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Stabilities of Kaolinite and Halloysite in Relation to Weathering of Feldspars and Nepheline in Aqueous Solution

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Abstract

Newly designed stability diagrams, which consider Al as a mobile, reactive component (including hydrated Al^{3+}, $Al(OH)^{2+}$, $Al_2(OH)^{4+}_2$, $Al(OH)^+_2$, and $Al(OH)^-_4$ species) as well as parameters, Na^+, K^+, H^+, and H_4SiO_4, show that in average river water halloysite and kaolinite are stable with respect to K-feldspar, albite, and nepheline. By contrast, in present sea water, kaolinite alone is stable in a system containing kaolins plus K-feldspar or albite, but both halloysite and kaolinite are stable in a system of kaolins and nepheline.

The geologic observations that kaolinites become more abundant than halloysites through geologic time are interpreted from solution chemistry, Gibbs free energy, and activation energy. Halloysite may crystallize from a solution supersaturated with respect to halloysite, but kaolinite may crystallize under these same conditions or also from a solution saturated with respect to kaolinite. Moreover, any halloysite formed will tend to be spontaneously transformed to kaolinite ($\Delta G_r{}^\circ$ being negative). Rate of transformation, however, is governed by the activation energy (not Gibbs free energy), the temperature, and the rate of kaolinite precipitation from such nutrient solutions as may be supplied from dissolution of halloysite through diagenetic processes. Geologic occurrences of kaolinite and halloysite in modern and ancient weathered products are consistent with these theoretical interpretations.

Introduction

Kaolin minerals have been formed in a number of different ways in geological environments, as reviewed recently by Keller (1970). The mechanisms for the formation of kaolin minerals include direct crystallization from solution, replacement, crystallization from colloidal gels, and weathering of layer or non-layer silicates. Geologic occurrences of kaolin minerals formed by weathering of non-layer silicates, particularly of feldspars, have been documented in Mesozoic weathered products in Minnesota (Parham, 1969), and in modern weathering products in the Southern Appalachian region (Sand, 1956), in Hawaii (Bates, 1962), in Hong Kong (Parham, 1969), and in Mexico (Keller *et al*, 1971). Minato and Utada (1972) even showed present-day formation of halloysite in Japan. Both kaolinite and halloysite have been found in recent weathering products, but kaolinite predominates in the ancient weathered products. Although many geological mechanisms have been suggested for the formation of kaolinite and halloysite from weathering of non-layer silicates, the relative abundances of these two minerals through geologic time, however, have not been fully explored. This paper therefore attempts to interpret from thermodynamic and kinetic relationships (1) the stabilities of kaolinite and halloysite formed by weathering of non-layer silicates, and (2) the relative abundances of these two minerals through geologic time.

Final judgment as to what minerals could form in nature could, of course, be better made if *all* potentially stable minerals were considered simultaneously, rather than two at a time, as done here. This present paper thus represents a step toward that goal.

Stability Diagrams

Relative stabilities of aluminum silicates (including primary rock-forming and clay minerals) in aqueous solution at 25°C, 1 atm. have been generally determined by thermodynamics and indicated graphically in stability diagrams. These stability diagrams are constructed primarily in terms of log of activities of K^+/H^+ or Na^+/H^+ and log of activity of H_4SiO_4 in aqueous solution, assuming Al_2O_3 as an *inert* component (Feth, Roberson, and Polyer, 1964; Garrels and Christ, 1965; Hess, 1966). Geologic observations of kaolin deposits indicate that kaolin minerals can be formed by weathering of aluminum

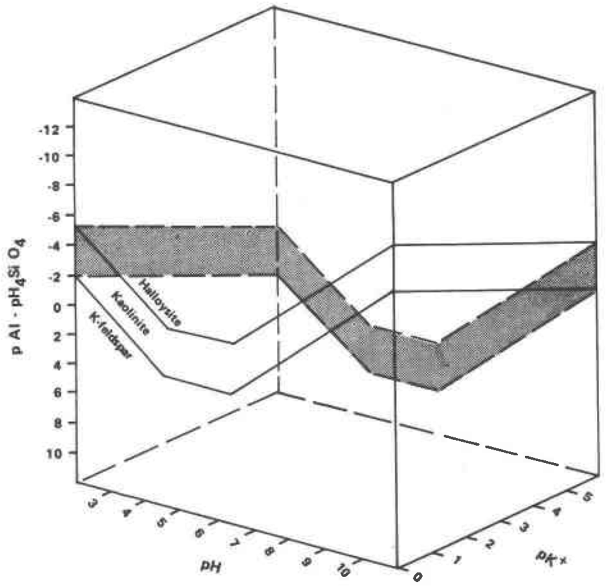

FIG. 1. Stability diagram of K-feldspar-kaolinite and K-feldspar-halloysite at 25°C and 1 atm., in which pAl-pH_4SiO_4 is plotted against pH and pK^+.

silicates either from solid-state transformation or solution-precipitation process. In either process, solute species of aluminum occur (Keller, 1970; Hem *et al*, 1973). Aluminum therefore should be considered as a mobile, active component rather than a fixed component in the stability diagrams of aluminum silicates (Huang, 1973; Huang and Keller, 1973a).

Because different Al species in a simple aqueous solution may be present in varying proportions (Huang and Keller, 1972a), relative stabilities of aluminum silicates should be expressed in terms of activities of the various species of Al (including Al^{3+}, $Al(OH)^{2+}$, $Al_2(OH)^{4+}_2$, $Al(OH)^+_2$, and $Al(OH)^-_4$, all hydrated) in addition to those of H_4SiO_4, K^+, Na^+, and H^+. The relative stability relationships in aqueous solutions between kaolin minerals and the non-layer silicates K-feldspar, albite, and nepheline can be obtained from the following two relationships.

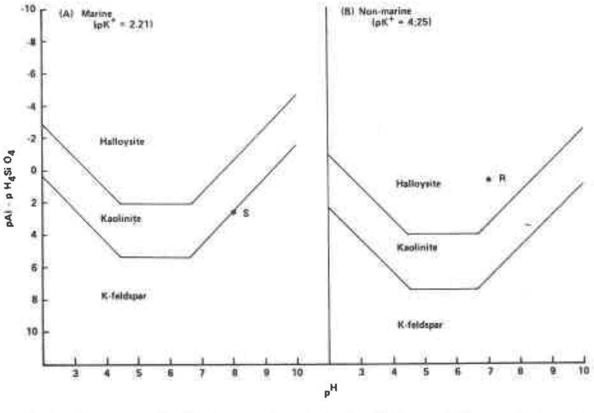

FIG. 2. Isoplethic sections of the stability diagram (K-feldspar—kaolinite and K-feldspar—halloysite) for marine (sea water) and non-marine (river water) environments. S and R are the compositions of sea water and average river water, respectively. (A) Marine ($pK^+ = 2.21$), (B) Non-marine ($pK^+ = 4.25$).

(1) $\Delta G_r°$ (standard free energy of reaction) $= \Sigma \Delta G_f°$(products)-$\Sigma \Delta G_f°$(reactant); where $\Delta G_f°$ is standard free energy of formation (the values of $\Delta G_f°$ are obtained from Robie and Waldbaum, 1968; Huang and Keller, 1972b; Hem *et al*, 1973; Huang and Kiang, 1973; Huang and Keller, 1973b).

(2) $\Delta G_r° = -1.364 \log K$; where K = equilibrium constant (activities of pure solids and liquids are equal to 1).

(1) Equilibrium reactions between K-feldspar ($\Delta G_f° = -892.6$ kcal/mole) and kaolinite ($\Delta G_f° = -902.9$ kcal/mole) and halloysite ($\Delta G_f° = -898.4$ kcal/mole) are written as follows:

(a) $KAlSi_3O_8 + Al^{3+} + 5 H_2O = Al_2Si_2O_5(OH)_4 + K^+ + H_4SiO_4 + 2 H^+$ $\log [Al^{3+}] - \log [H_4SiO_4] = 5.89$ (or 9.19 for halloysite) $+ \log [K^+ - 2pH]$

(b) $KAlSi_3O_8 + Al(OH)^{2+} + 4 H_2O = Al_2Si_2O_5(OH)_4 + K^+ + H_4SiO_4 + H^+$ $\log [Al(OH)^{2+}] - \log [H_4SiO_4] = 0.89$ (or 4.19 for halloysite) $+ \log [K^+] - pH$

(c) $KAlSi_3O_8 + Al(OH)^+_2 + 3 H_2O = Al_2Si_2O_5(OH)_4 + K^+ + H_4SiO_4$ $\log [Al(OH)^+_2 - \log [H_4SiO_4] = -3.16$ (or -0.14 for halloysite) $+ \log [K^+]$

(d) $KAlSi_3O_8 + 2 H^+ + H_2O + Al(OH)_4^- = Al_2Si_2O_5(OH)_4 + K^+ + H_4SiO_4$ $\log [Al(OH)^-_4 - \log [H_4SiO_4] = -16.53$ (or -13.23 for halloysite) $+ \log [K^+] + 2pH$

The stability relations of K-feldspar and kaolinite, and of K-feldspar and halloysite, can be expressed in terms of three measurable experimental parameters, namely pAl ($-\log$ [Al] minus pH_4SiO_4 ($-\log [H_4SiO_4]$), pK^+ ($-\log [K^+]$), and pH (see Fig. 1). Figures 2a and 2b, respectively, are two isoplethic sections of stability diagrams for present sea water ($pK^+ = 2.21$) and average river water ($pK = 4.25$) environments. The activities of Al (species generalized), H_4SiO_4, K^+, and H^+ in present sea water and average river water were calculated in earlier papers (Huang, 1973; Huang and Keller, 1973a).

As shown in Figure 2b where the activity of K^+ is small, such as in river water ($pK^+ = 4.25$), halloysite and kaolinite are stable with respect to K-feldspar. In present sea water (Fig. 2a), kaolinite (not halloysite) is stable with respect to K-feldspar. The occurrences of kaolinite and halloysite from alteration of feldspars in difference places, for example in the Southern Appalachian region (Sand, 1956), could be due to the differences in the activities of K^+, Al, H_4SiO_4 and H^+ in the environments. Sand (1956) also found that *river terraces* apparently are favorable locations for extensive deposition of hydrated halloysite from alteration of feldspars, as is consistent with the theoretical predictions from the stability diagrams in Figure 2. Furthermore, the diagrams show that halloysite, which is stable in river water, may become unstable and be transformed to kaolinite when halloysite is transported to marine environment. The stability fields are strongly controlled by pH below 4.2 or greater than 6.7, but between 4.2 and 6.7 they are independent of pH.

Three points should be noted, however, in applying these stability diagrams to natural geologic systems:

(a) Since naturally occurring kaolinite and halloysite have a wide range of stabilities depending on particle size, degree of crystallization, or hydration (halloysite), *etc*, standard free energy of formation for the minerals ($\Delta G_f°$) will be varied, and subsequently the stability boundary between K-feldspar and kaolinite (or halloysite) will be modified, depending on which $\Delta G_f°$ are used. In this paper $\Delta G_f°$ are chosen for those most stable clay minerals, and the diagrams should provide a base, and the subsequent modifications of the diagrams may be necessary to suit for individual needs.

(b) Before applying the diagrams to natural systems where the pH is higher than 5.6, activity of H_4SiO_4 should be corrected for the effect of dissolution from total activity of Si (Huang and Keller, 1973a).

(c) These calculations are made for fully dehydrated halloysite because $\Delta G_f°$ is available only for dehydrated halloysite. It has been recognized that typical halloysite may be slightly hydrated.

(2) Similar equilibrium reactions for albite ($\Delta G_f°$ = −884.0 kcal/mole), and kaolinite and halloysite are shown as follows:

(a) $NaAlSi_3O_8 + Al^{3+} + 5\,H_2O = Al_2Si_2O_5(OH)_4 + Na^+ + H_4SiO_4 + 2H^+$ $\log [Al^{3+}] - \log [H_4SiO_4] = 3.15$ (or 6.46 for halloysite) $+ \log [Na^+] - pH$

(b) $NaAlSi_3O_8 + Al(OH)^{2+} + 4\,H_2O = Al_2Si_2O_5(OH)_4 + Na^+ + H_4SiO_4 + H^+$ $\log [Al(OH)^{2+}] - \log [H_4SiO_4] = -1.84$ (or 1.46 for halloysite) $+ \log [Na^+] - pH$

(c) $NaAlSi_3O_8 + Al(OH)^+_2 + 3\,H_2O = Al_2Si_2O_5(OH)_4 + Na^+ + H_4SiO_4$ $\log [Al(OH)^+_2] - \log [H_4SiO_4] = -5.89$ (or −2.59 for halloysite) $+ \log [Na^+]$

(d) $NaAlSi_3O_8 + 2H^+ + H_2O + Al(OH)^-_4 = Al_2Si_2O_5(OH)_4 + Na^+ + H_4SiO_4$ $\log [Al(OH)^-_4] - \log [H_4SiO_4] = -19.26$ (or −15.96 for halloysite) $+ \log [Na^+] + 2pH$

Figure 3 is a three-dimensional plot of stability relations of albite and kaolinite and of albite and halloysite in terms of the experimental parameters—pAl, pH_4SiO_4, pNa^+, and pH. Figures 4a and 4b are two isoplethic sections at $pNa^+ = 0.48$, and 3.58, for average sea water and river water, respectively. The diagrams indicate that in non-marine environment (average river water) halloysite and kaolinite are stable with respect to albite, whereas in marine environment kaolinite (not halloysite) is a stable phase. This is consistent with the results obtained from the K-feldspar-kaolinite-halloysite system as shown in Figure 2.

(3) Equilibrium reactions for nepheline ($\Delta G_f°$ =

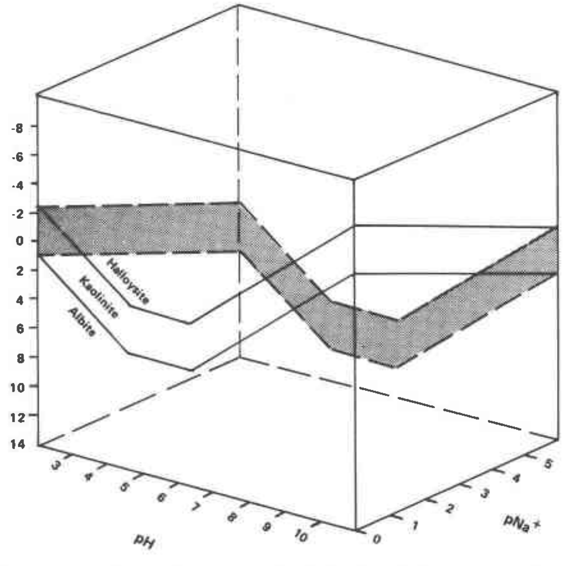

FIG. 3. Stability diagram of albite-kaolinite and albite-halloysite at 25°C and 1 atm., in which $pAl-pH_4SiO_4$ is plotted against pH and pNa^+.

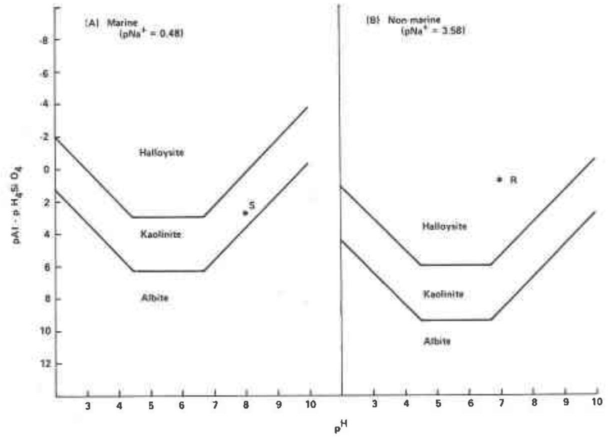

FIG. 4. Isoplethic sections of the stability diagram (albite-kaolinite and albite-halloysite) for marine (sea water) and non-marine (average river water) environments. S and R are the compositions of sea water and average river water respectively. (A) Marine ($pNa^+ = 0.48$); (B) Non-marine ($pNa^+ = 3.58$).

−469.7 kcal/mole) and kaolinite and halloysite are expressed as follows:

(a) $NaAlSiO_4 + Al^{3+} + H_4SiO_4 + H_2O = Al_2Si_2O_5(OH)_4 + Na^+ + H^+$ $\log [Al^{3+}] + \log [H_4SiO_4] = -8.26$ (or -4.96 for halloysite) $+ \log [Na^+] - 2pH$

(b) $NaAlSiO_4 + Al(OH)^{2+} + H_4SiO_4 = Al_2Si_2O_5(OH)_4 + Na^+ + H^+$ $\log [Al(OH)^{2+}] + \log [H_4SiO_4] = -13.26$ (or -9.96 for halloysite) $+ \log [Na^+] - pH$

(c) $NaAlSiO_4 + Al(OH)^{2+} + H_4SiO_4 = Al_2Si_2O_5(OH)_4 + Na^+ + H^+$ $\log [Al(OH)^{2+}] + \log [H_4SiO_4] = -17.31$ (or -14.01 for halloysite) $+ \log [Na^+]$

(d) $NaAlSiO_4 + Al(OH)^-_4 + H_4SiO_4 + 2H^+ = Al_2Si_2O_5(OH)_4 + Na^+ + 3\,H_2O$ $\log [Al(OH)^-_4] + \log [H_4SiO_4] = -30.68$ (or -27.38 for halloysite) $+ \log [Na^+] + 2pH$

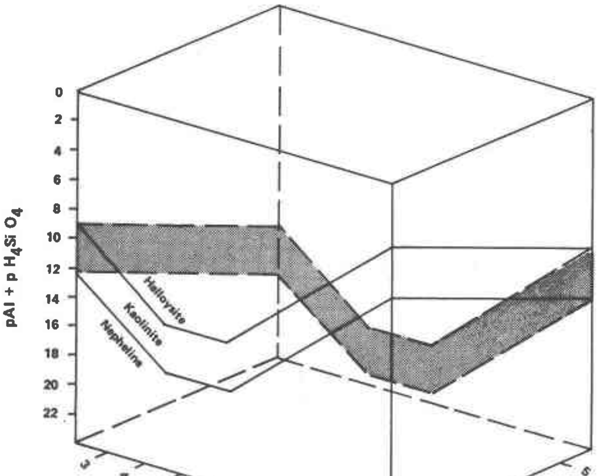

FIG. 5. Stability diagram of nepheline-kaolinite and nepheline-halloysite at 25°C and 1 atm., in which $pAl + pH_4SiO_4$ is plotted against pH and pNa^+.

Figure 5 is a phase diagram between nepheline and kaolinite and between nepheline and halloysite in terms of ($pAl+pH_4SiO_4$), pNa^+, and pH. Two isoplethic sections which show stability relations of these three minerals in marine ($pNa^+=0.48$) and non-marine environments are presented in Figures 6a and 6b. The diagrams show clearly that in either environment halloysite and kaolinite are stable with respect to nepheline, independent of activity of Na^+ (from marine to non-marine environment). The fact that nepheline from nepheline syenite in Arkansas has been altered to halloysite (Keller, personal communication) is consistent with the theoretical results obtained from such diagrams where Al is considered a mobile, active component. It should be pointed out, however, that since the more disordered halloysite can probably form more rapidly than kaolinite (kinetic consideration, discussed later), such differential rates of formation may mask the presence of any minor amount of kaolinite.

(4) Stability relations for albite and Na-montmorillonite, and K-feldspar and K-mica which are expressed in terms of pAl, pH_4SiO_4, pNa^+, pH, are also shown in Figures 7 and 8, respectively. In Fig-

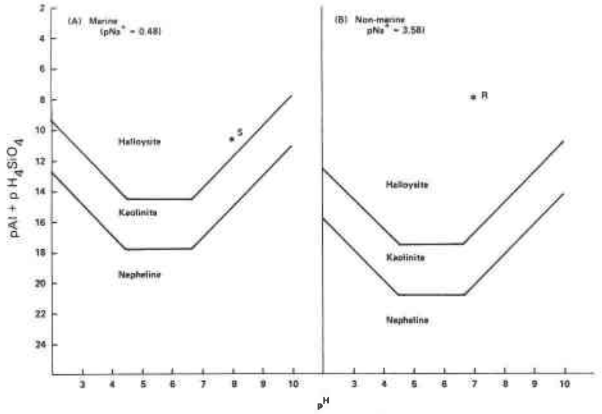

FIG. 6. Isoplethic sections of the stability diagrams nepheline-kaolinite and nepheline-halloysite for marine (sea water) and non-marine (average river water) environments. S and R are the compositions of sea water and average river water. (A) Marine ($pNa^+ = 0.48$); (B) Non-marine ($pNa^+ = 3.58$).

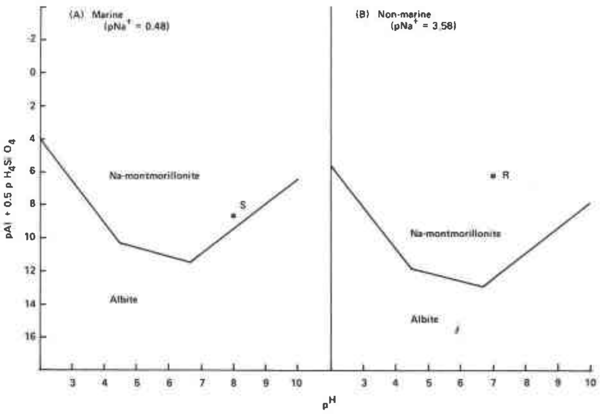

FIG. 7. Isoplethic sections of the stability diagram (Na-montmorillonite and albite) for marine (sea water) and non-marine (average river water) environments. S and R are the compositions of sea water and average river water. (A) Marine (pNa$^+$ = 0.48); (B) Non-marine (pNa$^+$ = 3.58).

ure 7, Na-montmorillonite is expected to be stable with respect to albite in either non-marine or marine environment. Likewise, K-mica (or illite) will be more stable than K-feldspar in either environment (Fig. 8).

Summary

In average river water, both halloysite and kaolinite are stable with respect to K-feldspar, albite, and nepheline. In present sea water kaolinite becomes stable with respect to K-feldspar and albite, whereas both halloysite and kaolinite are stable with respect to nepheline.

Discussions

Geologic field observations reveal that in the modern weathering products of non-layer aluminum silicates, both halloysite and kaolinite are formed together or independently, depending on (1) *geologic conditions*—climate, topography, the degree of leaching, *etc* (Sand, 1956; Parham, 1969; Keller, 1970); (2) *geochemical conditions*—activities of Al, H_4SiO_4, Na^+, K^+, and H^+. In the ancient weathered products, however, kaolinite is more abundant than halloysite. The question that remains to be answered is why the ratio of kaolinite over halloysite increases with an increase of geologic time. This may be explained from the following points:

(1) *From a viewpoint of Gibbs free energy* (ΔG°)

To simplify discussions here, assume both halloysite and kaolinite to have the composition, $Al_2Si_2O_5(OH)_4$. The values of ΔG_f° for halloysite and kaolinite with $Al_2Si_2O_5(OH)_4$ compositions respectively, are −898.4 kcal/mole and −902.9 kcal/mole.

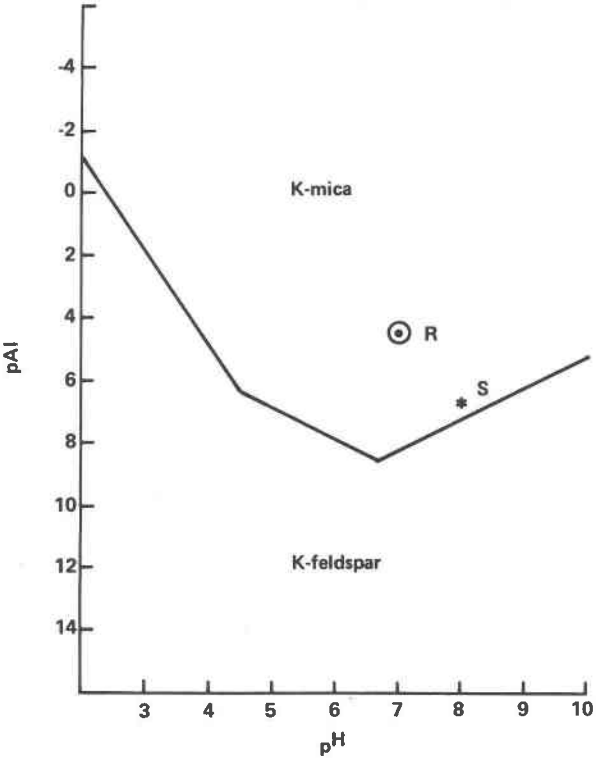

FIG. 8. Stability diagram of K-mica and K-feldspar at 25°C and 1 atm., in which pAl is plotted against pH. S and R are the composition of sea water and average river water.

(a) Because ΔG_f° for halloysite is larger than that for kaolinite (Fig. 9), a supersaturated solution of Al-silicate with respect to both halloysite and kaolinite, in which its molar Gibbs free energy exceeds those of both halloysite and kaolinite, will precipitate either halloysite or kaolinite, whereas a saturated solution with respect to kaolinite will equilibrate only with kaolinite. A similar solution phenomenon was

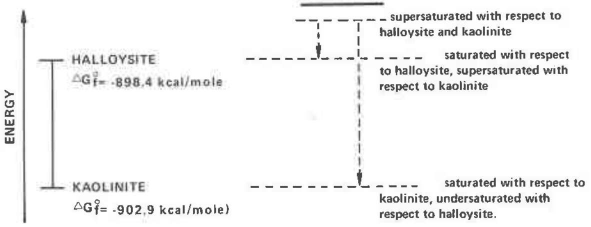

FIG. 9. Relative thermodynamic stabilities of kaolinite and halloysite.

pointed out by Ernst (1969) for crystallization of aragonite and calcite. Therefore, from a viewpoint of solution chemistry, halloysite will crystallize from a solution supersaturated with respect to halloysite, but kaolinite will crystallize under these same conditions or also from a solution saturated with respect to kaolinite. Furthermore, any halloysite formed will ultimately be transformed to kaolinite. This may be explained in section (b).

(b) Consider the equilibrium reaction between halloysite and kaolinite as follows:

$$\underset{\text{halloysite}}{Al_2Si_2O_5(OH)_4} = \underset{\text{kaolinite}}{Al_2Si_2O_5(OH)_4}$$

$\Delta G_r°$ (Gibbs free energy of reaction)

$= \Delta G_f°$ (Gibbs free energy of formation for kaolinite)

$- \Delta G_f°$ (Gibbs free energy of formation for halloysite)

$= -902.9 - (-898.4)$

$= -4.5$ kcal (<0)

Since the $\Delta G_r°$ is negative, the reaction is spontaneous; that is, the reaction will go from left to right. Therefore halloysite is a metastable phase, and will be ultimately transformed into kaolinite. This is analogous to the transformation of aragonite to calcite.

(2) *From a viewpoint of activation energy* (ΔH)

Although the transformation of halloysite to kaolinite is a spontaneous process, the question remains as to how long this transformation process will take. This is a kinetic problem, which involves activation energy (ΔH) rather than Gibbs free energy (ΔG), as shown in Figure 10. The magnitude of ΔH will depend on reaction mechanism, and the temperature of the reaction is a rate-decision factor for any given mechanism (Curtis and Krinsley, 1965). Thus the rate of transformation of halloysite to kaolinite will depend on (1) activation energy and (2) temperature. Geologically, the transformation may result from diagenetic processes. No data are available at this time for possible quantitative evaluation. If dissolution of halloysite and accompanying precipitation of kaolinite is the transformation mechanism, the rate of such transformation could be determined by the rate of such dissolution and precipitation. Further kinetic studies of such transformation is necessary before any definite interpretations may be made.

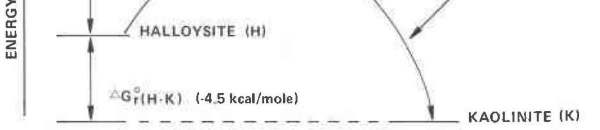

FIG. 10. Relationship between activation energy ($\Delta H_{(H-K)}$) and free energy of reaction ($\Delta G_{r(H-K)}{}^0$) for the kaolinite-halloysite system.

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