Solid solutions in I/S mixed-layer minerals and illite

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ABSTRACT

Chemographic analysis of suites of I/S minerals using M^+-$4Si$-R^{2+} coordinates reveals the existence of independent mineral series. The interlayered smectite is a montmorillonite whose composition and charge depends upon the *P*, *T*, and chemical conditions of formation. The charge can vary from near 0.33 to 0.66 depending upon the series. In each of the I/S series the montmorillonite is interlayered with an illite that has nearly the same composition for all I/S phases. The illite layer has a charge of 0.87. It appears that the members of the I/S mineral series are interlayered from a fully smectitic composition to a bulk composition with a charge of 0.75. Thus the interlayering does not reach the illite end-member with a charge of 0.87. This series can be treated as an incomplete solid-solution.

I/S mixed-layer minerals can be considered as a partial solid solution with three components: high-charge $ill_{0.87}$, low-charge $mnt_{0.33}$, and high-charge $mnt_{0.66}$. It is probable that the high-charge $ill_{0.87}$ component cannot replace the montmorillonite in all proportions from 0 to 100% because of crystallographic incompatibilities.

INTRODUCTION

The formation of I/S mixed-layer minerals through illitization of smectitic clay has been described in sedimentary basins (Perry and Hower, 1970; Weaver and Beck, 1971; Boles and Franks, 1979; Hower et al., 1976; Rettke, 1976), hydrothermally altered rocks (Steiner, 1968; McDowell and Elders, 1980; Horton, 1985; Inoue and Utada, 1983), contact-metamorphic environments (Nadeau and Reynolds, 1981; Pytte, 1982), and metasomatic bentonites (Velde and Brusewitz, 1982). Because the proportion of illite to smectite layers in I/S minerals and their layer ordering progressively increase with temperature, the thermal history of the I/S formation can be reconstructed (Hoffman and Hower, 1979; Nadeau and Reynolds, 1981).

Some chemical properties of both illitic and smectitic components in I/S mixed-layer minerals have been determined. The smectite is of the montmorillonite type, and the layer charge of the interstratified illite appears to be 0.75 per $O_{10}(OH)_2$ (Hower and Mowatt, 1966; Horton et al., 1985; Velde and Brusewitz, 1986; Środoń et al., 1986). However, these properties are not sufficient to accurately define the composition of these two components because both illite and montmorillonite, when they are discrete phases, form complex solid solutions with variable charge and composition of the octahedral layer ions. Velde and Brusewitz (1986) showed that the interlayer charge of the smectite component in I/S minerals also varies from 0.3 to 0.7, and this appears to be a function

of the bulk chemistry of the rock or the intensive variables of the regime under which they have been formed.

The phase relations between the two components of I/S mixed-layer minerals are not well known. Should they be considered as end-members of a solid solution (Aagaard and Helgeson, 1983) or as independent phases in equilibrium when interstratified (Garrels, 1984; Sass et al., 1987)? If the layer charge of the smectite is variable (Velde and Brusewitz, 1986), one can expect that compositions of both illite and montmorillonite components in I/S minerals are also variable. The purpose of this paper is to determine the chemical relationships between the two component layers in I/S minerals in different geologic environments and the relations between I/S minerals and illites.

METHOD

The published data used in this study concerning I/S mixed-layer minerals are bulk chemical composition, percentage of smectite component determined by XRD, and ordering degree of the layer types in the I/S structure. Only data from geologic occurrences with a continuous I/S mineral sequence have been used here. Analyses were rejected when the sum of octahedral cations was higher than 2.09 per $O_{10}(OH)_2$, which indicates a departure from the dioctahedral mineral structure, and when the layer charge required for the smectite component of the I/S mixed-layer clay minerals was higher than 0.66 per $O_{10}(OH)_2$, which is the upper limit of expandable phases (de la Calle and Suquet, 1988).

A M^+-4Si-R^{2+} ternary system is used to graphically represent the chemical compositions of discrete illites, smectites, and I/S mixed-layer minerals. Such a system allows one to separate beidellitic and montmorillonitic substitutions in the expandable phases. The M^+ pole indicates the layer charge of ideal mica, the 4Si pole represents the maximum Si content of the tetrahedral sheet, and the R^{2+} pole represents the amount of bivalent cations in the octahedral position. As an example, the coordinates of an ideal muscovite $(Si_3Al)O_{10}Al_2(OH)_2K$ are calculated as follows: $M^+ = 1$, $4Si = 0.75$, and $R^{2+} = 0$, which gives the percentages 57, 43, and 0%, respectively. Coordinates of low- and high-charge beidellites and montmorillonites are given in Table 1. For convenience, these different components will be designated by their mineral symbol with the layer charge in subscript. As an example, the illite with a layer charge of 0.87 per $O_{10}(OH)_2$ will be designated by $ill_{0.87}$.

RESULTS

I/S mixed-layer minerals from diagenetic series

The expandability of I/S mixed-layer minerals from a series of samples in the lower Eocene sediments of the Texas Gulf Coast decreases with depth (Perry and Hower, 1970). Chemical analysis from Howard (1981) shows that most I/S compositions are roughly distributed along a line between an illite and a low-charge montmorillonite in the M^+-4Si-R^{2+} system (Fig. 1). A high-charge expandable component, described by Howard (1981), is characterized by tetrahedral substitutions, as was determined by the Green-Kelly treatment. Figure 1A shows that this component cannot be of beidellitic type but rather is montmorillonite in an I/S mineral of high illite content.

The smectite component is in fact a low-charge montmorillonite, similar to that found by Horton et al. (1985) and Velde and Brusewitz (1986) in diagenetic shales. Its composition (Fig. 1) is remarkably similar to the average one given by Ramseyer and Boles (1986) for the highly expandable I/S from the San Joachin Valley Miocene sediments.

The maximum amount of illite in the I/S mixed-layer minerals does not exceed 82% according to Howard (1981). There is only a poor correlation between illite content (determined by XRD) and K (maximum value is 0.56) because the high interlayer charge appears to be compensated by the presence of large quantities of Na. Such a material might be called a vermiculite. Nevertheless, Figure 1 shows that the I/S composition line goes
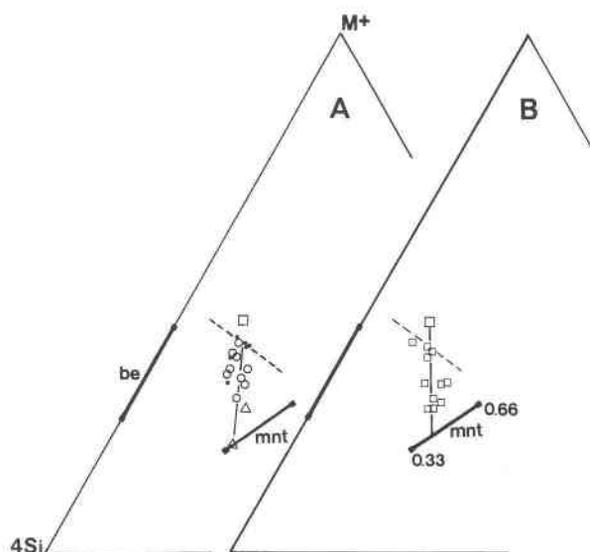

Fig. 1. Representation of I/S mixed-layer minerals in diagenetic formations (A) and hydrothermally altered tuffs (B) in the M^+-4Si-R^{2+} system. Compositions plotted here were given by Howard (1981) for I/S in sand (dots) and shale (circles) laminae of lower Eocene sediments of Texas Gulf Coast. Average compositions of smectite and I/S (triangles) in Miocene sediments in San Joachin Valley were found in Ramseyer and Boles (1986). The big square in A and in B represents the composition of pure illite from Rotliegend formation in the southern North Sea Basin (Nadeau and Bain, 1986). Compositions of I/S mixed-layer minerals plotted in B from Miocene volcanic glass in Waga-Omono district were found in Inoue et al. (1978). be = beidellite; mnt = montmorillonite; layer charges per O(OH) are given by numbers (0.33 and 0.66) and by the dashed line for 0.75.

toward the point representing the composition of an authigenic diagenetic illite similar to that from the Rotliegend formation in the southern North Sea Basin (Nadeau and Bain, 1986). This illite is characterized by a high interlayer charge, 0.87, but only 0.64 originates from the tetrahedral layer.

I/S mixed-layer minerals in a hydrothermal formation

I/S mixed-layer minerals from the Miocene tuffaceous sediments in Waga-Omono district in Akita Prefecture, Japan (Inoue et al., 1978), vary from 100 to 5% expandable layers (XRD determinations). Their compositions are roughly distributed along a line joining an $I/S_{0.75}$ and a montmorillonite (Fig. 1B). The smectite component has

TABLE 1. Coordinates of ideal muscovite, high-charge and low-charge beidellites, and montmorillonites in the M^+-4Si-R^{2+} system

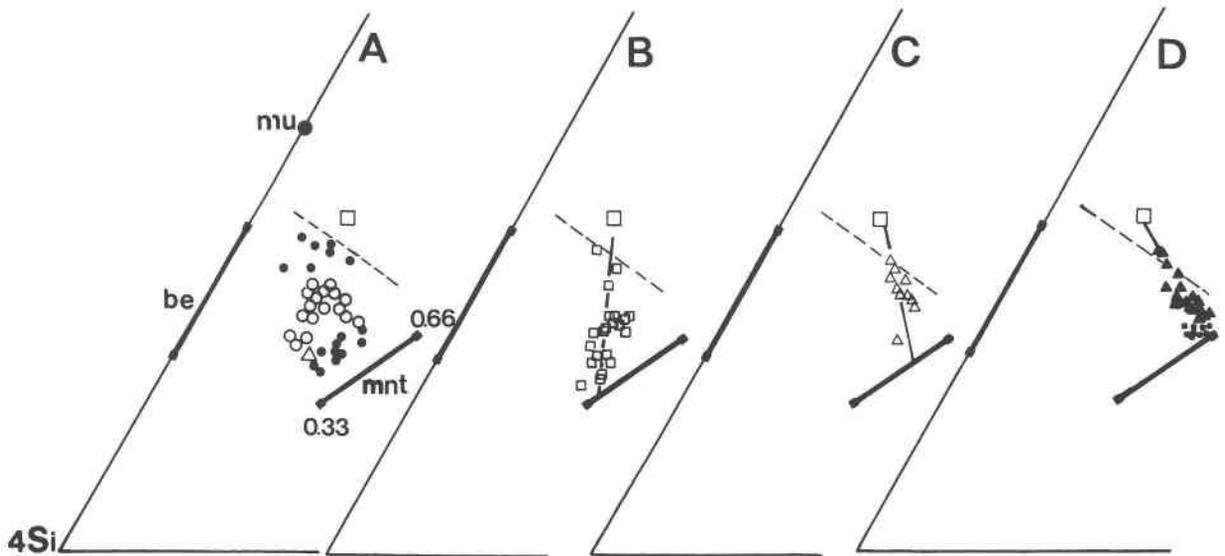|		M^+	4Si	R^{2+}
Muscovite	$Si_3AlO_{10}Al_2(OH)_2K$	57	43	0
Low-charge montmorillonite	$Si_4O_{10}Al_{1.67}R^{2+}_{0.33}(OH)_2M^+_{0.33}$	20	60	20
High-charge montmorillonite	$Si_4O_{10}Al_{1.34}R^{2+}_{0.66}(OH)_2M^+_{0.66}$	28	44	28
Low-charge beidellite	$Si_{3.67}Al_{0.33}O_{10}Al_2(OH)_2M^+_{0.33}$	26	74	0
High-charge beidellite	$Si_{3.34}Al_{0.66}O_{10}Al_2(OH)_2M^+_{0.66}$	44	56	0

Fig. 2. Representation of I/S mixed-layer minerals of different bentonite formations: Recent to Cretaceous (**A**) and Siluro-Ordovician (**B**, **C**, **D**) in the M^+-$4Si$-R^{2+} system. Big square = composition of Rotliegend illite; dots (Nadeau and Bain, 1986); circles (Eslinger et al., 1979); big triangle (Konta, 1986); small squares (part D only) = bentonite from Poland (Środoń et al., 1986); triangles = bentonites from the United Kingdom (Środoń et al., 1986); solid triangles (Brusewitz, 1986); solid squares (Huff and Türkmenoglu, 1981). mu = muscovite; be = beidellite; mnt = montmorillonite; dashed line = layer charge of 0.75.

a higher charge than the equivalent I/S minerals formed in diagenetic environments, as indicated by Horton et al. (1985) and Velde and Brusewitz (1986).

Nevertheless, in spite of the difference in composition of the montmorillonite component, the I/S composition line goes though the same high-charge illite point, which is very near that of the Rotliegend illite. As no 100% illite crystals were found in the Waga-Omono tuffaceous sediments, we do not know the maximum layer charge. The lowest detected expandability (XRD) in this sequence is 5% with a layer charge of 0.72.

I/S mixed-layer minerals in metabentonite formations

Several metabentonite deposits have been accurately studied from a mineralogical point of view (Huff and Türkmenoglu, 1981; Eslinger et al., 1979; Brusewitz, 1986; Środoń et al., 1986). The composition of nonmetamorphic bentonite is given in Konta (1986). Two populations of I/S mixed-layer minerals can be distinguished according to the age of their formation. It is interesting to note that the Cretaceous and Tertiary samples are characterized by a strong dispersion of compositions bounded by the smectite minerals beidellite and montmorillonite (Fig. 2A). On the contrary, the older Silurian and Ordovician samples show a linear relation between illite and montmorillonite components, thus corresponding to I/S compositions (Figs. 2B, 2C, and 2D). The layer charge of the smectite component is lowest in bentonites from Poland (Fig. 2B) and highest in the montmorillonite solid solution in bentonites from Sweden (Fig. 2D).

In extrapolating chemical data correlated with XRD de-

terminations, Środoń et al. (1986) showed that the fixed K in the illite component of I/S minerals from the older Paleozoic bentonites averages 0.75. This value was also found for I/S minerals from Ordovician bentonites from Sweden by Velde and Brusewitz (1986).

However, the lines joining the montmorillonite to the $I/S_{0.75}$ components of varying composition in the sequences converge toward a single composition that is a higher charge, $ill_{0.87}$ point, near the Rotliegend illite composition (Fig. 2).

I/S mixed-layer minerals and illite in metamorphic environments

Compositions of illites from nonmetamorphic to metamorphic environments in a continuous series were presented by Hunziker et al. (1986). Plotted in the M^+-$4Si$-R^{2+} diagram (Fig. 3), the nonmetamorphic illites are roughly distributed along the muscovite–high-charge montmorillonite line. These illites are in fact I/S mixed-layer minerals whose smectite content varies from 0 to 20% (determination by XRD). Their average layer charge is lower than 0.75. Hunziker et al. (1986) found that all of the nonmetamorphic illite-rich I/S minerals from his study area are of the *1Md* polytype.

Anchimetamorphic illites have a higher layer charge (between 0.80 to 0.87). The dominant polytype is *2M₁*. No evidence of I/S interstratification was detected by X-ray diffraction. In the M^+-$4Si$-R^{2+} diagram, the compositions of these illites are distributed along two lines: the high-charge $ill_{0.87}$-$mnt_{0.66}$ and the $ill_{0.87}$-phg_{max}, which is the mica of maximum phengite substitution composi-
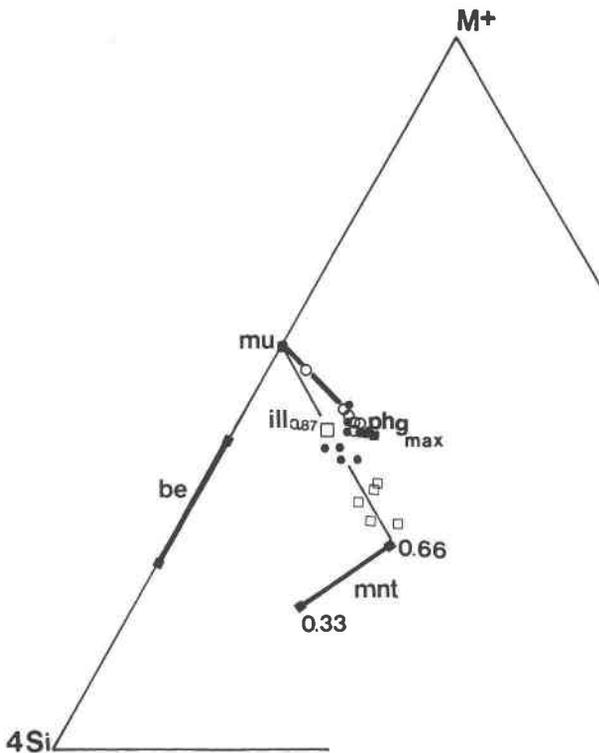
Fig. 3. Representation of nonmetamorphic $1M$ I/S mixed-layer minerals (small squares), anchimetamorphic illites (dots), and epimetamorphic micas (circles) from the Glarus Alps (Hunziker et al., 1986). mu = muscovite; phg_{max} = R^{2+}-rich phengite (Radoslovich, 1963); $ill_{0.87}$ = illite with a 0.87 layer charge per $O_{10}(OH)_2$; be = beidellite; mnt = montmorillonite.

tion in burial metamorphic rocks according to Radoslovich (1963): $(Si_{3.40}Al_{0.60})O_{10}(Al_{1.60}R_{0.40}^{2+})(OH_2)K$.

Epimetamorphic illites are very near true phengites as defined by Velde (1985). Their chemical domain fits well on the phengite line in the M^+-4Si-R^{2+} diagram (Fig. 4). They are a pure $2M_1$ polytype.

It is interesting to note that Inoue et al. (1988) have identified a change in mineral grain shape with change in polytype in hydrothermal I/S and illitic minerals. The low-charge, expandable minerals are lath shaped, whereas higher charged, illite minerals are basically hexagonal in shape. An electron micrograph presented by Nadeau and Bain (1986) shows that the Rotliegend mineral with a charge of 0.87 has both lath- and hexagonal-shaped crystals.

In summary, the representation of I/S mineral series from a given geologic environment shows that the smectite component is a montmorillonite of variable charge and that the high-charge I/S component is of constant charge, near 0.75. Epizone or metamorphic illites have a higher charge, 0.87. The most illitic I/S minerals have a lath-shaped, $1M$ structure, whereas higher-charge illites are of a hexagonal shape.
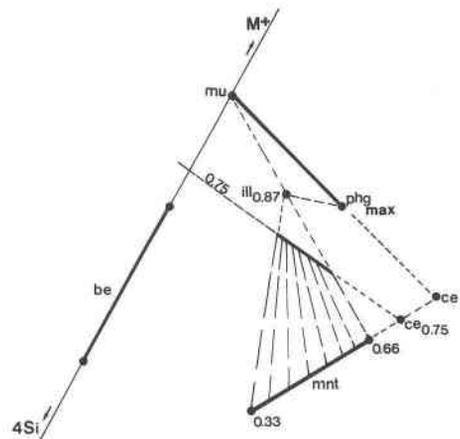

Fig. 4. Chemographic representation of smectites, I/S mixed-layer minerals, illite, and micas in the M^+-4Si-R^{2+} system. Bipole solid solutions are represented by heavy lines. Solid-solution tie-lines for I/S mixed-layer mineral series are symbolized by dashed lines. ce = celadonite.

DISCUSSION

The smectite component of I/S mixed-layer minerals

The geometric relations of I/S compositions in the M^+-4Si-R^{2+} system show that the smectite component of mixed-layer minerals is a montmorillonite whose interlayer charge varies between 0.33 and 0.66. The highest charge is found in metabentonites and the lowest in diagenetic formations (Velde and Brusewitz, 1986). Consequently, no beidellite component exists in most natural mixed-layer minerals. Thus, smectite of detrital or authigenic origin whose composition lies inside the beidellite-montmorillonite field must recrystallize or transform in order to join the $ill_{0.87}$-mnt line.

The compositions of end-members in the variable-charge montmorillonite solid solution in I/S mixed-layer minerals are found along the following low- and high-charge montmorillonites series:

$$Si_4O_{10}(Al_{1.34}R_{0.66}^{2+})(OH)_2M_{0.66}^+$$
$$Si_4O_{10}(Al_{1.67}R_{0.33}^{2+})(OH)_2M_{0.33}^+.$$
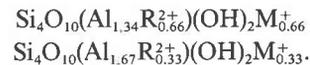
Intermediate compositions between these two poles of substitution in the smectite layer of the I/S minerals are governed by the $R^{2+}M^+ \leftrightarrow Al^{[6]}$ substitution.

The illite component of I/S mixed-layer minerals

In the I/S mixed-layer series from diagenetic, hydrothermal, or metasomatic environments, the extrapolated compositions of the illite component have a common characteristic: the interlayer charge is 0.87 and is mainly satisfied by K ions (Hower and Mowatt, 1966; Horton et al., 1985; Środoń et al., 1986; Velde and Brusewitz, 1986). When these I/S mixed-layer mineral series come from continuous geologic formations, their compositions plotted in the M^+-4Si-R^{2+} system are distributed along lines
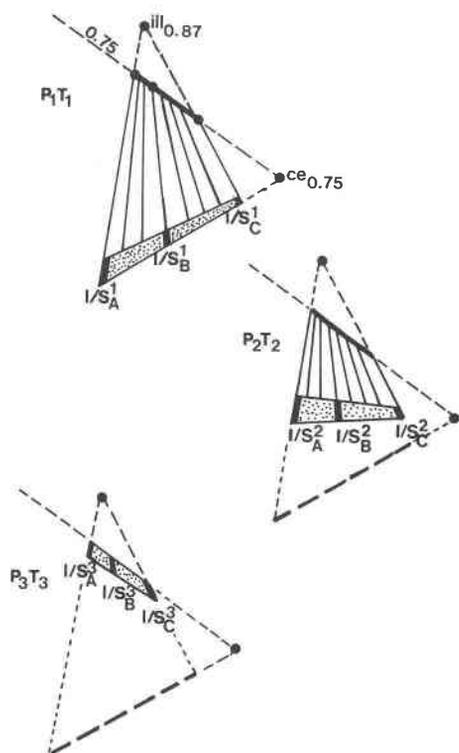
Fig. 5.   Representation of the I/S mixed-layer mineral solid solution (stippled areas) when P and T values vary from 1 to 3. The compositions of I/S phases are given for three series (A, B, C).

joining an I/S component having a constant layer charge of 0.75 with compositions along the $mnt_{0.33-0.66}$ solid-solution series. These lines of continuous I/S composition converge at a high-charge $ill_{0.87}$ point. However, the series does not reach the 0.87-charge illite end-member but stops at a value of 0.75 charge over a range of compositions in the different illite-montmorillonite series. The convergence to a common point means that this $ill_{0.87}$ (Fig. 5) is a pole of composition for I/S mixed-layer minerals while the 0.75 composition is only the end of each I/S series. We assume that the determinations by the several authors of 0% expandable layers at values below 0.87 charge is due to incorrect estimations from X-ray diffractograms. In fact, the mixed-layer minerals show an incomplete substitution between a highly illitic mineral and the illite end-member of 0.87 charge.

Solid solution and phase relationships in I/S mixed-layer minerals

One of the most important questions concerning mixed-layer minerals is whether the montmorillonite and the illite components should be regarded as independent phases or not (Zen, 1962). Garrels (1984), using ground water compositions in apparent equilibrium with the clay fraction of the rocks (data from Aagaard and Helgeson, 1983), concluded that the two-phase solubility model best

explained the data. This was substantiated by the experimental study of mineral solubilities by Sass et al. (1987).

From chemical and XRD data, it appears that there are series of I/S phases whose composition and structure vary continuously in composition (proportion of smectite and illite) between montmorillonites of different charge and layer composition and illite-rich phases whose charge is 0.75. The chemical substitution in the montmorillonite layers is of the Tschermak type ($AlAl = SiR^{2+}$). The end-member of the illite (high-K) component is of a unique composition, near that of the natural Rotliegend mineral. The I/S series thus form an incomplete mixed-layer solid solution.

In each I/S mixed-layer series the montmorillonite end-member maintains the same composition. This behavior is similar to a solid solution controlled by bulk chemical variables. Figure 5 shows the changing composition of each smectite end-point in the solid solution I/S mixed-layer mineral series as P and T change. The maximum smectite content of the series changes until the end-points of all of the series are an I/S of 0.75 charge. The illite end-member stays at constant composition, 0.87. In Figure 5 the points I_A-I_B-I_C represent the most illite-rich point in the I/S series and I/S_A, I/S_B, I/S_C the end-points of the mixed-layer series with the greatest amount of smectite permitted by the P and T conditions, which increase from 1 to 3. Thus each I/S phase from P_1, T_1 to P_3, T_3, i.e., I/S_A^1, I/S_A^2, and I/S_A^3, forms a chemical or chemographic series along the line I_A^1-S_B^1 in Figure 5. These are the same lines represented by natural mineral suites shown in Figures 1 and 2. The series of I/S mineral bulk compositions follows a line in M^+-$4Si$-R^{2+} space because the individual I and S layers do not change composition for a given geologic (chemical) environment. Only the proportion of I to S changes as a function of pressure and temperature. Such a behavior suggests that each suite of natural minerals follows a thermodynamic constraint that can be described as tie-line solid-solution behavior. When a bulk chemical composition is fixed, the phases change their composition in a regular manner as a function of P and T variations. Thus the I_A/S_A series of I/S minerals are chemically controlled by the presence of one or more other phases in the rock, all of which lie on the same chemical plane in chemical space. The series is incomplete (maximum charge of 0.75). This apparent solid-solution behavior contradicts the strict two-phase solubility model that seems to be indicated by data used in solution chemistry.

Low- and high-charge illite

The lowest expandable phase in the I/S mineral suite (Figs. 1 and 2) has a charge of 0.75. XRD generally indicates less than 10% expandability, and the crystal morphology is, at least in hydrothermal minerals, lath-shaped (Inoue, 1986; Inoue et al., 1988). However, higher-charge illites of low or zero expandability are found in high-grade diagenetic or epimetamorphic terranes. The diagenetic Rotliegend diagenetic mineral sample of high-

charge (0.87) illite (Nadeau and Bain, 1986) shows both lath and hexagonal crystal shape. Hydrothermal samples of lowest expandability show hexagonal shape (Inoue, 1986). The question must be asked as to why K-rich minerals change crystal shape near the mica composition.

A study of minerals in the transition of low-expandability I/S mixed-layer minerals to phengitic illites in metamorphic environments observed by Hunziker et al. (1986) gives a possible answer to this question. These authors determined that the b parameter decreases from 9.030 to 9.000 Å when the amount of interlayer increases from 0.70 to 0.90 per formula unit. The $1Md$ polytype disappears at very low expandability, and the $2M_1$ polytype becomes dominant. Thus, similar minerals have different cell dimensions. We propose that the morphological different—lath-shaped I/S minerals with a low charge (0.75) and hexagonal higher-charge illites (0.87)—indicates a miscibility gap in the I/S mineral series. There is no reason for a mineral to change its growth habit during normal crystal growth under the physical and chemical conditions as described by Inoue et al. (1988) except for a change in chemical, hence crystallographic, characteristics (b dimension). We suggest then that the lath shape $1M$ and hexagonal $2M_1$ minerals are separate phases.

The high-charge illite-phengite transition

The progressive transformation of smectite to a mica phase through mixed-layer minerals is not the only way to form illite. Direct precipitation from high-temperature solutions was observed in hydrothermal environments. Data from altered volcanic deposits in the Tertiary Silverton caldera (Eberl et al., 1987) show that illite compositions do not fall into the $ill_{0.87}$-$mnt_{0.33-0.66}$ subsystem but are dispersed toward the R^{2+}-poor side of the M^+-$4Si$-R^{2+} system (Fig. 6). Most of these illites precipitate with Al-rich phases (dickite), sulfides (pyrite), sulfates (jarosite), or oxides (goethite). The pH and R^{2+} amount in the hydrothermally altered rocks are probably too low for montmorillonite to form. In that case, the composition of the illite phase is not chemically buffered as it is when a continuous series of mixed-layer minerals is formed. Except for three samples, the Silverton caldera illites are of pure or dominantly $1M$ polytype. Their compositions lie between the beidellitic $ill_{0.85}$–phengitic $ill_{0.87}$ and I/S$_{0.75}$ lines (Fig. 6). The $2M$ phase lies to the K-rich side of this line.

Data from phyllic alteration in a porphyry copper deposit (Beaufort and Meunier, 1983) show that pure $2M_1$ polytype compositions lie between the muscovite-phg$_{max}$ and the beidellitic $ill_{0.85}$ and phengitic $ill_{0.87}$ lines (Fig. 6). The R^{2+} contents are probably somewhat overestimated because total Fe was arbitrarily considered as Fe^{2+}. Thus, the beidellitic $ill_{0.85}$–phengitic $ill_{0.87}$ line appears to be the boundary between the $1M$ and $2M_1$ polytype domains.

Figure 6 shows that the composition of the $ill_{0.87}$ corresponds to the maximum octahedral R^{2+} content possible in high-charge illite solid solution. Introduction of more R^{2+} component in octahedral position necessitates
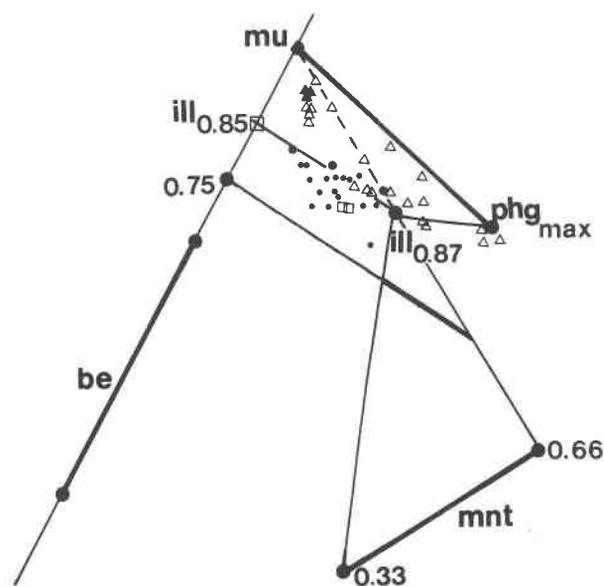

Fig. 6. Representation of the compositions of high-temperature illites. Silverton caldera hydrothermal system (Eberl et al., 1987): pure $1M$ polytype (squares); $1M$-dominated polytype (small dots); $2M_1$ polytype (big dots). Phyllic veins in the Sibert porphyry deposit, France (Beaufort and Meunier, 1983): $2M_1$ polytype from central vein deposit (solid triangle) and adjacent altered wallrock (triangles).

an increase of the layer charge (Velde, 1985). Then a phengitic phase crystallizes, as was shown by Bishop and Bird (1987) in the high-temperature zones of the Coso Hot Spring geothermal field. The compositions between $ill_{0.87}$ and phengite were also observed in metamorphic environments between the anchizone and the epimetamorphic zone in the Glarus Alps (Hunziker et al., 1986).

It appears that the compositions of illitic minerals lie between the beidellitic $ill_{0.85}$, phengitic $ill_{0.87}$, maximum phengite, and muscovite. These are $2M$ phases and would have a hexagonal growth form.

SUMMARY

It appears that I/S mineral suites (bentonites and diagenetic shale minerals) fall into linear series when plotted in M^+-$4Si$-R^{2+} coordinates. These series suggest that more or less identical chemical conditions occurred while P and T changed. The systems are buffered chemically, and the limit of solid solution toward smectite is determined by P and T.

The I/S series of phases, i.e., those showing significant expandability, appear to be lath shaped in the range of high illite content. Highest charge seems to be near 0.75 for this I/S series. It is incomplete toward the illite component.

High-charge $ill_{0.87}$ has a different crystal shape from that of the lowest expandable minerals in the I/S series. This suggests that a high-charge illite is crystallographically distinct from elements in the I/S minerals. Bulk chemical

constraints will control the presence or absence of I/S minerals, allowing the coexistence of illite and kaolinite at physical conditions that would normally produce an I/S mineral.

As the high-charge $ill_{0.87}$ is a compositional pole, the I/S $ill_{0.75}$-mnt mixed-layer minerals series can be considered as a partial solid solution between $ill_{0.87}$, low-charge $mnt_{0.33}$, and high-charge $mnt_{0.66}$.

ACKNOWLEDGMENTS

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