

## NEW STABILITY DIAGRAMS OF SOME PHYLLOSILICATES IN THE $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ SYSTEM

W. H. HUANG and W. D. KELLER

Department of Geology, University of South Florida, Tampa, Florida 33620, U.S.A.

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**Abstract**—Aluminum is treated as a mobile, reactive component in newly designed stability diagrams for the  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$  system. The diagrams show that the stability field of kaolinite is strongly dependent on pH at or below 6.7 but at 6.7 or greater the stability field is independent of pH, and also that in present sea water, K-mica is a stable phase with respect to kaolin minerals. Natural waters from present-day, kaolin-forming localities in Mexico and Kentucky are consistent with theoretical interpretations from these stability diagrams.

### INTRODUCTION

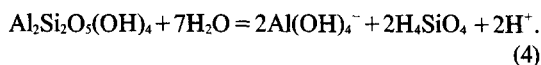
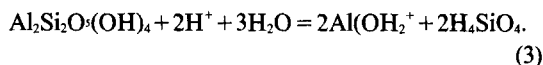
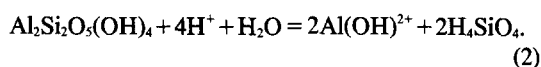
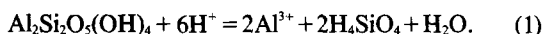
STABILITY diagrams for aluminum silicates applicable to conditions of weathering and diagenesis have been periodically modified so as to become more realistic and useful. Feth *et al.* (1964) pioneered with diagrams in terms of activities of  $\text{Na}^+/\text{H}^+$  or  $\text{K}^+/\text{H}^+$  and activity of  $\text{H}_4\text{SiO}_4$ , and modifications of the diagrams have been subsequently introduced (Garrels and Christ, 1965; Hess, 1966; Curtis and Spears, 1971). All of these diagrams treated Al as an inert component although in nature Al is known to be mobile. Kittrick (1970), however, recognized Al to be active in the system,  $\text{pH}-1/3\text{pAl}^{3+}$  vs  $\text{pH}_4\text{SiO}_4$ , although the determination of concentration or activities of  $\text{Al}^{3+}$  becomes difficult in systems near neutral pH. More recently Hem *et al.* (1973) used log activities of  $\text{Al}^{3+}$  or  $\text{Al}(\text{OH})_4^-$  plus  $\text{H}_4\text{SiO}_4$  versus pH to characterize halloysite which had been synthesized at room temperature.

This paper reports newer stability diagrams for kaolinite, halloysite, and K-mica with respect to activities of Al, in which Al has been differentiated into  $\text{Al}^{3+}$ ,  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_4^-$ , plus  $\text{H}_4\text{SiO}_4$  (or other species, such as  $\text{H}_3\text{SiO}_4^-$ ,  $\text{H}_2\text{SiO}_4^{2-}$ ,  $\text{H}_3\text{SiO}_4^{3-}$ ,  $\text{SiO}_4^{4-}$ , depending on pH), plotted against  $\text{H}^+$  (pH). Al is thereby treated as an active component in which its varied status is realistically recognized.

### SPECIES OF AL IONS AS ACTIVE COMPONENTS

Consider the systems in which kaolinite,  $\Delta G_f^\circ = 902.9$  kcal/mole (Robie and Waldbaum, 1968), is in

equilibrium with its dissociation products, notably the various species of hydrated Al as follows:



Equilibrium constants ( $K$ ) for these reactions can be obtained from the Nernst equation:  $\Delta G_f^\circ = -1.364 \log K$ , by the known values of standard free energies of formation ( $\Delta G_f^\circ$ ) (Reesman and Keller, 1965; Reesman *et al.*, 1969; Huang and Keller, 1972). The following relations are then obtained for the above four reactions, respectively:

$$\log [\text{Al}^{3+}] + \log [\text{H}_4\text{SiO}_4] = 3.46 - 3\text{pH} \quad (5)$$

$$\log [\text{Al}(\text{OH})_2^+] + \log [\text{H}_4\text{SiO}_4] = -1.54 - 2\text{pH} \quad (6)$$

$$\log [\text{Al}(\text{OH})_4^-] + \log [\text{H}_4\text{SiO}_4] = -5.59 - \text{pH} \quad (7)$$

$$\log [\text{Al}(\text{OH})_4^-] + \log [\text{H}_4\text{SiO}_4] = -18.97 + \text{pH}. \quad (8)$$

Figure 1 is a plot representing equations (5, 6, 7 and 8), and shows a stability field of kaolinite (above line K) delineated in terms of log activities

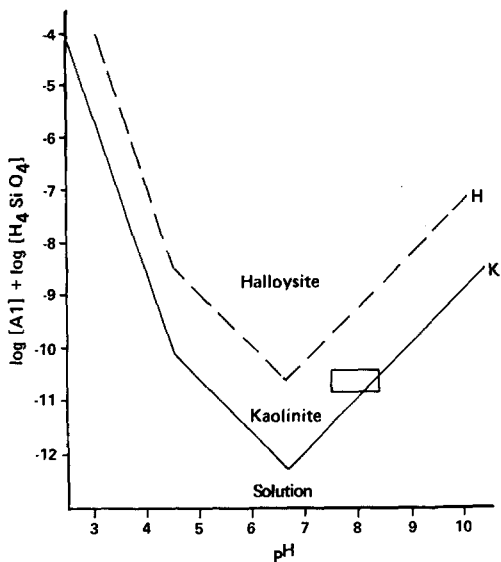


Fig. 1. Stability diagram of kaolinite and halloysite in terms of  $\log [Al] + \log [H_4SiO_4]$  plotted against pH at 25°C and 1 atm. The composition of present sea water is shown in a rectangle. *K* is a stability boundary between kaolinite and solution, whereas *H* is a stability boundary between halloysite and kaolinite.

of Al, as different Al species, plus log activity of  $H_4SiO_4$ , against pH. Figure 1 also shows a stability field of halloysite ( $\Delta G_f^\circ = -898.4$  kcal/mole, (Robie and Waldbaum, 1968)), above line *H*. The

composition of present sea water is shown in a rectangle. It is noteworthy that halloysite is a metastable phase with respect to kaolinite if the system is in present sea water.

Two points, especially, should be noted, in applying the stability relations of clay minerals in Fig. 1, and related Figs. 3, 4, and 5, to natural geologic systems:

(1) Since naturally occurring clay minerals have a wide range of stabilities depending on particle size, degree of crystallization etc. (Hem *et al.*, 1973), standard free energies of formation for the minerals ( $\Delta G_f^\circ$ ) derived will be varied, and subsequently the stability boundary of the minerals involved will be modified accordingly, depending on which values of  $\Delta G_f^\circ$  are used. In this paper  $\Delta G_f^\circ$  was chosen for those most stable clay minerals, and the diagrams should provide a fundamental base. Subsequent modifications of the diagrams may be made to suit for individual need.

(2) As shown in a distribution diagram of species from orthosilicic acid in Fig. 2,  $H_3SiO_4^-$  is present at  $pH = 5.6$  (0.01 per cent  $H_3SiO_4^-$  and 99.99 per cent  $H_4SiO_4$ ) and has a maximum value at  $pH = 10.7$ . Therefore, before applying the diagrams to natural systems where pH is higher than 5.6, activity of  $H_4SiO_4$  should be corrected for the effect of dissociation from total activity of Si as calculated from analytical data.

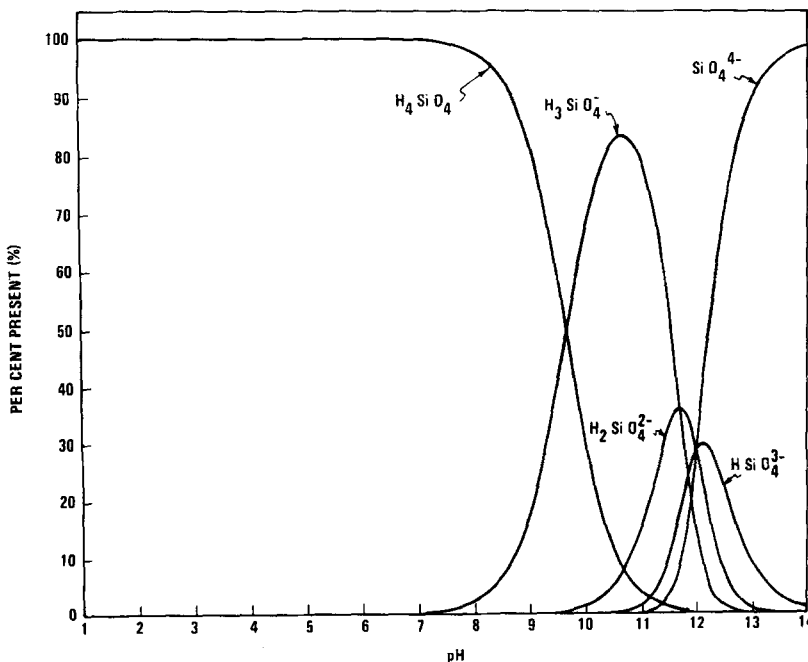
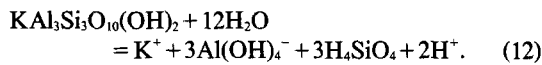
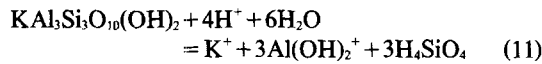
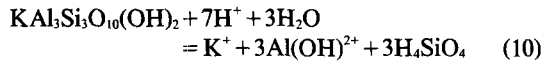
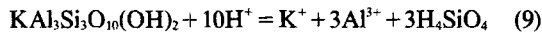


Fig. 2. Distribution diagram of species from orthosilicic acid.

For a system in which K-mica  $KAl_3Si_3O_{10}(OH)_2$ ,  $\Delta G_f^\circ = -1330.1$  kcal/mole, (Barany, 1964) is equilibrated with its dissociation product, the equilibrium equations can be written as for kaolinite as follows:



After equilibrium constants ( $K$ ) are calculated as in the case of kaolinite, the following relations are obtained for the above four reactions, respectively:

$$\log [Al^{3+}] + \log [H_4SiO_4] = 5.08 - 1/3 \log [K^+] - 10/3pH \quad (13)$$

$$\log [Al(OH)^{2+}] + \log [H_4SiO_4] = 0.08 - 1/3 \log [K^+] - 7/3pH \quad (14)$$

$$\log [Al(OH)_2^+] + \log [H_4SiO_4] = -3.97 - 1/3 \log [K^+] - 4/3pH \quad (15)$$

$$\log [Al(OH)_4^-] + \log [H_4SiO_4] = -17.34 - 1/3 \log [K^+] + 2/3pH. \quad (16)$$

By knowing an activity of  $K^+$  in the system,  $\log [Al]$  plus  $\log [H_4SiO_4]$  can be plotted against pH. Figure 3 is a plot representing equations (13, 14, 15 and 16), and shows a stability field of K-mica with respect to an activity of  $K^+$  for sea water (marine environment) taken as  $10^{-2.21}$  (Berner, 1971) bounded by line  $M$ , and for average river water (non-marine) with activity of  $K^+$ ,  $10^{-4.35}$  as line  $N$ . Activities of  $K^+$ ,  $Al(OH)_4^-$ , and  $H_4SiO_4$  for sea water were calculated from the data of Livingstone (1963), following the procedure outlined in an earlier paper (Huang and Keller, 1972). It is obvious from Fig. 3 that in present sea water (rectangle), K-mica is a stable phase.

In Fig. 4 are shown the stability relations of kaolinite, halloysite, and K-mica with respect to activities of different Al species,  $H_4SiO_4$ , and  $H^+$ , in marine and non-marine environments (Huang, 1973). Again, halloysite is stable below line  $M$  in marine water, and below  $N$  in river water. Kaolinite is stable below line  $M$ ,  $K^+ = 10^{-2.21}$  (marine water)

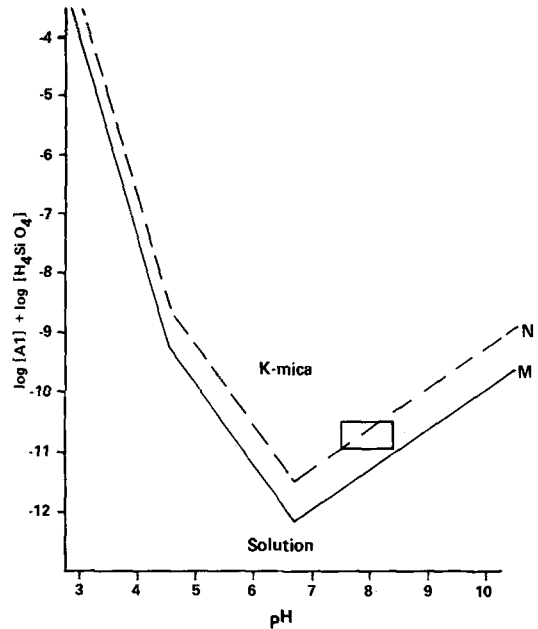


Fig. 3. Stability diagram, using the same variables as in Fig. 1, of K-mica with respect to sea water ( $M$ ) and average river water ( $N$ ). The composition of present sea water is also shown in a rectangle.

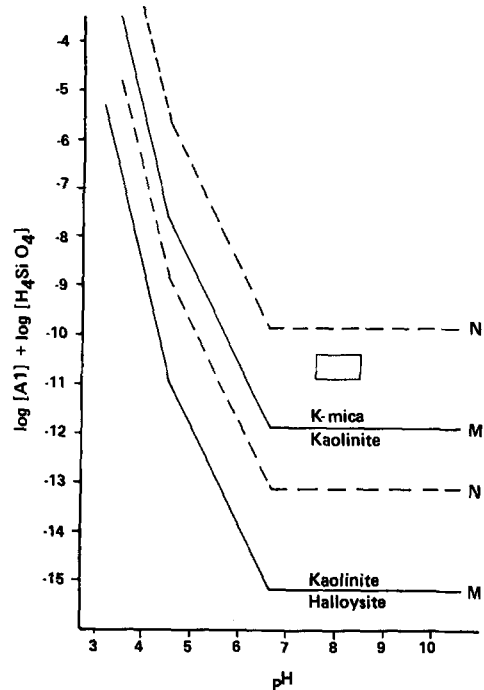


Fig. 4. Stability diagram of kaolinite, halloysite, and K-mica in terms of  $\log [Al] + \log [H_4SiO_4]$  plotted against pH at 25°C and 1 atm in sea water ( $M$ ) and average river water ( $N$ ). the composition of present sea water is shown in a rectangle. Activities of  $K^+$  are  $10^{-2.21}$  and  $10^{-4.35}$  for sea water and average river water, respectively.

and K-mica stable above it. Kaolinite and K-mica are stable, respectively below and above line  $N, K^B = 10^{-4.35}$  (river water).

In either marine or river water, the stability field of kaolinite is strongly dependent on pH at or below 6.7 (also the isoelectric point of Al in an aqueous system), but at 6.7 or greater, the stability field is totally independent of pH. In present sea water, K-mica is a stable phase with respect to kaolinite or halloysite.

#### GEOLOGIC EXAMPLES

A geochemical development or device is meaningful to a geologist when it accords with geological field examples. It is not easy as might appear at first thought to apply, unequivocally, stability diagrams of clay minerals to natural systems. Only uncommonly are systems known where clay minerals are observably being formed *now* and the associated solutions are truly the reactants producing the particular variety of clay mineral present. Even in large deposits of clay minerals, the waters extracted from them do not necessarily represent the composition of waters operative at the time of their formation. Furthermore, waters emerging from rocks undergoing "kaolinization" (in general), for example, can not be specifically tied to kaolinite, or to halloysite, or to possibly an intermediary film of "K-mica" generated between the feldspar and kaolin, unless detailed observations are made and appropriate restrictions imposed.

We cite two occurrences in which altering solutions are currently producing endellite in the process of formation: one from Michoacan, Mexico, and the other from Kentucky. We will illustrate with 8 other spring-water samples taken from Hem *et al.* (1973), quoting Feth *et al.* (1964), although the specific clay minerals with which these solutions are in equilibrium are not identified.

At Ojo Caliente de Laguna Larga, Michoacan, Mexico, a large hot spring, 45°C, rises through multiple orifices within country rock of rhyolitic composition. Masses of clean, relatively pure endellite are in the process of formation from the rock by this water, (Keller *et al.*, 1971). Thus, this natural system and stability diagram No. 4, Fig. 5, presumably are compatible. The composition of the water is located at L on the diagram.

Near Stanford, Kentucky, in a road cut through middle Paleozoic rocks, white, relatively pure endellite is being formed as connected nodular masses in a reddish-brown ancient residuum from weathered Silurian Brassfield limestone (Keller *et al.*,

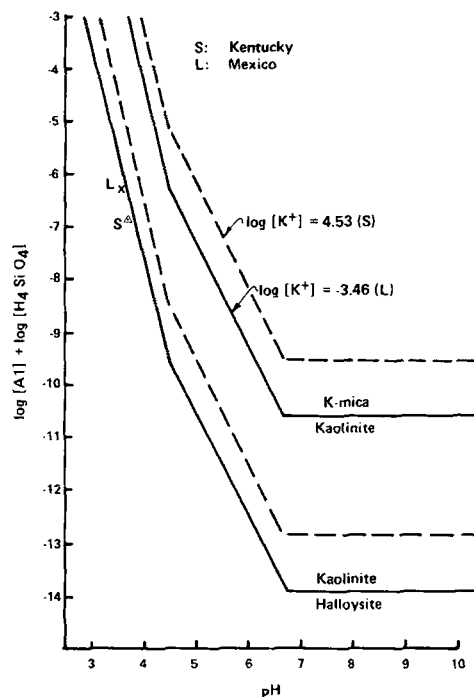


Fig. 5. Stability diagram of kaolinite, halloysite, and K-mica. L represents the composition of water from a hot spring in Mexico; S represents a vadose solution in Kentucky.

1966). The reacting solutions are acidic, seeping downward from oxidizing iron sulphide in the overlying Devonian New Albany shale. This natural system appears indubitably to be active in argillation, and is compatible with the stability diagram. Water leached from the sticky, wet endellite yields a composition plotted at S on Fig. 4. The halloysite field and boundary of the diagram are clearly consistent with these two natural occurrences.

Hem *et al.* No. 1 (Feth *et al.*, No. 1218), water from an ephemeral spring, is plotted on Fig. 6, as "1" in a solid circle. It is in a K-mica field. The solid circles are referable to the solid boundary lines, which are located on the graph by calculation with  $\log [K^+] = 4.5$ . The analyses of  $K^+$  are taken from the paper by Feth *et al.* (1964). Spring-water numbers marked X are referable to the dashed lines located with respect to  $\log [K^+] = 5.0$ . Nos. 6, 9, 10, 14, are from "quartz monzonite" springs; they lie within the kaolinite field. No. 26 is from a "granodiorite" spring; it lies in the kaolinite field. Nos. 34 and 36 are from "granitic rock springs"; No. 34 lies in the K-mica field, barely above the kaolinite-mica boundary, whereas No. 36 falls in the halloysite field.

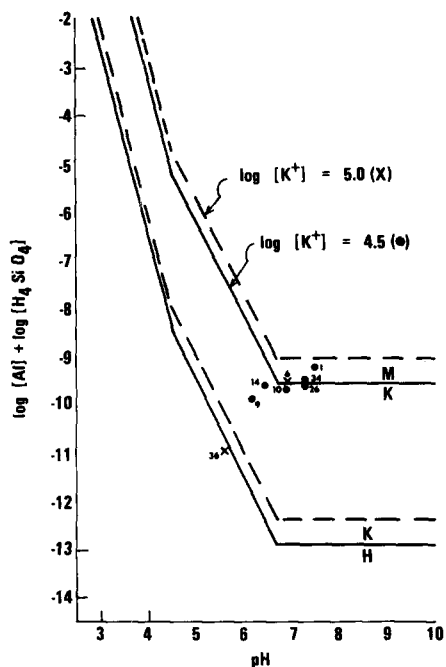


Fig. 6. Ground-water compositions related to clay-mineral stabilities. *H*: Halloysite stability field. *K*: Kaolinite stability field. *M*: K-mica stability field. Solid line and circle, where  $\log [K^+] = 5.0$ . Dashed line and X, where  $\log [K^+] = 4.5$ . No. 1, Ephemeral spring. Nos. 6, 9, 10, 14, Quartz monzonite springs. No. 26, Granodiorite springs. Nos. 34, 36, Granitic rock springs. Spring-water data from Hem *et al.* (1973).

Because the compositions of all of these waters lie within potential or probable equilibrium-clay areas, the stability diagrams appear to be well applicable to geologic systems. Only if the *unique* clay mineral being developed in the weathering crystalline rock is known can exact equilibrium correlation be established.

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**Résumé**—L'aluminium est traité comme un composant mobile et réactif, dans le cadre de diagrammes de stabilité nouveaux concernant le système  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ . Les diagrammes montrent que l'halloysite et le mica -K ne peuvent pas coexister à l'équilibre, que le domaine de stabilité de la kaolinite dépend fortement du pH en dessous de 6, 7 mais qu'il n'en dépend plus au dessus de cette valeur, et que, en présence d'eau de mer, le mica K est une phase stable par rapport aux minéraux du type kaolin. Les eaux naturelles actuelles et les sites où se forme le kaolin au Mexique et dans le Kentucky présentent des conditions en accord avec les interprétations théoriques tirées de ces diagrammes de stabilité.

**Kurzreferat**—Aluminium wird in neu entworfenen Stabilitätsdiagrammen für das  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ -System als beweglicher, reaktionsfähiger Bestandteil behandelt. Die Diagramme zeigen, daß Hal-

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loysit und K-Glimmer im Gleichgewicht nicht koexistieren können, daß das Stabilitätsfeld von Kaolinit eine starke pH-Abhängigkeit bei Werten von 6,7 oder darunter aufweist, daß das Stabilitätsfeld bei pH-Werten über 6,7 dagegen pH-unabhängig ist, und schließlich, daß im heutigen Seewasser K-Glimmer im Verhältnis zu Kaolinmineralen eine stabile Phase darstellt. Natürliche Wässer von Gegenden in Mexico und Kentucky, in denen heute Kaolinbildung erfolgt, stimmen mit den theoretischen Auswertungen dieser Stabilitätsdiagramme überein.

**Резюме** — Во вновь составленных диаграммах устойчивости системы  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O-H}_2\text{O}$ , алюминий рассматривается как мобильный реакционноспособный компонент. По диаграммам видно, что галлузит и К-слюда не могут сосуществовать в равновесных соотношениях и, что поле устойчивости каолинита преимущественно зависит от pH равному или ниже 6,7, но при 6,7 или выше поле устойчивости не зависит от pH, также видно, что в морской воде К-слюда является устойчивой фазой по отношению к каолиновым минералам. Природные воды Мексики и Кентукки образующие в настоящее время каолин не противоречат теоретическим интерпретациям этих диаграмм устойчивости.