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MONTMORILLONITE/ILLITE STABILITY DIAGRAMS

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Abstract—Chemical activity diagrams, prepared to illustrate the properties expected if mixed-layer montmorillonite/illite is regarded as a solid solution, are compared to those derived from a treatment of these materials as a mixture of two phases. If the system is a solid solution, the coexisting aqueous solution should range from higher dissolved silica contents in the presence of kaolinite and a montmorillonite end member to lower dissolved silica in the presence of kaolinite and an illitic end member. Silica concentration in the aqueous solution might vary by a factor of as much as six. If the system is two phase, the silica content of a solution in equilibrium with kaolinite and both phases would be fixed at a given T and P, as would a solution equilibrated with both phases and K-feldspar. In the absence of a third phase, silica in equilibrium with both phases should be nearly constant, but increase with increasing ratio of K^+/H^+ in solution. Available data on coexisting aqueous solutions apparently are more nearly consistent with two phases than with a solid solution.

Key Words—Chemical activity diagram, Illite, Mixed layer, Montmorillonite, Phase, Solid solution, Stability.

INTRODUCTION

The genesis and phase relations of mixed-layer montmorillonite/illite clays have been the subjects of much research and comparable controversy over the last 20 years. The following aspects of genesis, taken chiefly from the works of Hower and his colleagues (Hower and Mowatt, 1966; Perry and Hower, 1970; Hower *et al.*, 1976), seem to be generally accepted.

Illite/montmorillonite interlayered materials are composed of two discrete species; one is montmorillonite with low interlayer charge. Its interlayers are hydrated by at least two layers of water molecules and have interlayer spacings at unit water activity of 15 Å or more. Most of the negative charge of montmorillonites is attributable to substitution of divalent cations in octahedral positions; in some montmorillonites there is no substitution of other ions for silicon in tetrahedral positions and hence no resultant tetrahedrally based negative charge. Cations exchange freely in the hydrated interlayers of montmorillonites; exchange energies for divalent cations are usually less than 1 kJ per formula weight (Garrels and Tardy, 1982). Energies for exchange between smaller, hydrated ions, such as Na^+, and larger, slightly hydrated ions, such as Cs^+, may be as large as 3 kJ, but the overall selectivity among cations by hydrated interlayers is so slight that montmorillonite interlayers characteristically are occupied simultaneously by several cations in significant percentages (>10%).

The second species, illite, is made up of layers interstratified with the montmorillonite layers and formed by diagenetic alteration of original montmorillonite layers. Illite layers have a 10-Å spacing. The interlayers are dry and are occupied almost exclusively by K^+. The K^+ is exchangeable, but so slowly and only by such strong solutions that it is usually described as "fixed potassium." Illitic layers have a total interlayer charge of −0.80 to −0.82 per formula weight (Hower and Mowatt, 1966). Most of the charge stems from replacement of tetrahedral silicon by trivalent cations, chiefly Al^{3+}.

In nature, a typical layer of montmorillonite is converted to a typical layer of illite by a reaction such as the one below:

$$\underset{\text{montmorillonite}}{K^+_{0.33}(Al_{1.50}Fe^{3+}_{0.23}Mg^{2+}_{0.27})(Al_{0.06}Si_{3.94}O_{10}(OH)_2} + \underset{\text{feldspar}}{0.47KAlSi_3O_8} = \underset{\text{illite}}{K^+_{0.80}(Al_{1.50}Fe^{3+}_{0.23}Mg^{2+}_{0.27})(Al_{0.53}Si_{3.47})O_{10}(OH)_2} + \underset{\text{quartz}}{1.88SiO_2}.$$

In the above reaction, no change in the composition of the octahedral layer takes place in the conversion of montmorillonite to illite. This is true in many natural assemblages; the extensive data of Hower and Mowatt (1966) show no trends of octahedral composition with increasing percentage of mixed-layer illite. Thus, the change to illite layers does not *require* octahedral change. Other investigators (e.g., Inoue *et al.*, 1978) have noted octahedral compositional changes accompanying the formation of illite layers. In the ongoing discussion only the simpler case of constant octahedral composition will be considered.

The conversion of a single, isolated montmorillonite layer to an illite layer would clearly be a phase change—there are marked structural differences between them.

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The basic question, discussed clearly by Zen (1962), is whether interlayering of two phases on an essentially molecular scale should be considered one phase or two. The question resolves as to whether, in an intimate mixture, there is so much interaction between the substances that the properties of the constituent phases are modified strongly. The phase rule can be applied in devising tests to distinguish a two-phase mixture and a one-phase solid solution. A two-phase system restricts the composition of a coexisting aqueous solution in equilibrium with it more than does a solid solution. The ensuing discussion attempts to determine the characteristics of aqueous solutions coexisting with interlayered montmorillonite/illite that might permit resolution of the controversy.

SOME COMPOSITIONAL RELATIONS OF REAL MIXED-LAYER MONTMORILLONITE/ILLITES

As indicated above, the data of Hower and Mowatt (1966) consist of a large number of analyses of mixed-layer montmorillonite/illites. Also, they constitute a system for which no change in octahedral composition is required to change a montmorillonite into an illite. Figure 1 is an adaptation of Hower and Mowatt's Figure 10 with a few analyses added from Tardy and Fritz (1981). The bulk compositions of the mixed-layer montmorillonite/illites are described by Hower and Mowatt in terms of the components, $KAl_3Si_3O_{10}(OH)_2$, $KAlMgSi_4O_{10}(OH)_2$, and $Al_2Si_4O_{10}(OH)_2$. End-member minerals with these compositions are typically muscovite, celadonite, and pyrophyllite. Consequently, the components will be identified as *mus, cel,* and *pyr*. The compositions shown can be bounded by a clearly defined trapezoid ABCD and represent, at one extreme of interpretation, a mixture of the minerals celadonite, pyrophyllite, and muscovite, and at the other extreme a limited but continuous solid solution of the components *cel, mus,* and *pyr*.

In the interpretation given here, based on the genesis of mixed-layer minerals, "true" montmorillonites have compositions lying along the line AB and are solid solutions of *cel* and *pyr,* with a small component of *mus.* Illite layers lie along the line CD and are characterized by a total negative charge of the silicate framework of −0.8 per formula weight. The solid arrows on the diagram indicate that for the data chosen, the change from montmorillonite to illite takes place at a constant *cel.* Minerals with compositions along AB show no evidence of mixed layering. Therefore it is assumed that they are solid solutions of *pyr* and *cel.*

The next question is whether the continuous range of compositions between AB and CD are mixtures of phases with compositions close to AB and CD, or a single-phase solid solution over the compositional range AB → CD. To simplify the complex chemistry of montmorillonites and illites, a theoretical montmorillonite and a theoretical illite can be created. The end-member

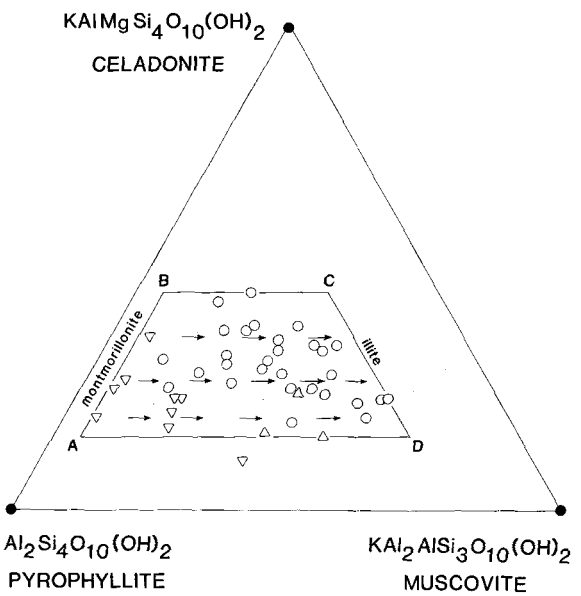


Figure 1. Compositions of montmorillonite and mixed-layer montmorillonite/illites. Open circles are data for mixed-layer minerals from Hower and Mowatt (1966), triangles are mixed-layer compositions, and inverted triangles are montmorillonite compositions from Tardy and Fritz (1981). Arrows indicate presumed direction of compositional change of original montmorillonite to illite.

component of montmorillonite composition and the end-member component of illite composition presented here permit representation of phase relations in the system K_2O-Al_2O_3-SiO_2-H_2O. This simplification permits discussion of the problem of one or two phases for the montmorillonite/illite system, without being so simple that it has no relation to nature. The iron content of the mixed-layer minerals of Hower and Mowatt (1966) is fairly constant, as is the magnesium content. The important differences between montmorillonite and illite involve K_2O, Al_2O_3, SiO_2, and H_2O.

THEORETICAL MONTMORILLONITE AND ILLITE

The idealized smectite for which free energy of formation values are commonly cited in the literature is one that has only Al in the octahedral positions, and low substitution of Al for Si in tetrahedral positions. The composition most commonly cited is:

$$K_{0.33}(Al_2)(Al_{0.33}Si_{3.67})O_{10}(OH)_2$$

(e.g., Helgeson and Mackenzie, 1970).

A negative charge of 0.33 for the silicate framework is certainly reasonable, but the data of Hower and Mowatt show that the negative charge of montmorillonites stems chiefly from substitutions in the octahedral layer, rather than in the tetrahedral layer. Furthermore, the theoretical occupancy of the octahedral layer by exactly

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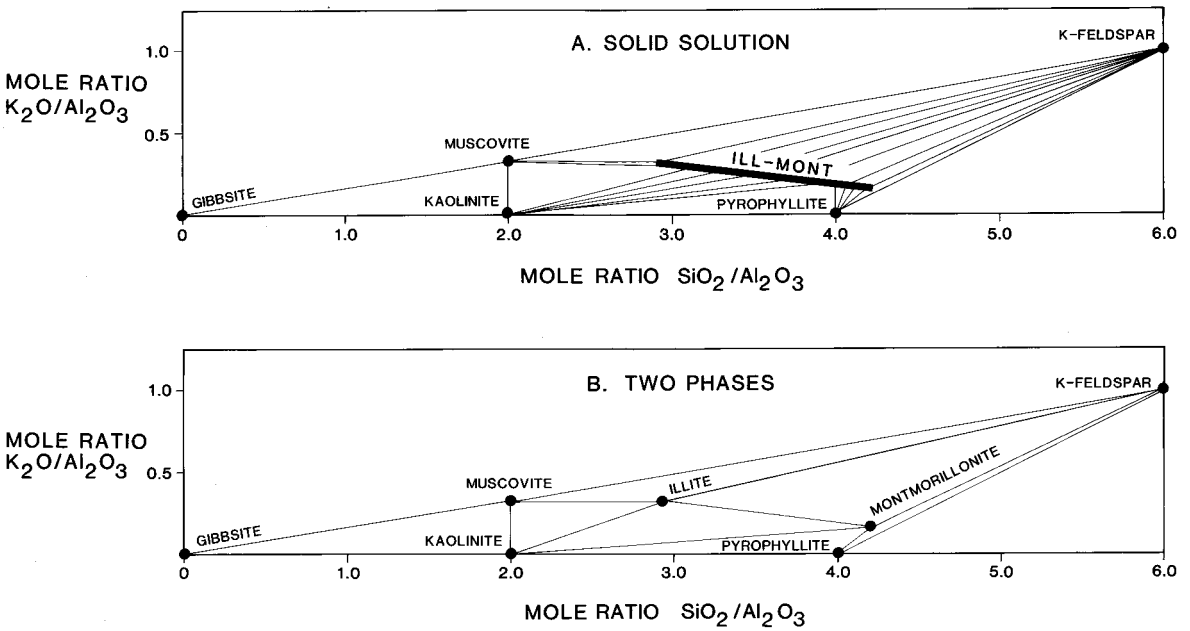


Figure 2. Mole ratio plots of the major phases that occur with mixed-layer montmorillonite/illite minerals in the system K_2O-Al_2O_3-SiO_2-H_2O. Figure 2A shows compositional relations if montmorillonite and illite are considered to be a single mineral phase exhibiting solid solution. Figure 2B shows the relations if they are considered to be two discrete mineral phases. The tie lines reflect commonly observed associations.

two cations is rarely observed. Usually there are more than two, sometimes fewer. At any rate, it seemed more reasonable to create a montmorillonite with 1.9 Al^{3+} in the octahedral layer, with a vacancy of 0.1 ions equal to 0.3 charge units, creating a negative charge on the silicate framework with its origin in the octahedral layer, rather than in the tetrahedral layer. The resultant composition is $K_{0.3}(Al_{1.9})(Si_4)O_{10}(OH)_2$.

To make the illite layers, this montmorillonite composition is changed by substituting 0.5 Al^{3+} for 0.5 Si^{4+} in the tetrahedral positions, giving a formula $K_{0.8}(Al_{1.9})(Al_{0.5}Si_{3.5})O_{10}(OH)_2$.

COMPOSITIONAL RELATIONS OF THEORETICAL MONTMORILLONITE AND ILLITE IN THE SYSTEM K_2O-Al_2O_3-SiO_2-H_2O

Figures 2A and 2B show compositional relations in the system K_2O-Al_2O_3-SiO_2-H_2O for the major phases that occur with mixed-layer montmorillonite/illite minerals. The plot is the classical mole ratio plot used by Korzhinski (1959). In Figure 2B it is assumed that only phases of fixed composition are involved; the tie lines reflect commonly observed associations.

In Figure 2A it is assumed that the illite and montmorillonite components form a continuous solid solution. The tie lines have been drawn in an attempt to conform with the suggestions of J. J. Hemley (U.S. Geological Survey, Reston, Virginia 22092, personal communication, 1981). The chief change that might be made would be a restriction of the coexistence of kaolinite and montmorillonite/illite solid solution, but the nature of the geometry of the system and the many reports of kaolinite occurrences with mixed-layer minerals would make it difficult to change the tie lines drastically.

ION ACTIVITY DIAGRAMS COMPARING MONTMORILLONITE AND ILLITE AS SEPARATE PHASES AND AS A SOLID SOLUTION

The composition diagrams can be converted into ion activity diagrams by geometric procedures described by Korzhinski (1959). These procedures do not specify numerical values for the logarithm of the ratio of $(a_{K^+}/a_{H^+})^2$ used as the ordinate in Figures 3 and 4, nor for the logarithm of the activity of dissolved silica, shown as the abscissa. The numerical values have been obtained from thermodynamic data on the minerals involved. Values for the theoretical montmorillonite and illite proposed here are constrained by the geometry of the system. For example, quartz + kaolinite + mixed-layer clay is a common association in sedimentary rocks, as is the K-feldspar + mixed-layer association. The free energy of formation values used here for the various species involved are given in Table 1.

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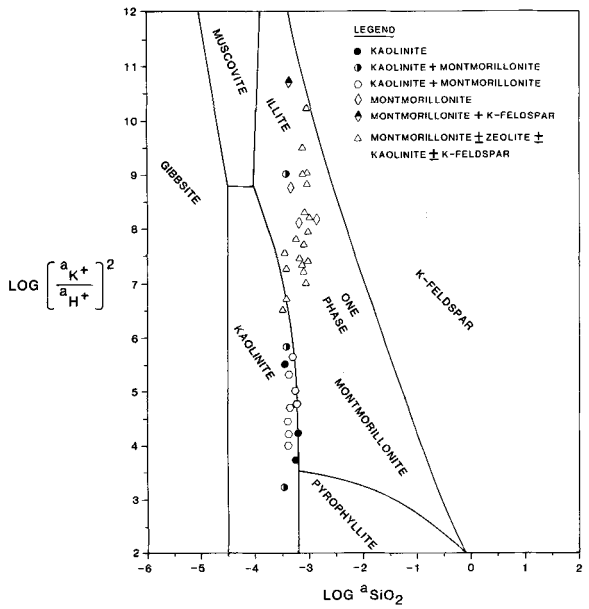


Figure 3. Ion activity diagram derived from the relationships in Figure 2 and the thermodynamic data listed in Table 1. The figure illustrates the general relations between solids and aqueous solution to be expected if montmorillonite and illite form a continuous solid solution. The symbols plotted on the diagram are from a compilation of water analyses of solutions in contact with clays by Aagaard and Helgeson (1983).

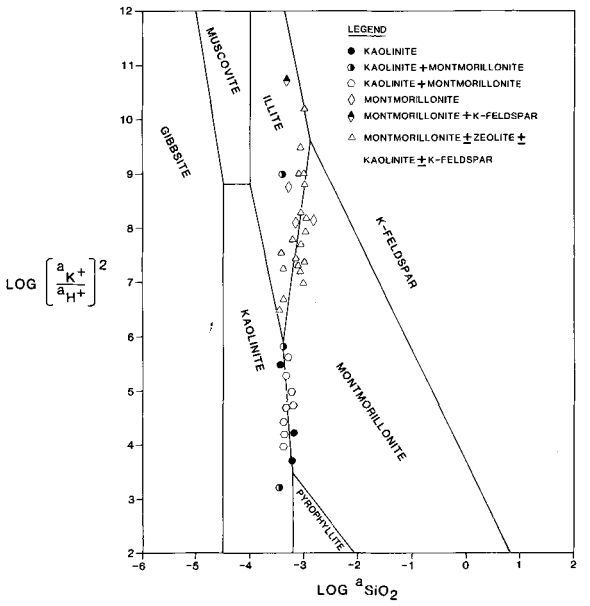


Figure 4. Ion activity diagram similar to Figure 3, but illustrating the relations to be expected if montmorillonite and illite behave as two discrete phases.

Montmorillonite/illite as solid solution

Figure 3 illustrates the general relations between solids and aqueous solution to be expected if montmorillonite/illite is a continuous solid solution. Kaolinite should coexist with a wide range of solid solution compositions, and the dissolved silica in equlibrium with the kaolinite association should decrease from high values, if kaolinite is associated with a mixed-layer mineral containing a large percentage of the montmorillonite component, to low values if it is associated with a mixed-layer mineral containing a large percentage of the illite component. K-feldspar should occur with the high illite-component species at high ratios of K^+/H^+ in the aqueous solution. A K-feldspar + high montmorillonite-component, mixed-layer mineral may well be precluded by the requirement of very high dissolved silica content.

The various symbols plotted on the diagram are taken from a compilation of water analyses of solutions in contact with clays compiled by Aagaard and Helgeson (1983). The low a_{K^+}/a_{H^+} values fall nicely on the kaolinite + montmorillonite-rich, solid solution boundary, but at higher ratios of a_{K^+}/a_{H^+} the analyses drift across the field of the solid solution. Aagaard and Helgeson (1983) stated that no compositions are available in the literature for waters that are known to coexist with illite.

Table 1. Gibbs energies of formation used to construct the activity-activity diagrams.

Species or mineral	G_f^1 (kcal/mole)	G_f^2 (kcal/mole)
K^+	−67.52	
H_2O	−56.68	
$SiO_{2(aq)}$	−199.3	
$KAlSi_3O_8$	−894.44	
$KAl_3Si_3O_{10}(OH)_2$	−1338.6	
$Al_2Si_4O_{10}(OH)_2$		−1258.7
$Al_2Si_2O_5(OH)_4$	−908.07	
$K_{0.8}Al_{1.9}(Al_{0.5}Si_{3.5})O_{10}(OH)_2$		−1307.77
$K_{0.3}Al_{1.9}Si_4O_{10}(OH)_2$		−1267.46
$Al(OH)_3$		−276.96

[1] Values from Robie *et al.* (1978).
[2] Values derived from Figures 3 and 4.

Montmorillonite and illite as two phases

Figure 4 shows the phase relations expected if the theoretical montmorillonite and illite are discrete phases. For phases of fixed composition, boundaries between phases on diagrams utilizing logarithms of activities are straight lines. As above, the analytical data from Aagaard and Helgeson (1983) seem in harmony with this interpretation of mixed-layer montmorillonite/illite as a two-phase system. Low values of the logarithm of (a_{K^+}/a_{H^+}) are consistent with equilibrium be-

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tween kaolinite and montmorillonite. Higher values of the logarithm of (a_{K^+}/a_{H^+}) are consistent with a phase boundary between illite and montmorillonite, and there is a suggestion that high values of the logarithm of (a_{K^+}/a_{H^+}) lie on the K-feldspar-illite boundary.

DISCUSSION

The solution compositions shown on Figures 3 and 4 fit the two-phase system better than they fit solid solution relations. The minerals listed in the legend as being present in the waters agree well with the phase relations of Figure 4, except for those represented by open triangles. It would be interesting to look carefully for mixed-layer minerals in the minerals exposed to the open-triangle solutions. The evidence from the water compositions is more consistent with the two-phase, mixed-layer concept than with continuous solid solution, but it is certainly not definitive. In a multimineralic clay system, which minerals dominate the solution compositions?

Figures 3 and 4 can be used to devise tests of the alternate hypotheses of solid solution or two phases for montmorillonite/illite, mixed-layer minerals. If the solid solution interpretation is correct, as shown in Figure 3, equilibration of kaolinite with mixed-layer minerals should yield progressively lower dissolved-silica values with increasing illite component, with perhaps a six-fold *range* of silica concentration from high montmorillonite-component to high illite-component. On the other hand, if montmorillonite and illite are two phases, as shown in Figure 4, the degrees of freedom of the aqueous solution are reduced by one, and if kaolinite is in equilibrium with a mixed-layer mineral, the dissolved silica in the aqueous solution should be fixed. Similarly, a solution in equilibrium with K-feldspar, an illite phase, and a montmorillonite phase also should have a fixed equilibrium concentration of silica. Furthermore, the (a_{K^+}/a_{H^+}) ratio for kaolinite + mixed-layer phase equilibrium should be fixed (all at constant temperature and pressure), as should that for K-feldspar + mixed-layer phase equilibrium.

At the moment, the experimental difficulties of performing the tests suggested above are formidable, but long-term experiments designed to meet the tests might resolve the problem.

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REFERENCES

Aagaard, P. and Helgeson, H. C. (1983) Activity/composition relations among silicates and aqueous solutions II. Chemical and thermodynamic consequences of ideal mixing of atoms among energetically equivalent sites in montmorillonites, illites, and mixed layer clays: *Clays & Clay Minerals* **31,** 207–217.

Garrels, R. M. and Tardy, Y. (1982) Born-Haber cycles for interlayer cations of micas: in *Proc. 7th Int. Clay Conf., Bologna and Pavia, 1981,* H. Van Olphen and F. Veniale, eds., Elsevier, Amsterdam, 423–440.

Helgeson, H. C. and Mackenzie, F. T. (1970) Silicate-seawater equilibria in the ocean system: *Deep-Sea Research* **17,** 877–892.

Hower, J., Eslinger, E. V., Hower, M. E., and Perry, E. A. (1976) Mechanism of burial metamorphism of argillaceous sediment: mineralogical and chemical evidence: *Geol. Soc. Amer. Bull.* **87,** 725–737.

Hower, J. and Mowatt, T. C. (1966) The mineralogy of illites and mixed-layer illite/montmorillonites: *Amer. Mineral.* **51,** 825–854.

Inoue, A., Minato, H., and Utada, M. (1978) Mineralogical properties and occurrence of illite/montmorillonite mixed layer minerals formed from Miocene volcanic glass in Waga-Omono District: *Clay Science* **5,** 123–136.

Korzhinski, D. S. (1959) *Physiochemical Basis for the Analysis of the Paragenesis of Minerals:* English translation, Consultants Bureau, New York, 142 pp.

Perry, E. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: *Clays & Clay Minerals* **18,** 165–177.

Robie, R. A., Hemingway, B. S., and Fisher, J. R. (1978) Thermodynamic properties of minerals and related substances at 298.15K and 1 bar (10^5 pascals) pressure and at higher temperatures: *U.S. Geol. Surv. Bull.* **1452,** 456 pp.

Tardy, Y. and Fritz, B. (1981) An ideal solid solution model for calculating solubility of clay minerals: *Clay Miner.* **16,** 361–373.

Zen, E-An (1962) Problem of the thermodynamic status of the mixed-layer minerals: *Geochim. Cosmochim. Acta* **26,** 1055–1067.

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Резюме—Диаграммы химической активности, подготовленные для показания ожидаемых свойств в случае, когда смешано-слойный монтмориллонит/иллит считается как твердый раствор, сравнивались с диаграммами полученными для этих материалов, рассматриваемых как смесь двух фаз. Если эта система рассматривается как твердый раствор, ожидается, что сосуществующий водный раствор имеет большие содержания растворенного кремнезема в присутствии каолинита и монтмориллонитового конечного члена и меньшие содержания в присутствии каолинита и иллитового конечного члена. Концентрация кремнезема в водных растворах может изменяться даже в шесть раз. Если эта система рассматривается как смесь двух фаз, тогда содержание кремнезема в растворе в состоянии равновесия с каолинитом и двумя фазами будет неизменяющимся при данных температуре и давлении, так как раствор в равновесии с двумя фазами и К-фельдшпатом. В отсутствии третьей фазы, содержание кремнезема в равновесии с двумя фазами будет почти постоянное, но увеличивается с увеличением отношения K^+/H^+ в растворе. Доступные данные по сосуществующим водным раст1

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ворам, по-видимому, являются более согласующимися в случае двух фаз, чем в случае твердого раствора. [E.G.]

Resümee—Chemische Aktivitätsdiagramme, die hergestellt wurden, um die Eigenschaften, die man erwartet, wenn man Montmorillonit/Illit-Wechsellagerungen als feste Lösungen betrachtet, zu beschreiben, werden mit denen vergleichen, die man erhält, wenn man diese Substanzen als eine Mischung aus zwei Phasen behandelt. Wenn das System eine feste Lösung ist, dann sollte die koexistierende wässrige Lösung von höheren gelösten SiO_2-Gehalten in der Gegenwart von Kaolinit und einem Montmorillonit-Endglied bis zu niedrigeren gelösten SiO_2-Gehalten in der Gegenwart von Kaolinit und einem illitischen Endglied reichen. Die SiO_2-Konzentration in der wässrigen Lösung kann bis zu einem Faktor von sechs variieren. Wenn das System als aus zwei Phasen bestehend betrachtet wird, dann wäre der SiO_2-Gehalt einer Lösung im Gleichgewicht mit Kaolinit, und beide Phasen wären bei einem gegebenen T und P fixiert, wie auch eine Lösung mit beiden Phasen und K-Feldspat ins Gleichgewicht gebracht wäre. In Abwesenheit einer dritten Phase sollte das SiO_2, das im Gleichgewicht mit beiden Phasen ist, nahezu konstant sein, aber mit wachsendem K^+/H^+-Verhältnis in der Lösung ansteigen. Die zur Verfügung stehenden Daten über koexistierende wässrige Lösungen stimmen offensichtlich eher mit der Annahme von zwei Phasen als mit der Annahme einer festen Lösung überein. [U.W.]

Résumé—Des diagrammes d'activité chimique, préparés pour illustrer les propriétés attendues si une montmorillonite/illite à couches mélangées est considérée comme une solution solide, sont comparés à ceux dérivés d'un traitement de ces matériaux en tant que mélange de deux phases. Si le système est une solution solide, la solution aqueuse coexistante devrait s'étager de contenus en silice dissoute plus élevés en la présence de kaolinite et d'un membre final de montmorillonite, à des contenus en silice dissoute moins élevés en présence de kaolinite et de l'illite comme membre final. La concentration en silice dans la solution aqueuse peut varier d'un facteur aussi élevé que six. Si le système est à deux phases, le contenu en silice d'une solution en équilibre avec la kaolinite et les deux phases serait fixé à des T et P données, comme le serait une solution equilibrée avec les deux phases et du feldspar-K. En l'absence d'une troisième phase, la silice en équilibre avec les deux phases devrait être presque constante, mais devrait augmenter proportionnellement à la proportion croissante de K^+/H^+ en solution. Les données sur les solutions coexistantes sont apparemment plus consistantes avec deux phases qu'avec une solution solide. [D.J.]

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