

## CHEMIOGRAPHIC ANALYSIS OF TRIOCTAHEDRAL SMECTITE-TO-CHLORITE CONVERSION SERIES FROM THE OHYU CALDERA, JAPAN

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**Abstract**—The chemical compositions of chlorite-smectite mixed-layered minerals (C/S) from the Ohyu caldera (Inoue, 1985) are analyzed using  $M^{+}-4Si-3R^{2+}$  diagrams. The assumed original saponite has the following composition:  $Si_{3.54}Al_{0.46}O_{10}Al_{0.173}Fe^{2+}_{1.385}Mg_{1.295}Mn_{0.02}(OH)_2M^{+}_{0.56}$ . Random C/S minerals (100 to 80% expandable layers) are interpreted as an interstratification of the starting 2:1 smectite layer with a  $Al_xR^{2+}_{3-x}$  interlayer. The 2:1 smectite layer charge remains constant but Ca, Na, K cations are replaced by a  $Al-R^{2+}$  complex ion. The brucitic layer (produced by the polymerization of the complex ions) and the 2:1 smectite layer form a 14 Å non-expandable phase having a composition different from a true chlorite.

The true chlorite layers first appear in the ordered (corrensite) phase composed of a high charge saponite:  $Si_{3.35}Al_{0.65}O_{10}R^{2+}_3(OH)_2M^{+}_{0.65}$  and an octahedral vacancy-free chlorite  $Si_{2.90}Al_{1.10}O_{10}Al_{1.10}R^{2+}_{4.90}(OH)_8$ . The recrystallization of the original trioctahedral smectite into a high-charge saponite decreases the b-dimension difference with the chlorite component.

From these data, it is suggested that the trioctahedral smectite-to-chlorite conversion is controlled by three reactions: 1. fixation and polymerization of  $Al-R^{2+}$  complex ions in the interlayer region of the original smectite producing a 14 Å non-expandable phase (the interlayering of this phase with the original smectite gives the randomly interstratified C/S mineral. 2. dissolution of these random mixed-layered minerals and precipitation of corrensite. 3. dissolution of corrensite and growth of Fe-rich chlorite.

**Key Words**—Chlorite/smectite mixed layer, Corrensite, Ohyu caldera, Smectite-to-chlorite conversion.

### INTRODUCTION

The conversion of trioctahedral smectite to chlorite through the ordered interstratified structure (corrensite) has been documented in sedimentary rocks (April, 1981), in diagenetic series (April, 1981; Chang *et al.*, 1986; Bodine, 1985), in contact metamorphic environments (April, 1980), and in hydrothermal areas (Kristmannsdottir, 1979, 1983; Inoue *et al.*, 1984; Inoue, 1985, 1987). In spite of the fact that the structural aspect of chlorite-smectite interlayering has been well characterized by XRD analysis (Reynolds, 1988), the chemical processes by which an original smectite is converted to a chlorite via corrensite have not been clearly established. Indeed, the most detailed study is that of Bodine and Madsen (1987) who proposed a set of reactions based on mass balance considerations and on the chemical compositions of end products. Unfortunately, the equations that apply to the particular evaporitic environment they studied are difficult to extrapolate to other diagenetic or hydrothermal series.

Among studies of the smectite-to-chlorite conversion in diagenetic or hydrothermal series, the chlorite/smectite mineral sequence from the Ohyu caldera (Inoue, 1985) is one of the best documented because both chemical composition and percent expandability mea-

sured by XRD are available for 36 samples. The conversion is characterized by a discontinuous change in smectite layer percent. Three types of chlorite/smectite interstratified minerals were identified: highly expandable (100 to 80% smectite layers), corrensite (50 to 40% smectite layers) and highly chloritic (15 to 0% smectite layers). On the other hand, the microprobe analyses of the C/S minerals indicated a continuous change in chemical composition (Inoue, 1985, 1987). Inoue presented the following scheme for the smectite-to-chlorite transformation: (1) increase of the tetrahedral layer charge in precursor smectite layers takes place parallel to the formation of brucite-like layer in the interlayer position, (2) beyond the 20% chlorite layer limit, brucite precipitates in every second interlayer and corrensite is formed, (3) chlorite crystal growth includes corrensite domains.

Several critical points remain unclear in the above scenario, such as whether or not the compositions of component layers in C/S stay constant during the transformation, and how the formation of the brucite-like layer influences the charge distribution of precursor smectite. Detailed chemiographic analysis can provide answers to these questions, if the structure and chemical composition of a continuous sequence involving the transformation of smectite to chlorite are well

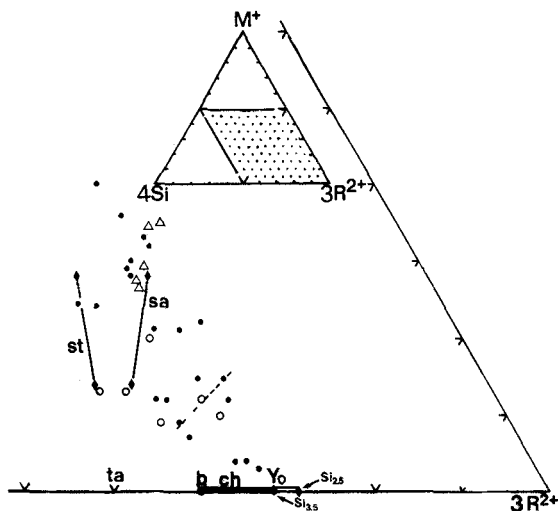


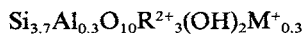
Figure 1. Trioctahedral phyllosilicate compositions are plotted in the  $M^+-4Si-3R^{2+}$  system; high-charge (circles) and low-charge (dots) corrensitite from Brigatti and Poppi (1984); vermiculite (triangles) from de la Calle and Suquet (1988); Silent Valley chlorite (b) from Deer *et al.* (1971); ta: talc; sa: saponite; st: stevensite; ch: chlorite solid solution; Y<sub>0</sub>: octahedral vacancy-free chlorite domain limited by the following compositions:  $Si_{3.5}Al_{0.5}O_{10}Al_{0.5}R^{2+}_{10.5}(OH)_8$  and  $Si_{2.5}Al_{1.5}O_{10}Al_{1.5}R^{2+}_{4.5}(OH)_8$ . The theoretical 50-50 corrensitite composition is given by the dotted line.

known. In this paper, the data given by Inoue (1985) are used for the chemiographic analysis. The goal is to determine the individual compositions of smectite and chlorite layers in C/S and to identify the chemical reactions that occurred during the transformation of smectite to chlorite.

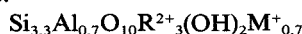
#### $M^+-4Si-3R^{2+}$ DIAGRAM

The compositions of corrensitite, trioctahedral expandable minerals (i.e., smectite, vermiculite), and chlorite are expressed on  $O_{10}(OH)_5$ ,  $O_{10}(OH)_2$  and  $O_{10}(OH)_8$  basis, respectively, and are plotted in a  $M^+-4Si-3R^{2+}$  diagram (derived from the  $M^+-4Si-R^{2+}$  diagram; Meunier and Velde, 1989) in which  $M^+ = Na^+ + K^+ + 2Ca^{2+}$ ;  $4Si = Si/4$ ;  $3R^{2+} = (Mg + Fe^{2+} + Mn)/3$ . The following end member compositions are:

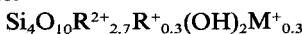
Low-charge saponite:



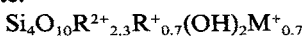
High-charge saponite:



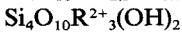
Low-charge stevensite:



High-charge stevensite:



Talc:



Chlorite:  $Si_{4-x}R^{3+}_xO_{10}R^{2+}_{6-x-3y}R^{3+}_{x+26y}(OH)_8$

where ■ represents a vacancy (Bailey, 1988).

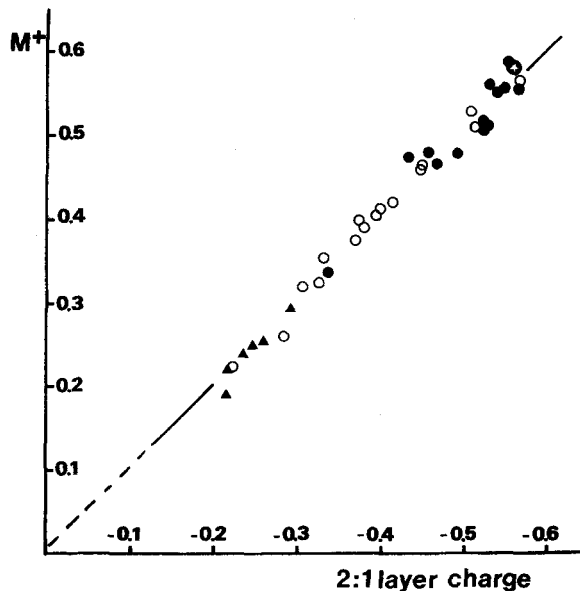


Figure 2. Relation between the 2:1 layer charge and the interlayer charge ( $M^+$ ) assuming that total Fe is in the  $Fe^{2+}$  state and that there is no exchangeable Mg. Star: original trioctahedral smectite (100% expandable); dots: highly expandable random mixed-layered minerals (100 to 80% expandable); circles: corrensitite (55 to 40% expandable); triangles: highly chloritic mixed-layer minerals (15 to 10% expandable).

When  $y = 0$ , the composition of chlorites from  $Si_{3.5}$  to  $Si_{2.5}$  is represented by the Y<sub>0</sub> domain (Figure 1). The maximum amount of octahedral vacancies (the boundary of the solid solution toward the 4Si pole) was constrained to that shown by brunsvigite from Silent Valley (Figure 1, point b; Deer *et al.*, 1971). Compositions of trioctahedral vermiculites (de la Calle and Suquet, 1988) are plotted in order to analyze the compositions of the ordered chlorite-vermiculite (i.e., high-charge corrensitite) compiled by Brigatti and Poppi (1984).

The compositions of the theoretical end members in the trioctahedral smectite solid solution (saponite and stevensite series) were deduced from a compilation of data by Güven (1988). Theoretically, the chemical composition of corrensitite must lie between the trioctahedral smectite and chlorite domains. The chemical compositions of brucite ( $Mg_3(OH)_6$ ) or "brucitic-layer" in chlorite ( $Mg_{3-x}Al_x(OH)_6$ )<sup>x+</sup> are projected on the  $3R^{2+}$  pole.

Data from Brigatti and Poppi (1984) are used to illustrate the usefulness of the  $M^+-4Si-3R^{2+}$  diagram. When plotted, the data suggest that corrensitite has a broad chemical composition field (Figure 1). Excluding analyses that show abnormally high layer charge, most of the compositions lie between the saponite and chlorite end members, and some of them between the saponite and stevensite end members.

Diffraction patterns of the samples selected by Brigatti and Poppi (1984) show a 31–33 Å reflection after

Table 1. Compositions of chlorite-smectite mixed-layered minerals in the Ohyu caldera formations (from Inoue, 1985) expressed on an  $O_{10}(OH)_2$  basis for samples 1–17, and on an  $O_{10}(OH)_5$  basis for samples 18–36. Samples 1–17: random mixed-layered minerals (100–80% smectite); samples 18–30: random mixed-layered (80% smectite) + corrensite + highly chloritic mixed layer (20–15% smectite); samples 31–36: corrensite + highly chloritic mixed-layered clay (15–10% smectite).

	Si	Al(IV)	Al(VI)	Fe <sup>2+</sup>	Mg	Mn	Octahedral occupation	Octahedral charge	Ca	Na	K	Interlayer charge
1	3.540	0.460	0.175	1.385	1.295	0.020	2.875	-0.075	0.250	0.030	0.030	0.560
2	3.005	0.995	0.100	1.685	1.445	0.050	3.280	0.660	0.160	0.000	0.015	0.335
3	3.055	0.945	0.070	2.140	0.945	0.050	3.205	0.480	0.220	0.015	0.010	0.465
4	3.000	1.000	0.105	1.890	1.130	0.060	3.185	0.475	0.250	0.000	0.005	0.505
5	3.085	0.915	0.155	1.525	1.400	0.030	3.110	0.375	0.270	0.000	0.010	0.550
6	3.220	0.780	0.170	1.550	1.310	0.040	3.070	0.305	0.250	0.000	0.010	0.510
7	3.075	0.925	0.075	1.750	1.300	0.055	3.180	0.435	0.230	0.000	0.010	0.470
8	3.105	0.895	0.085	1.570	1.485	0.050	3.190	0.465	0.235	0.000	0.005	0.475
9	3.105	0.895	0.150	1.555	1.400	0.040	3.145	0.440	0.235	0.000	0.010	0.480
10	3.235	0.765	0.190	1.470	1.330	0.035	3.025	0.240	0.240	0.015	0.020	0.515
11	3.215	0.785	0.245	1.420	1.285	0.035	2.985	0.215	0.270	0.010	0.005	0.555
12	3.260	0.740	0.180	1.385	1.405	0.035	3.005	0.190	0.275	0.000	0.005	0.555
13	3.200	0.800	0.230	1.470	1.265	0.040	3.005	0.240	0.280	0.010	0.010	0.580
14	3.150	0.850	0.095	1.475	1.500	0.030	3.100	0.295	0.290	0.000	0.005	0.585
15	2.935	1.065	0.070	1.665	1.530	0.045	3.310	0.690	0.155	0.055	0.010	0.375
16	2.935	1.065	0.085	1.720	1.445	0.040	3.290	0.665	0.205	0.000	0.005	0.415
17	2.935	1.065	0.085	1.660	1.490	0.030	3.265	0.615	0.230	0.000	0.005	0.465
18	3.370	0.630	0.605	2.035	1.555	0.060	4.255	0.115	0.245	0.000	0.020	0.510
19	3.380	0.620	0.640	1.825	1.705	0.035	4.205	0.050	0.280	0.000	0.005	0.565
20	3.225	0.775	0.620	2.090	1.650	0.065	4.425	0.470	0.150	0.000	0.020	0.320
21	3.165	0.835	0.720	2.195	1.420	0.060	4.395	0.510	0.160	0.000	0.005	0.325
22	3.035	0.965	0.635	2.570	1.280	0.070	4.555	0.745	0.110	0.000	0.005	0.225
23	3.295	0.705	0.605	2.020	1.685	0.050	4.360	0.325	0.195	0.000	0.000	0.390
24	3.150	0.850	0.640	1.950	1.785	0.045	4.420	0.480	0.185	0.000	0.005	0.375
25	3.120	0.880	0.580	2.095	1.745	0.065	4.485	0.550	0.175	0.000	0.005	0.355
26	3.090	0.910	0.540	2.130	1.735	0.055	4.460	0.460	0.220	0.010	0.010	0.460
27	3.250	0.750	0.625	2.035	1.650	0.055	4.365	0.355	0.200	0.000	0.005	0.405
28	3.300	0.700	0.595	1.980	1.725	0.045	4.345	0.285	0.210	0.000	0.000	0.420
29	3.315	0.685	0.625	1.910	1.695	0.045	4.275	0.175	0.260	0.000	0.010	0.530
30	3.045	0.955	0.540	2.215	1.745	0.065	4.565	0.670	0.130	0.000	0.000	0.260
31	3.105	0.895	0.565	2.125	1.750	0.055	4.495	0.555	0.170	0.000	0.005	0.345
32	2.995	1.005	0.550	2.285	1.710	0.075	4.620	0.790	0.110	0.000	0.005	0.225
33	2.950	1.050	0.605	2.270	1.675	0.065	4.615	0.835	0.095	0.000	0.000	0.190
34	2.985	1.015	0.565	2.350	1.615	0.070	4.600	0.765	0.115	0.005	0.010	0.245
35	3.025	0.975	0.580	2.360	1.560	0.080	4.580	0.740	0.115	0.000	0.010	0.240
36	2.950	1.050	0.510	2.200	1.865	0.065	4.640	0.790	0.125	0.000	0.005	0.255

glycolation. This means that the chlorite-to-smectite ratio in the corrensite must not be very different from unity since the intensity and the sharpness of the superlattice reflection should decrease markedly were this not the case (Reynolds, 1988). Figure 1 shows that the compositions compiled by Brigatti and Poppi (1984) do not correspond to pure corrensite but to mixtures of corrensite with a discrete trioctahedral expandable clay (e.g., saponite, stevensite, vermiculite) or chlorite.

#### PLOTS OF THE OHYU C/S SEQUENCE IN THE $M^{+}-4Si-3R^{2+}$ DIAGRAM

The chemical compositions of the three types of chlorite/smectite were measured assuming that total Fe is in the  $Fe^{2+}$  state and that there is no exchangeable Mg (Table 1). These assumptions seem to be reasonable because there is no discrepancy between the 2:1 layer charge and the interlayer charge:  $(M^{+}) = 0.97$  2:1 layer

charge + 0.02 (correlation coefficient = 0.98; Figure 2). The caldera profile contains one clay phase present from the surface to 600 m depth (highly expandable mixed-layered minerals which do not contain more than 20% of 14 Å nonexpandable layers; samples 1–14) and three phases between 600 m and 800 m depth (highly expandable mixed-layered, corrensite, and chlorite-rich, mixed-layered clay that does not contain more than 15% expandable layers; samples 15 to 30). Below 800 m, the highly expandable phase disappears (samples 31–36). Based on the chemical analyses, the 100% expandable smectite (sample 1) has the following composition:  $Si_{3.54}Al_{0.46}O_{10}Al_{0.17}5Fe^{2+}_{1.385}Mg_{1.295}Mn_{0.02}(OH)_2M^{+}_{0.56}$ . The calculated total layer charge (-0.54) of the 2:1 layer is mainly compensated by interlayer Ca. It is slightly inferior to the measured interlayer charge. For homogeneity, the interlayer charge will be considered to compensate exactly the 2:1 layer charge (+0.54 instead of 0.56). Sample 1 was assumed to

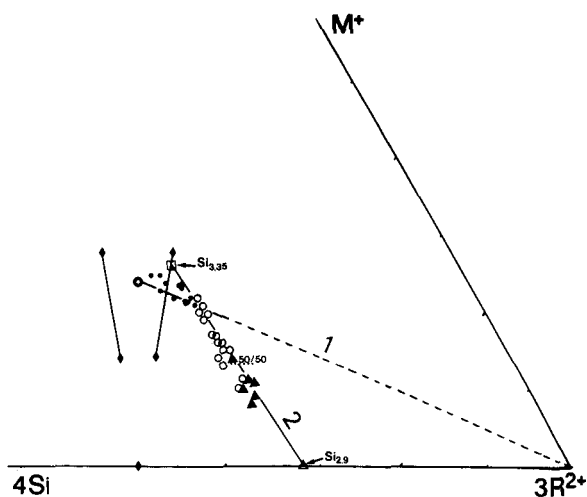


Figure 3. Projection in the  $M^+-4Si-3R^{2+}$  system of the compositions of the "chlorite-smectite" mixed-layer minerals from Ohyu caldera formation (Inoue, 1985). Symbols are the same as in Figure 2; line 1: mixture of original smectite with an Al-Mg brucitic layer; line 2: interlayering of high-charge saponite with octahedral vacancy-free chlorite; extrapolation of line 2 gives the saponite composition (square) and the chlorite composition (triangle). The intersection with the dashed line represents the ideal 50-50 corrensite composition.

represent the starting material for the smectite-to-chlorite transformation in the Ohyu area.

Plotted in the  $M^+-4Si-3R^{2+}$  system, the chemical compositions of these mineral assemblages are not linearly distributed between the original trioctahedral smectite composition and a chlorite end member. They seem to follow two lines: 1. the original trioctahedral smectite-brucite (or brucitic layer) line for the highly expandable mixed-layer minerals; 2. a saponite (0.65  $M^+$  charge)-chlorite without octahedral vacancy trend for corrensite (Figure 3).

The  $M^+$  charge decreases from 0.56 (original smectite) to about 0.2 (chlorite-rich mixed-layer) while the  $Al/R^{2+}$  and  $Fe^{2+}/(Fe^{2+} + Mg)$  ratios increase. These ratios seem to be linearly correlated with the layer charge (Figure 4a-b) with  $Al/R^{2+} = -0.17 M^+ + 0.43$  (correlation coefficient = 0.69) and  $Fe^{2+}/(Fe^{2+} + Mg) = -0.15 M^+ + 0.60$  (correlation coefficient = 0.71).

## DISCUSSION

### Random "chlorite-smectite" mixed-layer minerals

Line 1 (Figure 2) for the  $M^+-4Si-3R^{2+}$  coordinates shows that the random mixed-layered "chlorite-smectite" series consisting of 100 to 80% smectite layers is composed of original smectite layers associated with a brucitic interlayer. This means that the composition and the total charge of the 2:1 layer remains constant whatever the proportion of the brucitic interlayer in the random C/S. The amounts of  $Ca^{2+} + Na^+ + K^+$  cations ( $M^+$ ) decreases, so the 2:1 layer charge is pro-

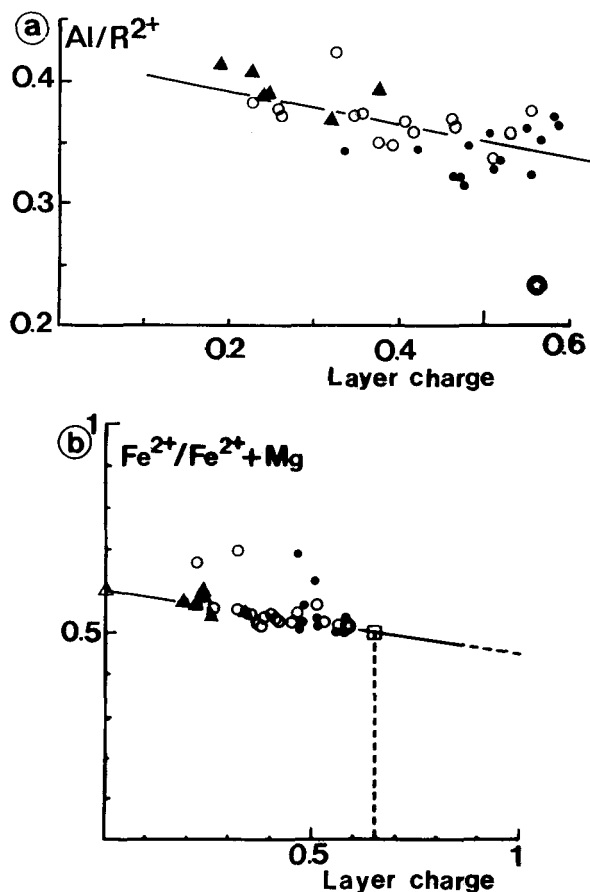


Figure 4. (a)  $Al/R^{2+}$  versus layer charge (L.C.) diagram for the chlorite-smectite mixed layer mineral series (Ohyu caldera formations). Symbols are the same as in Figure 2. (b)  $Fe^{2+}/(Fe^{2+} + Mg)$  versus layer charge (L.C.) diagram for the chlorite-smectite mixed-layer mineral series (Ohyu caldera formations). Symbols are the same as in Figure 2.

gressively compensated by the formation of additional brucitic interlayers. This is the case for chlorite in which the stable state of the brucitic interlayer is considered reached for the following composition:  $(Al Mg_2(OH)_6)^+$  (Bailey, 1988). The presence of Al in the brucitic layer explains the strong increase of the  $Al/R^{2+}$  ratio between the original smectite and the random mixed-layered phases (Figure 4a). The association of Al and  $R^{2+}$  components ( $R^{2+}$  predominately Mg) in a brucitic layer was explained by the formation of a complex ion that is fixed in the interlayer region of the smectite in place of Ca, Na and K (Elderfield, 1976). When a certain quantity of these complex ions is fixed in the interlayer region, polymerization occurs and a brucitic layer is produced.

The new-formed, non-expandable 14 Å phase which is composed of the brucitic layer associated with the original 2:1 smectite layer is chemically different from a true chlorite. The random C/S series is produced

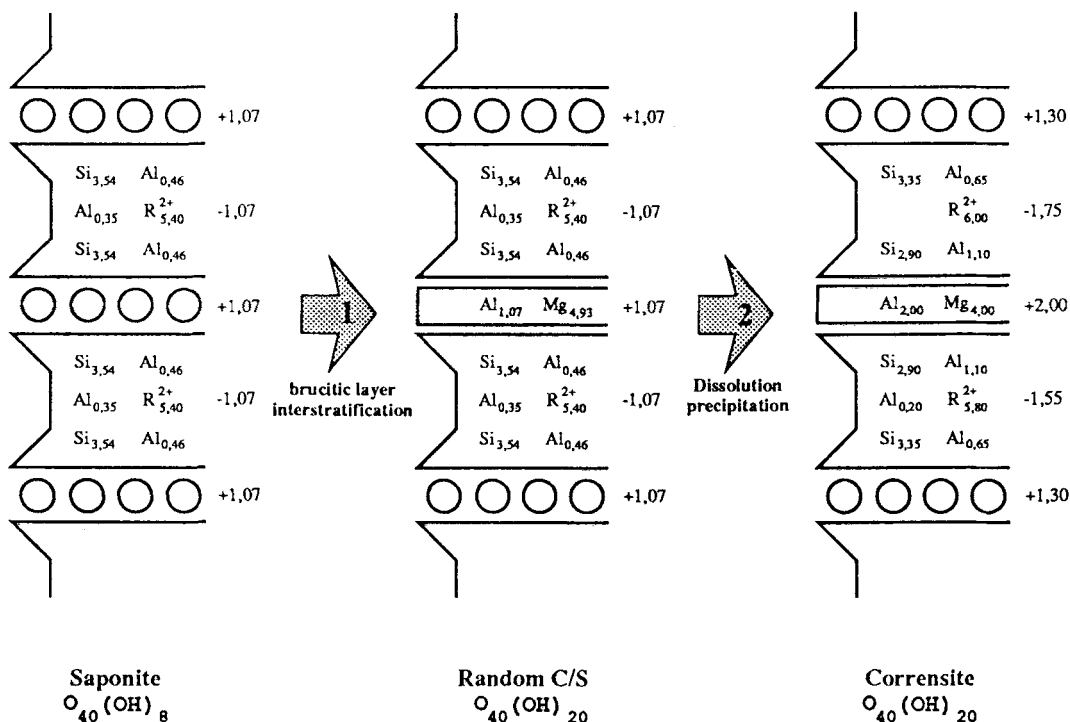
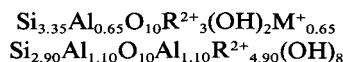


Figure 5. Schematic structural model showing possible layer structures, and distribution of elements and electrical charges in saponite, random mixed-layered minerals (14 Å nonexpandable layer interstratified with the original smectite) and corrensite. The structures of random mixed-layered mineral and corrensite are considered to have tetrahedral charges symmetrical across the brucitic interlayer. Arrows indicate the chemical process involved: 1. growth of a brucitic interlayer; 2. dissolution of the random mixed-layered minerals and crystallization of corrensite.

without any chemical change involving the remaining 2:1 smectite layers. As a consequence, the increase of tetrahedral aluminium in a structural formula calculated on a  $O_{10}(OH)_2$  basis is due to underestimation of the amount of Si atoms. Because of the presence of variable quantities of 14 Å non-expandable layers, the formula must be calculated on a  $O_{10}(OH)_8$  basis.

#### Corrensite

The chemical compositions of smectite and chlorite layers in corrensite can be deduced by extrapolation of line 2 (Figure 2) which intersects, respectively, the saponite and chlorite domains. Assuming that the octahedral layers are vacancy free, the saponite and chlorite compositions are respectively the following:



From Figure 3b, one can extrapolate the  $Fe^{2+}/(Fe^{2+} + Mg)$  ratio of the saponite and chlorite layers: 0.5 and 0.6 respectively. One can deduce the  $Fe^{2+}$  and Mg contents for saponite:  $R_{3.00}^{2+} = Fe_{1.50}^{2+} + Mg_{1.50}$  and chlorite:  $R_{4.90}^{2+} = Fe_{2.94}^{2+} + Mg_{1.96}$ . In both cases, the 2:1 layer of these two end members has a chemical composition different from the 2:1 layer of the original trioctahedral smectite. This suggests that the 2:1 structure of the

saponite and chlorite components is not inherited from the crystalline structure of the original smectite. In other words, corrensite crystallizes when the random mixed-layer clay dissolves and Fe is preferentially fixed in the chlorite component.

The question is why the corrensite cannot be formed by a progressive interstratification of the Al-R<sup>2+</sup> interlayer in the original saponite. Inoue (1985) showed that there is a large difference in the b-dimension between the original smectite (9.234 Å) and the chlorite-rich mixed-layered minerals (>9.270 Å). This suggests that the misfit of cell dimensions between the original smectite and the chlorite may hinder production of a regular interstratified structure. However, the crystallographic constraints may be reduced because the b-dimension of trioctahedral smectite increases with increasing tetrahedral charge (Suquet *et al.*, 1981).

The formation of the ordered mixed-layered clay does not proceed by a progressive interstratification of the Al-R<sup>2+</sup> interlayers in the original smectite as is the case for the random phases. Corrensite appears to crystallize in the Ohyu caldera series by a two-step mechanism: 1. dissolution of the random mixed-layered minerals and, 2. crystallization of high-charge saponite layers with chlorite. Figure 5 summarizes the possible structures of the random mixed-layered minerals and



the corrensite, assuming that both have tetrahedral charges symmetrical across the brucitic interlayer (Yen-Hong Chau *et al.*, 1990).

#### *Chlorite-rich, mixed-layered minerals*

In the studied sequence, Inoue showed that a gap exists in the percent expandability between corrensite and chlorite rich, mixed-layered minerals from 40 to 20% smectite layers. This gap is not obvious from the chemical data alone because XRD results show that corrensite coexists with highly chloritic mixed-layer minerals in the analyzed samples. The compositions of the mixture (corrensite + highly chloritic, mixed-layered clay) and of the highly chloritic, mixed-layered minerals are linearly distributed in the  $M^{+}4Si-3R^{2+}$  coordinates (Figure 2). This indicates that the composition of the saponite and the chlorite components are identical in the corrensite and the highly chloritic, mixed-layered clay (Figure 2).

#### CONCLUSION

It appears that the trioctahedral smectite-to-chlorite conversion is not a simple process controlled by the formation of brucite in the smectite interlayer region as classically proposed (Bodine and Madsen, 1987). Two reactions proceed successively (Figure 5): (1) formation of a brucitic layer by fixation and polymerization of complex  $Al-R^{2+}$  ions in the interlayer region of the original smectite and, (2) dissolution of the random mixed-layered minerals and recrystallization of an ordered chlorite-saponite phase. The random mixed-layered minerals conserve the composition of the original 2:1 smectite layer and, as a consequence, they are not direct precursors of corrensite in which the non-expandable layer is a true chlorite. The random mixed-layered phase is not progressively transformed into an ordered phase implying that it probably dissolves when corrensite crystallizes. This explains why there is not a continuous series from 100 to 50% expandable minerals in the Ohyu caldera sequence. As corrensite is the product of a dissolution-recrystallization reaction, it behaves thermodynamically as an independent phase. This was suggested by Velde (1977) and Inoue (1985).

In the Ohyu caldera sequence, the expandable component of corrensite is a high-charge saponite. The increase of tetrahedral charge in the expandable layer reduces the difference in the b-dimension between the smectitic and the chloritic layer. This may be a general rule in the smectite-to-chlorite conversion. At present, we do not know how low-charge trioctahedral smectites would behave.

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