. The phylllosilicate zonation roughly parallels the calc-silicate paragenesis, in which smectite and interlayered C/S occur in zeolite and pumpellylite facies volcanic rocks and epidote occurs with chlorite in the dike unit. HRTEM investigations of 5 samples from the Point Sal suite are reported by Bettison-Varga et al. (1991). TEM observations generally confirm the percentage of chlorite layers determined using XRD and microprobe analyses and the existence of randomly interlayered chlorite(<0.5)/smectite has been confirmed in 1 specimen.

**EXPERIMENTAL METHODS**

Sample 1A-25, from the Upper Lava unit of the Point Sal ophiolite (Bettison and Schiffman 1988), was selected for study. Preparation of oriented aggregates for XRD analyses is described in Bettison and Schiffman (1988). Clay mineral separates were analysed on a Diano 8000 X-ray diffractometer using graphite-monochromated CuKα radiation. The existence of irrational (001) basal reflection positions from XRD patterns of the Mg-saturated, glycerol-solvated samples is the basis for identification of interlayering of smectite and chlorite in sample 1A-25.

Sections 3 mm in diameter were cut from doubly polished thin sections and thinned by argon milling using a Gatan duo ion mill. This technique allows for correlation between optical petrography and HRTEM images. Ion-milling conditions were 5 kV and 25° incident angle until perforation, followed by 15° and 1 kV milling for more than 8 h. Samples were analyzed at 400 kV using a Jeol 4000FX analytical electron microscope (AEM).

Compositional analyses were performed using a Cameca SX-50 electron microprobe. Wavelength dispersive analyses were performed using a 1-μm beam at 15 kV and 10 nA beam current. The silicate and oxide standards used with “ZAF” matrix corrections are as follows: bytownite (Na), tremolite (Mg, Si), anorthite (Al), orthoclase (K), wollastonite (Ca), TiO2 (Ti), rhodonite (Mn) and fayalite (Fe).

**RESULTS**

X-ray Diffraction and Petrography

As previously reported by Bettison and Schiffman (1988), XRD results for sample 1A-25 indicate the presence of randomly interlayered C/S, discrete chlorite and celadonite. Sample preparations that were air-dried, MgCl2-saturated, glycolated and heated to 350 °C produced identifiable reflections of the above minerals (Figure 1). Randomly interlayered C/S is identified by the presence of nonintegral (001) and (002) spacings. However, Shau et al. (1990) suggest that nonintegral spacings such as these can be produced from mixed-layered chlorite/corrensite.

Phylllosilicates in the basalt occur primarily as vesicle and vein fillings and as replacement of fine-grained mesostasis. Green-colored chlorite completely fills vesicles and shows a coarse grain size from rim to core. Pale green-colored mixed-layered C/S and minor chlorite occur as fine-grained patches within the groundmass. Chlorite has anomalous blue interference colors and weak birefringence, whereas mixed-layered C/S has weak to moderate birefringence and 1° interference colors. Analcime and laumontite occur as vesicle fillings and plagioclase is not albitionized.
High-Resolution Transmission Electron Microscopy

Guthrie and Veblen (1989) have shown that, for layer silicate structures, HRTEM images can be reliably interpreted with the aid of computer simulation packages that incorporate multi-slice calculations developed from the theory of Cowley and Moodie (1957). Simulation of corrensite phase contrast images at 70 μm defocus using the multi-slice program by Stadelmann (1991) shows the correlation between the 1:1 structure for chlorite and the TEM images that follow (Figure 2a). In this analysis for chlorite, the darkest fringes correspond to the brucite-like interlayer of the structure. Under the experimental conditions used, the combination of 3 light fringes and 2 dark fringes correlates with the tetrahedral-octahedral-tetrahedral layers of chlorite and/or smectite.

TEM images of phyllosilicates replacing glassy groundmass show 2 distinctive morphologies. The 1st morphology consists of thin crystallites less than 200 Å across arranged in a mesh-like manner. Periodicities of 10 Å, 14 Å and 24 Å are common and an example is shown in Figure 2b. In addition, larger, more coherent crystals up to 1000 Å in width occur within the groundmass. Examination of vesicle-filling phyllosilicates indicate that chlorite is the predominant phase as shown for pore-filling chlorite in Figure 3. The crystals are large and coherent, with rare layer mistakes (10 Å); but, more commonly, they show layer defects at the edges.

Figure 4 shows a sequence of chlorite-like and smectite-like fringes with no apparent ordering for any of the following arrangements: smectite and chlorite, smectite/corrensite or chlorite/corrensite. The sequence as shown in the image is as follows from upper right to lower left arrow: CSCCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSCSSCCS (C = chlorite-like and S = smectite-like layers). This sequence could either be interpreted as corrensite (SC alternations) interlayered with discrete smectite and chlorite, or as randomly interlayered C/S. The latter interpretation is supported by the occurrence of adjacent smectites within the sequence. Both CCS and SSC repetitions occur within the sequence shown in Figure 4. The sequence comprises 48% 10-Å and 52% 14-Å layers. This approximate 50:50 distribution of chlorite and smectite is characteristic of the groundmass mixed-layered phyllosilicates imaged with TEM. A selected area electron diffraction (SAED) pattern from this area (Figure 4, inset) shows irrational reflections, consistent with an interpretation of random interlayering of chlorite and smectite sequences.

Figure 5 is a higher-magnification image that shows predominantly chlorite. In this figure, a change in sequence, in which a 28-Å spacing is reduced to a 24-Å spacing at both ends, is evident. A brucite-like interlayer appears to terminate into the boundary between the 10-Å and 14-Å fringes. The presence of the brucite-like layer necessitates a volume increase and involves the transformation of smectite-like interlayers to the brucite-like interlayer of chlorite. Layers on either side of the brucite-like layer are continuous and bend with the distortion.

Figure 6 shows a sequence of chlorite-like and smectite-like fringes with no indication of ordering. Adjacent smectite layers occur in this packet of 74% chlorite and 26% smectite; the figure shows a magnification of that sequence composed of 46% smectite and 54% chlorite. Within this area 2 changes in sequence occur between chlorite-like layers that are unlike the transformation shown in Figure 5. As shown...
in Figure 6, the 1st transformation occurs between a pair of brucite-like interlayers. For example, between the heavy black fringes (the brucite-like layers) shown by the black arrows on the left is the sequence B T-O-T T-O-T B T-O-T B T-O-T B which converts to B T-O-T T-O-T T-O-T B as the middle brucite-like layer ends within a smectite-like T-O-T sequence (T = tetrahedral, O = octahedral and B = brucite-like layers). The 2nd change in sequence, shown between the 2 black arrows on the right, again results in the brucite-like interlayer ending within a T-O-T, indicating the conversion of a smectite (T-O-T) layer to a T-O-T B T-O-T sequence. Layers on either side of the brucite layer remain intact and bend around the expanded area.

Electron Microprobe Analysis

Table 1 presents microprobe data for vesicle-filling and groundmass replacement phyllosilicates. Note that chlorite analyses show the presence of Ca, Na and K, indicating some minor contamination by corrensite or smectite-like expandable layers (Bettison and Schiffman 1988; Shau et al. 1990). Potassium contents are higher than normal, suggesting the presence of celadonite in the groundmass phyllosilicates. Celadonite is present in the sample, as determined petrographically and using XRD data. However, a comparison of K2O content of samples with high K with octahedral cations (Gallahan and Duncan 1994) combined with the total Al indicates that these specific analyses are not characterized by significant amounts of a dioctahedral phase.

Smectite, corrensite and chlorite should have non-interlayer cation totals of 15.9, 17.0 and 17.85, respectively, when calculated on a 25 oxygen equivalent basis (Schiffman and Staudigel 1995). As indicated by cation totals, vesicle-filling phyllosilicates are chlorite (17.46–17.73), whereas groundmass phyllosilicates are chlorite and mixed-layered C/S (16.4–17.71). Two analyses have noninterlayer cation totals of approximately 17.0. However, corrensite cannot be identified from the XRD pattern. TEM images confirm the lack of significant $R = 1$ S/C ordering. The Al content increases with an increase in noninterlayer cations, as shown in Figure 7a. The range in Mg/(Mg + Fe) content of the phyllosilicates (Figure 7b) is narrow and most likely reflects the bulk rock composition (Bettison and Schiffman 1988).

DISCUSSION

Random Interlayering

The existence of randomly interlayered C/S has been disputed by some (Roberson 1988, 1989) while other workers suggest that random, mixed-layered chlorite and smectite forms at low temperatures under nonequilibrium conditions favoring disorder rather
than order (e.g., Shau et al. 1990). Interfingering of S-C repetitions in packets of either smectite or chlorite can result in nonintegral spacings on XRD patterns that give rise to the classic interpretation of an $R = 0$ structure, as determined using the program NEW-MOD® (Reynolds 1985; Roberson 1989). Shau et al. (1990) and Roberson (1989) propose that such structures are more accurately described as smectite/corrensite and chlorite/corrensite interstratifications.

Images showing large packets of regular alternation of chlorite-like and smectite-like layers (such as those several hundred Å in extent shown by Shau et al. 1990 and Schiffman and Staudigel 1995) and which exhibit sharp superlattice peaks on XRD patterns are strong evidence for the existence of corrensite. However, the occurrence of SC alternations within packets of either smectite- or chlorite-like layers may not warrant the interpretation of those interlayerings as smectite/corrensite or chlorite/corrensite. In the images obtained in this study (Figures 4 and 5), the relative proportions of smectite and chlorite are each approximately 50%. However, none of the images records long repetitions of structurally coherent alternating layers of 10 Å and 14 Å. Instead, this 50:50 composition appears to be the result of random mixing of smectite and chlorite. Both adjacent 10-Å and adjacent 14-Å layers are common in the sequences imaged.

If one were to consider 5 repetitions of SC alternations as evidence for corrensite, then one might con-
sider several repetitions of SSC or CCS (Figures 4 and 5) as evidence for long-range ordering. In fact, Jiang and Peacor (1994) report limited occurrences of long-range ordering, R2 and R3 C/S interstratifications, in samples from pelitic units of the Gaspe Peninsula. TEM analyses of serpentine/chlorite interlayered minerals led Banfield et al. (1994) to suggest that transitions of layer silicates occur sequentially in which the 1st interstratified mineral to form is a 50:50 mixture of the 2 layer silicates, followed by a sequence of longer-range ordering (for example, transformation of “a” to “b” produces a, ab, abb, abbb). While this suggestion might be applied to the S/C transformation and be supported by the lack of significant occurrences of smectite(<0.50)/chlorite interlayering in sequences studied to date, there is still no compelling evidence for long-range ordering of S/C interstratifications. The images recorded here must be interpreted as random interlayering in view of the statistical insignificance of the SC, SSC, CCS repetitions.

Several workers have suggested that corrensite has a unique compositional range that differs from the combined composition of chlorite and smectite layers (Brigatti and Poppi 1984; Inoue et al. 1984; Shau et al. 1990; Inoue and Utada 1991). Shau et al. (1990) suggest that the Mg/(Mg + Fe) totals for smectite, corrensite and chlorite decrease in that order. However, work by Schiffman and Staudigel (1995) shows significant overlap in the Mg/(Mg + Fe) totals for these

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<th>Table 1. Representative electron microprobe analyses of chlorite and randomly mixed layered chlorite-smectite.</th>
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<td><strong>Mg#</strong></td>
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† Total iron reported as FeO.
Figure 7. A) Noninterlayer cations Mg + Fe + Al + Si versus total Al. B) Mg/(Mg + Fe) versus Si for phyllosilicates from 1A-25 calculated on the basis of 25 oxygens. Key: □ = groundmass replacement, ○ = vesicle-filling.

Transformation Processes

Recent studies suggest that the transformation of smectite to chlorite is not simply related to an increase in temperature during hydrothermal metamorphism. Instead, water/rock ratios and the mode of occurrence of phyllosilicates may be more important factors in controlling the structure of the stable layer silicate (Alt et al. 1986; Shau and Peacor 1992; Schiffman and Staudigel 1995). Observations from previous studies show that the transition may occur in a stepped progression of smectite to chlorite via corrensite or as a gradual change involving randomly and regularly interlayered structures, as dictated by the environment of formation.

Assuming that the phases present are the result of alteration, the reaction mechanism would be found in the layer transition boundaries. Figure 8 shows 3 possible mechanisms for the transition, 2 of which are based on models by Veblen and Ferry (1983) for the reaction of biotite to chlorite. The 1st involves the formation of a brucite-like interlayer in the interlayer region between the smectite-like layers. This reaction, causing an increase in volume, would result from primary growth or replacement of the interlayer region of the smectite. Terminations such as this have been found in a variety of phyllosilicates, including talc (Veblen and Buseck 1980, 1981; Veblen 1980). In the 2nd possible mechanism, the dissolution of tetrahedral sheets from smectite and conversion of the octahedral sheet to a brucite-like layer, involves an overall volume decrease. Veblen and Ferry (1983) observed this consumption of mica layers in the alteration of biotite to chlorite.
Veblen and Ferry's (1983) 1st mechanism, as applied to the transformation of smectite to chlorite, would describe the growth of a brucite-like layer within the interlayer of a smectite as shown in Figure 5. To approximate this reaction, a chlorite composition from this study was chosen as the product phyllosilicate. Pure saponite analyses for Point Sal samples have not been obtained, so the composition of smectite was set using Al and Si contents from Shau et al. (1990), while keeping the Mg/Fe ratio similar to that of the chlorite produced. In this study, data for mixed-layered chlorite(0.50)/smectite and chlorite indicate that, with decreasing Si and increasing Al, the Mg# slightly increases, although it generally remains constant due to the control of bulk rock chemistry on phyllosilicate composition. The Fe and Mg distribution in the reaction would be controlled by local availability from the surrounding host sample. The reaction is written as 1 smectite being transformed to 1 chlorite. For example:

\[
\begin{align*}
\text{Ca}_{0.20}(\text{Mg}_{1.46}\text{Fe}_{1.34}\text{Al}_{0.20})(\text{Si}_{3.40}\text{Al}_{0.60})\text{O}_{10}(\text{OH})_2 \\
+ 6.16\text{H}_2\text{O} + 1.06\text{Fe}^{++} + 1.14\text{Mg}^{++} + 1.20\text{Al}^{+++} \\
= (\text{Mg}_{2.8}\text{Fe}_{2.4}\text{Al}_{1.0})(\text{Si}_{3.0}\text{Al}_{1.0})\text{O}_{10}(\text{OH})_8 \\
+ 0.04\text{H}_4\text{SiO}_4 + 0.20\text{Ca}^{++} + 6.16\text{H}^+ \quad [1]
\end{align*}
\]

The reaction progresses with addition of Fe++, Mg++, and Al+++ while Si, Ca++, and H+ are released. Modification of the tetrahedral layers on either side of the brucite-like layer would be necessary.

The 2nd mechanism for the transformation may progress by the following reaction:
This reaction would require the input of minor Al$^{3+}$ in an acidic environment and the loss of substantial Si, as 1 smectite unit is transformed to 0.5 chlorite crystals. In comparison with the 1st mechanism, the dissolution of the tetrahedral layers of a smectite layer to form the brucite-like interlayer would require the release of Fe and Mg in the phyllosilicate microenvironment in proportion to their abundance in the system and the release of substantial amounts of silica into solution. Modification of the tetrahedral layers on either side of the brucite layer would be necessary. Mechanism 1, on the other hand, would result in a much smaller loss of silica but necessitates input of Mg and Fe from the environment. No evidence for mechanism 2, such as brucite-like layer terminations within a T-O-T sequence with an associated volume decrease, has been found in this study.

The image in Figure 6 suggests a 3rd possible mechanism for the reaction of smectite to chlorite. This transformation involves a volume increase as one 10-Å layer is transformed to a 10-Å and 14-Å unit (Figure 8). This reaction requires input of the elements necessary to form the chlorite-like layer, but would obviously result in significant structural modification of the original smectite layers. Addition of Fe and Mg in abundances controlled by the host rock composition, along with the addition of OH, Si and Al, would be necessary for progress of this reaction. The steps involved in this transformation may be 1) dissolution of the smectite layer and 2) reprecipitation of those elements plus the additional materials as the chlorite layer. Meunier et al. (1991) and Shau et al. (1990) also suggest that dissolution and redistribution of elements within the microenvironment of the phyllosilicates produces corrensite and then chlorite. Differences between Groundmass Replacement and Vesicle-Filling Phyllosilicates

Some studies have documented the variation of discrete phases (such as smectite or chlorite) and interlayer structures with occurrence in temperature-dependent sequences or with inferred transformation processes. For example, Inoue (1985) presents a sequence with a high percentage of smectite layers (100–80%), corrensite (50–40% smectite layers) and chlorite (15–0% smectite) and suggests that the lack of intermediate intercalated phases indicates that corrensite is a discrete phase. Likewise, Schiffman and Staudigel (1995) report on the occurrence of smectite, smectite + corrensite, corrensite and chlorite + corrensite with increasing depth in samples from the La Palma seamount. However, a gradual transformation, with increase in the component of nonexpandable layers with depth, has been shown from a number of environments, although commonly the lack of S/C with >50% smectite characterizes these sequences. The transition from smectite to chlorite in the Point Sal sequence appears to be accommodated in this gradual manner, as indicated by the presence of randomly interstratified C/S (Bettison and Schiffman 1988). Only 1 sample from Point Sal has R = 0 S/C with greater than 50% expandable layers. Liou et al. (1985) report the increase in percent chlorite layers with depth in the Onikobe geothermal system. Their study supports the existence of a compositional gap between smectite and 50:50 C/S. However, Schiffman and Fridleifsson (1991) also report a gradual transformation, without the compositional gap suggested by the previous 2 studies, for phyllosilicates in the Nesjavellir geothermal system in Iceland.

What factor(s) determine whether or not a sequence is characterized by discrete layer or interlayered phases? Schiffman and Staudigel (1995) argue that the pervasiveness of alteration in La Palma samples, indicated by the lack of relict igneous phases and high-variance mineral assemblages, supports a high water/rock ratio attending the alteration. They suggest that it is this high integrated fluid flow that allows for the stabilization of the discrete layer phases. While differences in pervasiveness of alteration may not be quantifiable, comparison between the Point Sal and La Palma sequences suggest that fluid/rock ratios were probably smaller in the alteration of the former than the latter (P. Schiffman, personal communication). This supports the suggestion by several workers (Alt et al. 1986; Shau and Peacor 1992; Schiffman and Staudigel 1995) that formation of randomly interlayered C/S would be favored in low fluid flux environments.

In this study, a notable difference exists between phyllosilicate phases in vesicles and groundmass of a basalt sample from the Point Sal ophiolite. Chlorite is the predominant vesicle phase, whereas randomly interlayered C/S characterizes groundmass replacements. Clearly, the mechanism of formation is different for the 2 occurrences: precipitation in voids versus transformation of a pre-existing phyllosilicate or silicate mineral. Shau and Peacor (1992) found a correlation between mixed-layered phases and mode of occurrence as well, indicating that ill-defined packets of interlayered C/S occur as replacements of olivine or interstitial materials. Our results show that the thick packets of smectite-like and chlorite-like layer alternations are well defined. While the void phases are characterized by large, coherent crystals of chlorite.

\[
\begin{align*}
\text{Ca}_{0.2}(\text{Mg}_{1.46}\text{Fe}_{1.34}\text{Al}_{0.20})(\text{Si}_{3.40}\text{Al}_{0.60})\text{O}_{10}(\text{OH})_2 & \quad \text{smectite} \\
+ 0.20\text{Al}^{3+} + 4.6\text{H}_2\text{O} + 0.4\text{H}^+ & \quad \text{corrensite} \\
= (\text{Mg}_{1.1}\text{Fe}_{1.2}\text{Al}_{0.5})(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_5(\text{OH})_4 & \quad \text{chlorite} \\
+ 1.9\text{H}_2\text{SiO}_4 + 0.16\text{Mg}^{++} + 0.14\text{Fe}^{++} & \\
+ 0.20\text{Ca}
\end{align*}
\]

\[\text{[2]}\]
that precipitated from fluid flowing through these zones of permeability, the groundmass replacement of pre-existing material would progress at a slower rate with lower fluid/rock ratios.

Studies of the transformation of smectite to ilite are far more advanced in their consideration of the mechanism and the control of ordering than are studies of the smectite-to-chlorite conversion. Recent work by Huang et al. (1993) on the kinetics of the conversion resulted in the development of a simple rate law for conversion of smectite to ilite. Their work indicates that temperature, time and K concentration are the most important factors controlling the conversion. Abercrombie et al. (1994) suggest that reduction in silica activity as a result of quartz precipitation controls the smectite-to-ilite reaction. They also note that in metabasalts the transition from corrensite to chlorite is accompanied by the precipitation of quartz. Similarly, the activity of Mg has been suggested to be an important factor in the development of corrensite by Velde (1977), as has the activity of Al due to albitionization of plagioclase (Shau and Peacor 1992). How can we distinguish between controls of elemental availability and kinetic factors in the conversion of smectite to chlorite?

The existence of chlorite in the vesicles of the Point Sal metabasalt argues for progressive transformation of smectite in the groundmass to mixed-layered C/S and against the retrograde alteration of chlorite to C/S. As chlorite precipitates from solution, the transformation progresses in the groundmass with less access to fluids, although presumably the activity of Mg would be similar in both microenvironments as shown by the narrow range in Mg# shown in Figure 7. Since Mg# is controlled by the bulk rock composition, the difference is most clearly related to 2 possible factors: the fluid/rock ratio and the time available for the formation or conversion process. Temperature would play a secondary role, since both the randomly interlayered phase and discrete chlorite can coexist.

CONCLUSIONS

The varying interstratifications in images shown here are consistent with structural disequilibrium between chlorite, corrensite and smectite. That growth of the interstratifications occurred by modification of the original layer silicate is suggested by the similar morphology of the regions affected. The modification of smectite and inheritance of pre-existing structural units are supported by the TEM data. However, the majority of the observations argue for the dissolution of smectite and recrystallization of 10-Â and 14-Â units within this sample.

The evidence from phyllosilicates in the groundmass of these samples results in the formation of metastable mixed-layered C/S. Within the microenvironment of the pore space, chlorite precipitates. The bulk rock chemistry controls the Fe/Mg ratio of both the chlorite and mixed-layered C/S. However, the structure of the phase depends on the microenvironment of formation. Observations from the samples in this study support the suggestion by Alt et al. (1986), Shau and Peacor (1992) and Schiffmann and Staudigel (1995) that structural differences reflect the achievement of textural equilibrium in zones of high permeability (chlorite in this case) and that randomly interlayered S/C represents a metastable phase formed in the less-permeable glassy groundmass of the metabasalts. The low water/rock ratios and less-pervasive alteration are implied by the lack of albitionization of the plagioclase in this sample. While chlorite formed from crystal growth in the pores of this metabasalt, randomly mixed-layered C/S formed from dissolution/reprecipitation events in the groundmass. Given the control of permeability on the phase formed, the use of mixed-layered C/S phases as geothermometers in variably altered basalts may be problematic.

The statistical significance of apparently ordered sequences must be considered when addressing the question of whether or not a repeat sequence of smectite-like and chlorite-like layers can be adequately described as corrensite. What is the probability that 5 repetitions of SC will occur in a random distribution of 100 phyllosilicate layers? Are the arrangements of these layers the result of random mixing, or do thermodynamic properties and/or reaction processes control the sequence produced? Understanding the probability of limited numbers of SC repetitions in a string of layers is necessary to answer the question of random versus regular ordering in phyllosilicate phases.

REFERENCES


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