COMPOSITIONAL VARIATION IN COMPONENT LAYERS IN NATURAL ILLITE/SMECTITE

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Abstract—Published chemical data for suites of mixed-layer minerals from diagenetic sedimentary rocks, hydrothermally altered tuffs, and a metasomatic bentonite bed indicate that the layer charge and composition of the different components of illite/smectite (I/S) differ from one geological environment to another. It appears that the composition of the elemental smectite and illite layers in the I/S is more or less constant for samples within each geologic setting. In the examples considered, the smectite layers are predominantly montmorillonitic in character (i.e., the charge is in the octahedral site), whereas the illite layers show different types of charge sites, depending upon the suite studied. Illite layers appear to have about the same charge in all three suites studied, slightly more than 0.7 per $O_{10}(OH)_2$ unit, whereas the smectite layers in the different suites range in charge from about 0.3 to 0.7 per $O_{10}(OH)_2$ unit. Cation-exchange capacities reflect these differences in charge, although not ideally. The differences in the composition of the component layers in each geologic suite of mixed-layer clays are probably due either to differences in the bulk chemistry of the rocks in the different suites or to differences in intensive variables, such as temperature and pressure, of the regime under which they have formed.

Key Words—Bentonite, Cation-exchange capacity, Diagenesis, Hydrothermal, Illite, Interstratification, Smectite.

INTRODUCTION

Mixed-layer clay minerals have been reported in many low-temperature geological environments. Their distinctive X-ray powder diffraction diagrams have led to the rather widespread use of illite/smectite (I/S) to determine mineral facies at low temperatures (see Velde, 1985, for a survey of this problem). I/S, however, does not occur in sedimentary rocks of all bulk compositions; the host material must be dominated by silica and alumina. The geological environments in which the I/S is formed include burial diagenesis in sedimentary rocks, hydrothermal alteration of acidic rocks, high geothermal activity where acidic or pelitic rocks are present, and metasomatic alteration of glassy acidic materials (bentonites and metabentonites).

The most striking characteristic of the I/S is the gradual change in composition brought about by a variation in the proportion of the mixed-layer components. The almost universal occurrence of this continuous variation allows I/S to be described in terms of the solid solution of two components; in fact, it is useful to treat these minerals as a solid solution series when considering their thermodynamic properties (see, e.g., Aagaard and Helgeson, 1983). If such use is to be made of the chemical properties of mixed-layer minerals, however, the component layers should have the same compositions in all occurrences; i.e., each layer of

smectite should have the same composition as each other smectite layer in the mineral, and each smectite layer in a given mixed-layer mineral should be of much the same composition as the smectite layers in the I/S found in a different geologic setting. In other words, the component layers in the I/S formed during burial diagenesis should have the same compositions as those formed by hydrothermal alteration. If the compositions of mixed-layer components are different in different environmental settings, even though the bulk composition of the systems are similar, the thermodynamic information cannot be used interchangeably from one series to another. If the compositions of the mixed-layer components are the same for different series, however, intensive and extensive variables will act on the minerals in the same way, and these minerals can be used as indicators of paleoconditions.

Inoue and Utada (1983) suggested that differences between the charge on the illite layers of hydrothermal I/S and the illite layers in the I/S in the shale suite of Hower and Mowatt (1966) could be due to differences in the geological environment. The present paper attempts to define these differences to a greater extent and to demonstrate the importance of variations in layer composition of the smectite and illite components of I/S.
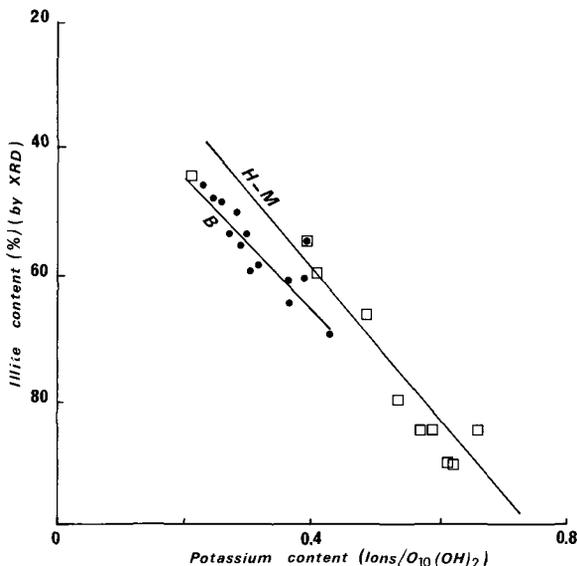
Figure 1. Summary of relations between smectite content as determined by X-ray powder diffraction and K content. H-M = correlation of Hower and Mowatt (1966). Solid circles show data for samples used in the present study, B = data (shown as squares) from Brusewitz (1986). Data from Inoue *et al.* (1978) fall between these lines.
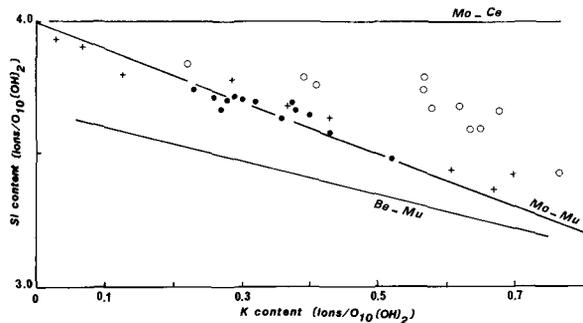

Figure 2. K vs. Si content of mixed-layer minerals, calculated for $O_{10}(OH)_2$. Solid circles = metasomatic bentonites (Brusewitz, 1986); crosses = tuffs from Inoue *et al.* (1978); circles = diagenetic shale minerals from Hower and Mowatt (1966). Lines show beidellite-muscovite (Be-Mu), montmorillonite-muscovite (Mo-Mu), and montmorillonite-celadonite (Mo-Ce) compositional trends.

METHODOLOGY

Type of data obtained

Three commonly measured properties of I/S are: bulk chemical composition, exchangeable ions and cation-exchange capacity (CEC), and X-ray powder diffraction (XRD) estimates of the smectite component in the clay. These independent determinations are generally sufficient to establish the character of the layer types in the I/S structure. The range in composition of the minerals of a geologic suite, however, must be sufficiently great to extrapolate the values to the endmember compositions. In the present study, three sets of published data have been used to compare the compositions of the different component layers of I/S minerals. The CEC was obtained using Sr as the exchanged ion, and the Reynolds-Hower computer program (Reynolds, 1984) or an equivalent was used to estimate the smectite content by XRD. Identification of the I/S polytype was made using the criteria described by Reynolds (1984).

The first data set is from the classic study of Hower and Mowatt (1966) on minerals affected by burial metamorphism or diagenesis. The samples selected for use here were designated by the authors as shales. All material labeled as metabentonites was excluded. Interlayer ion estimates, designated as "x" by the authors, were used for the M⁺ or exchange-ion component. The minerals occur commonly with chlorite and also with kaolinite (five samples). Mixed-layer mineral stacking types were R=1 and R=3.

The second data set was reported by Inoue *et al.* (1978) for minerals formed in acidic tuffs by hydrothermal alteration. Here, I/S is accompanied by alkali zeolites, analcime, kaolinite, and locally chlorite. Samples reported on pages 131 and 127 of Inoue *et al.* (1978) were used in the present study. Because some samples lack exchange-capacity determinations, the number of data points on the illustrations is not the same for all comparisons of chemical and physical properties. Estimates of the smectite content of the highly expandable material (samples A and B, p. 127) were corrected using the methods of Reynolds for nonordered minerals (Reynolds, 1980). Mixed-layer mineral stacking types were R=0, R=1, and R=3.

The third data set used was from samples described as bentonites of metasomatic origin (i.e., isothermal process occurring under chemical gradients) investigated by Bystrom (1956) and Velde and Brusewitz (1982). Details of the determinations are given in Brusewitz (1986). The samples are from the Stora Mossen locality at Kinnekulle, Sweden; the material in the thick "B" bed and the Kullatorp core "C" layers was used. The accompanying mineral is kaolinite; I/S stacking types were R=0 and R=1.

INTERPRETATION

Chemistry

The relation between the K content and the composition of the mixed-layer minerals is examined in Figure 1. The K content of the minerals is assumed to be closely related to the percentage of nonexpandable (illite) layers in the mineral, as has been found by Hower and Mowatt (1966), Inoue and Utada (1983), and Brusewitz (1986). Figure 1 shows the Hower and Mowatt and Brusewitz data sets; the data from Inoue and Utada (not plotted) fall between these lines.
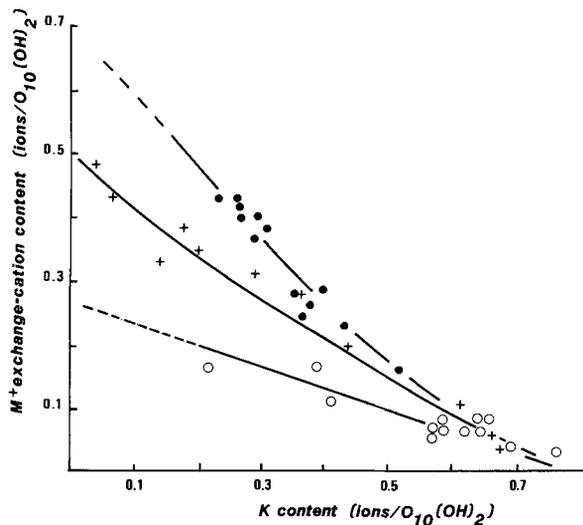
Figure 2 shows the relations between the Si and K

Figure 3. K content vs. M^+ exchangeable cations, i.e., Na^+ + $2 \times Ca^{2+}$ content. Trend lines were visually estimated; the data are obviously slightly nonlinear. Solid circles = metasomatic bentonites; crosses = tuffs; open circles = shales.

Figure 4. Correlation of illite content as estimated by X-ray powder diffraction and using the K/K_{max} ratio, i.e., K ions, for a sample divided by the maximum potassium content ($K = 0.75$) for a pure illite structure estimated from the data presented in Figure 3. Solid circles = metasomatic bentonites; crosses = tuffs; open circles = shales. The resulting curves, visually estimated correlation line is drawn through the 0 and 100% illite points.

contents of I/S from the three suites. The lines in the illustration indicate ideal series between (1) a tetrasilicic montmorillonite having no tetrahedral charge and muscovite (i.e., an aluminous mica having a tetrahedral occupancy of 3 Si); (2) beidellite (having 3.7 tetrahedral Si) and muscovite; and (3) tetrasilicic montmorillonite and the tetrasilicic mica, celadonite. The I/S samples examined plot between the montmorillonite-muscovite and the montmorillonite-celadonite lines.

At the potassic (mica) end of the mixed-layer mineral series, the scatter of compositions indicates a tendency towards a celadonite component (i.e., charge originating in the octahedral layer) in the illite layers of the I/S from diagenetic shales. The line joining the muscovite and the tetrasilicic montmorillonite types seems to fit best the I/S in the tuff and bentonite suites. The data points slightly below the muscovite-montmorillonite line at the low K end of the series suggest that a small amount of charge originates in the tetrahedral site as well. In the smectite layers of the I/S minerals, most of the charge is due to octahedral (montmorillonite-type) substitution. Thus, the composition of the illite component in I/S from the different suites differs, whereas a certain convergence can be seen in the illustration for the site of charge for the smectite component (low K composition). It is apparent that the illite layers of the I/S contain different sites of ionic substitution depending upon the geological environment in which they formed.

The K (illite) content also correlates with the other interlayer ions present. A certain amount of exchangeable K must, however, belong to the illite layers, but
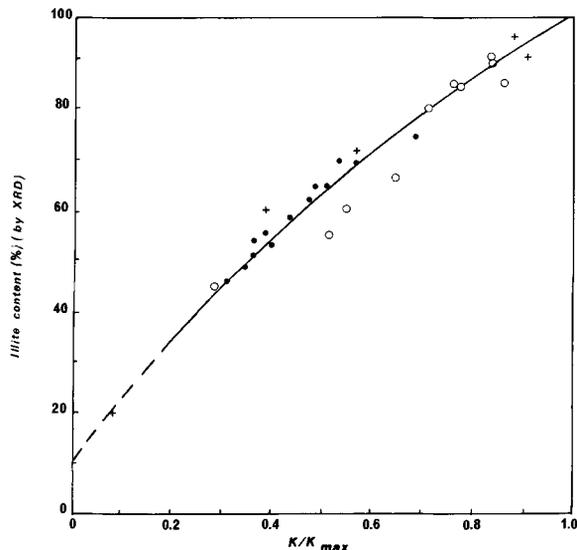
the quantities are not large, as was established by Hower and Mowatt (1966) and Inoue et al. (1978). Inasmuch as neither paragonite nor margarite appear to form at low temperatures in nature (Velde, 1985), all of the Ca and Na ions were assumed to be present in the smectite layers. Figure 3 is a plot of K vs. Ca + Na (M^+) for the three data sets and may be considered to represent illite vs. smectite.

The relationships shown in Figure 3 are remarkable in that the three trends converge at high K content (~ 0.7 $K/O_{10}(OH)_2$), as found for I/S minerals from shales and metabentonites by Hower and Mowatt (1966). This convergence indicates that the illite layer of the I/S has the same charge regardless of its origin. In addition, each data set gives a different extrapolated value for interlayer ion occupancy for the smectite component (at essentially zero K content). The bentonite samples give the highest M^+ values, and the I/S minerals from shales, the lowest M^+ values. These extremes represent nearly a threefold difference in M^+ content. This result suggests that a large difference exists in the charge on the smectite layers of the I/S of the different suites. The smectite layer charge does not vary greatly, however, for I/S samples within a given suite.

Correlations of physical and chemical properties

To corroborate the compositional trends in the I/S discussed above, other structural parameters had to be
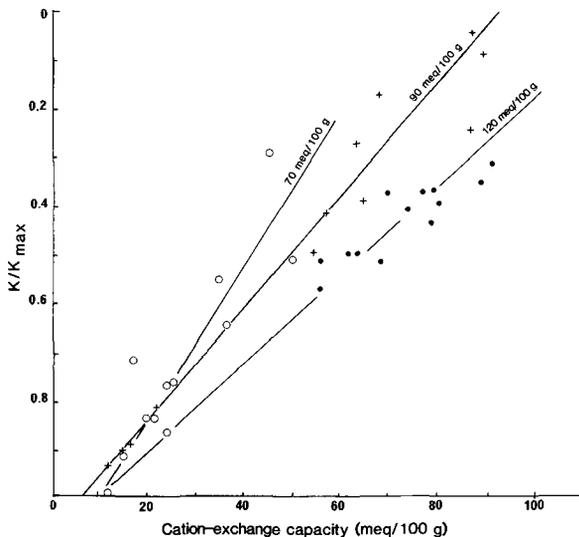
Figure 5. Cation-exchange capacity vs. percentage of illite estimated by the K/K_{max} method. A minimum cation-exchange value of 5–10 meq/100 g was found for the micaceous end member of each series. Dots = metasomatic bentonites; crosses = tuffs; circles = shales.
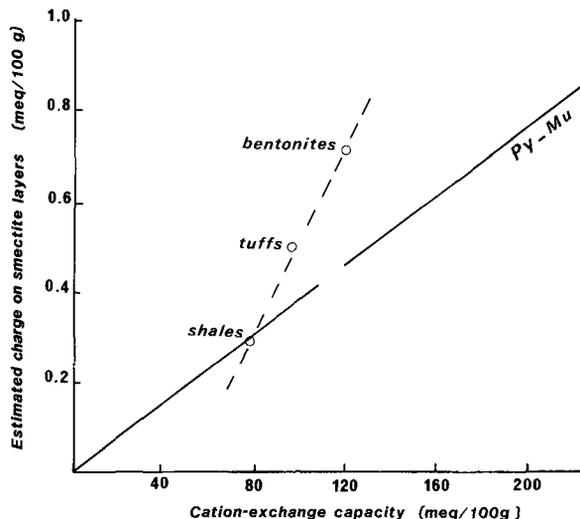

Figure 6. Extrapolated cation-exchange capacity for pure smectite layers vs. estimated charge on smectite layers using extrapolated values from Figures 2 and 3. Dashed line shows trend for natural samples; full line shows ideal values for a hypothetical series of 2:1 layers between muscovite (Mu) and pyrophyllite (Py) compositions, i.e., having a charge ranging from 1.0 to 0.0 per $O_{10}(OH)_2$.

measured that did not depend on the chemical composition of the samples. Two independent measurements were made to characterize the percentage of smectite or illite layers in the I/S, namely, X-ray powder diffraction characteristics and cation-exchange capacity. Ideally, these two parameters should be interrelated because they both depend on the chemical and physical character of the individual layers in the structure. Thus, each measurement should have been related to the percentage of smectite and illite layers in the I/S.

Illite and potassium content. Hower and Mowatt (1966) showed a nearly linear relation between the K content and the XRD estimate of the proportion of illite layers in I/S which they investigated (i.e., those used in the present study, as well as some metabentonites). Another method of assessing the smectite content of I/S, based on the conclusions of Hower and Mowatt (1966), makes use of an estimate of the composition of the pure illite component using Figure 3 which indicates that pure illite will contain 0.75 K ions/$O_{10}(OH)_2$ for all I/S minerals (at least for all those studied here). The expression K/K_{max} can be used to give the percentage of illite layers in each sample, where $K_{max} = 0.75$ and K = the value for the sample. To test the validity of this estimate, the illite content based on K/K_{max} was plotted against that determined by XRD (Figure 4). A correlation between the two methods exists for samples from all of the three suites examined here; the plot is reasonably linear in the range 30–100% illite layers. These data yield a maximum deviation of 12% illite layers about the visually estimated correlation line. The correlation

line passes through 10% illite layers using the XRD method when the chemical method shows no illite present.

An estimate of the smectite content was made using the extrapolated interlayer ion content of the samples (Na + 2Ca) compared with the percentage of smectite layers estimated by XRD for each of the suites of I/S (0.3 for shales, 0.5 for tuffs, and 0.7 for bentonite). A plot of percentage of smectite layers (chemical) vs. percentage of smectite layers (XRD) shows the same correlation as for the illite estimates, suggesting that the interlayer ion concentrations reflect the proportion of smectite layers in the I/S.

Because chemically analyzed samples are more abundant than those characterized by XRD in the studies used here, the chemical data have been used to estimate I/S composition. To this end, the relationship of K content and percentage of illite layers seems to be more widely used than the estimates of smectite content; however, a slight difference will exist depending upon which method is used to estimate the illite content of the mixed-layer mineral.

Cation-exchange capacity and illite content. Using K/K_{max} as a measure of the illite content of each I/S sample, the CEC appears to be a function of the illite content of the I/S in each of the three suites. Because the remaining layers in a mixed-layer phase should represent the smectite content of the structure, the illite content will be inversely related to the CEC if the CEC is proportional to percentage of smectite layers. Figure
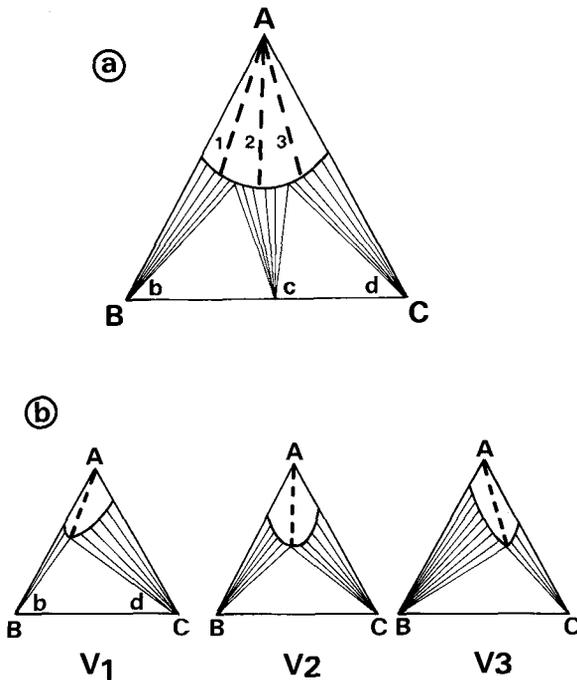
Figure 7. Representation of the possible controls which give rise to the three series of mixed-layer minerals investigated in this paper. (a) Bulk chemistry controls the solid solution series. Solid solution composition varies between the dashed lines in the presence of phases b and c, or c and d toward A as temperature increases. Tie lines remain the same for all conditions of intensive variables. (b) Variations in the intensive variable V_i affect the solid solution composition. Mineral assemblage is a + b + d for all conditions of intensive variables. Increase in temperature gives a decrease in solid solution.

5 shows the relation between the illite content, as determined by the K/K_{max} method, and the CEC of the samples. Even though the data are somewhat scattered, a different trend can be seen for each of the three geologic suites investigated. The extrapolated values of exchangeable ions ($M^+ = Ca + Na$) in Figure 3 indicate that the charge on the smectite layers is fundamentally different in the different suites; thus, the CEC of each smectite layer should be different in the different suites. The low-charge smectite units in the I/S have a lower CEC than do other smectite units. The highest CEC value was 120 meq/100 g for the bentonite samples; the tuff sequence gave a maximum value of 90 meq/100 g; and the shale smectite layers gave a value of 70 meq/100 g.

Cation-exchange capacity and charge on the smectite layer. The relationship between charge on the smectite layers and CEC of these layers is shown in Figure 6. From comparison of measured CEC values with the value calculated for an ideal beidellitic structure (the muscovite-pyrophyllite compositional trend), the CEC

of higher charged minerals is lower than ideal. Similar nonideal CEC can be seen in the data of Grim and Kulbicki (1961) and Chen and Brindley (1976) for natural, fully expandable minerals. Similar CECs were found for synthetic dioctahedral smectites in the beidellite-montmorillonite series (Velde, unpublished). The ideal and observed values correspond to a charge of about 0.3 $K/O_{10}(OH)_2$ in both synthetic and natural smectites. Descriptions of inhomogeneities in charge density and amount of charge on natural smectites have been given by many authors recently (see, e.g., Talibudeen and Goulding, 1983; Stul and Mortier, 1974). Whatever the reason for the differences in charge on the smectite layers in the I/S, the CEC does not appear to follow layer charge in an ideal manner for the three suites of I/S examined here.

Recapitulation. The observations made on the compositions of the minerals in the three suites of I/S clays considered here can be summarized as follows:

1. Illite layers have a charge which is satisfied by about 0.75 $K/O_{10}(OH)_2$ for all of the I/S minerals in the three suites.
2. The site of charge in the illite layers varies, some having an octahedral and others a more tetrahedral charge. These substitutions can be considered as celadonite- and muscovite-type substitutions.
3. Smectite layers in all of the I/S have a charge concentrated in the octahedral site (montmorillonite-like).
4. The charge on the smectite layers varies from one suite to the other, but is apparently constant within a given suite. Smectite layer charges range from 0.3 to 0.7 per layer in the samples considered here.
5. The CEC per smectite layer in the mixed-layer minerals follows the charge on each layer, but not in an ideal manner.

DISCUSSION

The individual component layers in the I/S appear to be more or less constant in composition within each suite; a conclusion indicated by the strong linear relationships between the chemistry and the physical properties of the minerals shown in Figures 1-5. Thus, the factors that caused a given I/S to form appear to have been the same in all three environments. In other words, for a given kind of parent material or geologic setting—diagenetically modified shale, hydrothermally altered tuff, or metasomatic bentonite—the chemistry of each kind of component layer in the mixed-layer I/S clays is essentially the same over a wide range of I/S proportions.

Based on the geologic environments of the samples examined here, it is apparent that the tuff I/S formed over a range of temperatures that accompanied the hydrothermal alteration. Such a thermal variation must

have caused the differences in solid solution (smectite content), according to Hower *et al.* (1976). The shales of Hower and Mowatt (1966) most likely show the same effects although they come from different areas and are of different geologic age. On the other hand, the bentonites represent minerals formed at the same temperatures as a result of variation in the K activity of the altering solutions (Velde and Brusewitz, 1982). It is evident that the differences in the composition of the smectite and illite layers of an I/S can be of either chemical or physical origin, i.e., due to the effects of extensive and intensive variables of the system.

These two effects can be represented schematically assuming the intensive and extensive parameters to be the agents which produce the differences in chemistry of the smectite and illite layers. In Figure 7a, extensive variables fix the type of solid solution, which does not change with temperature. The phases present are a function of bulk composition. The extent of solid solution is determined by the temperature, and its composition lies between the dashed lines in the figure for a given assemblage of accompanying phases. From petrographic observation, the phase assemblage will determine which line of solid solution will occur for the phase of variable composition. For example, if phases c and b are present, as seen in Figure 7a, the solid solution composition will lie between the dashed lines 1 and 2.

A second effect on the composition of a solid solution series can be that of an intensive variable, such as pressure or the chemical potential of a species, such as silica or K⁺. In Figure 7b, a change in the type of substitution of a solid solution series is affected by differences in the intensive variable V_i, whereas temperature changes the extent of solid solution towards A without changing the substitutional type. The different orientation of the dashed line of the solid solution mineral shows the effect of differences in V_i. In this example, the phases present (A + b + c) are always the same even though the composition of the solid solution will change depending upon the different values of the intensive variables V_i.

The above examples are of more than theoretical interest. From the available data for diagenetic pelitic series and those occurring under geothermal gradients in volcano-sedimentary materials, a definite tendency is present for diagenetic minerals to be significantly transformed (i.e., an increase in the illite content of the I/S) at temperatures near 50°–80°C (Perry and Hower, 1970; Hower *et al.*, 1976; Schmidt, 1973; Boles and Franks, 1979; Weaver and Beck, 1971). The same change has been noted at higher temperatures in series of altered tuffs and other volcanic rocks (Steiner, 1968; Aoyagi and Kazama, 1980; Pevear *et al.*, 1980). From the discussion presented here, the composition of the minerals or their general chemical system could be the

primary cause of this difference in thermal stability. The data of Hoffman and Hower (1979) show significantly different smectite contents of the I/S in adjacent shales and metabentonites. Rock type clearly played a role in the composition of the mixed-layer clay, because the P-T conditions of the adjacent rocks were the same during diagenesis. In any event, the role of the starting compositions of the materials must be considered when attributing a paleotemperature to a given suite of argillaceous rocks.

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