AQUEOUS DISSOLUTION STUDIES OF ILLITE UNDER AMBIENT CONDITIONS

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Abstract—Dissolution data on five of the six illites reported by Reesman and Keller (1968) indicate that these illites are more stable than was previously thought. The revised Gibbs free energies of formation (ΔG_f^0) with respect to the 'ideal' illite formula and the muscovite formula are:

Sample	ΔG_f^0 'illite formula'	ΔG_f^0 'muscovite formula'
Fithian illite	−1319·7 kcal/fw	−1334·8 kcal/fw
Grundy illite	−1322·7	−1338·0
Rock Island illite	−1307·3	−1333·2
Marblehead	−1310·8	−1334·2
Gage	(No formula)	−1337·6

Use of muscovite formula as an indirect comparator provides a means of predicting the relative stabilities of these chemically complex materials.

The response of illite-equilibrated solution to a kaolin ΔG_f^0 was found in all samples in which a 7 Å mineral phase was detected by X-ray diffraction. Stability diagrams based upon the ΔG_f^0 with respect to ideal muscovite and kaolin formulas show a rather wide range in chemical conditions through which illites and kaolin minerals with differing ΔG_f^0 would be stable. However, in carbonate rocks and sea water illite is stable relative to kaolin. During the weathering of carbonates the lower pH zones in the clay-rich residuum above the carbonates favor the transformation of illite to kaolin minerals.

INTRODUCTION

Marblehead, Fithian, Rock Island, and Grundy (grundite) illites, used by Gaudette *et al.* (1966), and the Gage illite were studied by aqueous dissolution techniques to determine the solubility constants (*Ks*) and standard free energies of formation (ΔG_f^0). This paper covers the same illites studied by Reesman and Keller (1967), but is based upon newly collected solution data. Five factors that led to this re-study of illite dissolution and stability are: (1) new analytical data, believed to be superior, were available; (2) variability in the data of the original study led to an undesirable degree of certainty in the results; (3) one previously reported value was wrong; (4) the extent to which unremoved colloidal material in the sample solution affected the analytical results was poorly understood; and (5) extensive manipulation of solubility data indicates that very useful information can be obtained by simplifying illite formulas.

The mineral samples used in this study are the same ones that were studied by Reesman and Keller (1967), except that samples of the Beavers Bend illite were lost by the author in the course of subsequent moves. In the previous study 100 ml aliquots were extracted from the mineral–water containers, centrifuged, and the resul-

tant solutions analyzed. The containers were small (500 ml) and the sample aliquots were replaced with fresh deionized water for further (renewed) equilibration. Thus, the study system was of an open–closed extractive nature that was opened periodically by the addition of new deionized water. From three to eleven separate equilibrations were made with the mineral samples. Another problem in the study was that solutions were equilibrated, 100 ml aliquots withdrawn and centrifuged in one location then transported to a second laboratory for analyses. All subsequent analyses were made with this 100 ml aliquot. Because of the time necessary to run the various analyses, the prolonged separation of solution from the solid, and the fact that numerous separate equilibrations were made, there was a rather large variation in the calculated ΔG_f^0 for the minerals as determined from the dissolution data.

In the current study, the mineral–water samples from the previous study, which had been stored in their original equilibration bottle for 2 yr in 200 ml of solution, were transferred to large plastic bottles and a solution volume of about 2 l. was formed by adding deionized water. The initial mineral–water ratio was about 1–200, but the final ratio was about 1–20. The

Table 1. Analytical data for solutions equilibrated with illites for 42 months

Sample	K	Na	Ca	Mg	SiO$_2$	Al	Fe	SO$_4$	HCO$_3$	PO$_4$	pH
Grundite	1·9	0·40	0·02	0·008	6·6	0·094	0·02	29·0	—	—	3·70
	(4·33)	(4·77)	(6·35)	(6·53)	(3·96)	(5·47)	(6·50)	(3·57)			
Gage	0·58	0·20	—	—	2·2	0·047	0·014	10·0	—	—	4·49
	(4·84)	(5·07)			(4·44)	(5·77)	(6·63)	(4·01)			
Fithian	2·7	0·30	0·02	0·023	1·90	0·032	0·026	2·0	3·0	—	5·00
	(4·17)	(4·89)	(6·17)	(6·04)	(4·50)	(5·93)	(6·35)	(4·70)	(4·30)		
Rock Island	1·80	0·13	0·13	0·056	1·90	0·0085	0·020	—	5·0	—	5·77
	(4·34)	(5·25)	(5·50)	(5·65)	(4·50)	(6·50)	(6·50)		(4·09)		
Marblehead	1·65	0·12	0·36	0·64	2·07	0·0009	0·037	—	15·0	0·56	7·42
	(4·38)	(5·29)	(5·07)	(4·60)	(4·46)	(7·48)	(6·20)		(3·62)	(5·25)	

Absence of analytical data indicates that concentrations of ion were below the levels of detection.
Upper values given in ppm and enclosed values are p values (negative logarithm of activities as determined by the Debye–Hückel method).

original intention was to obtain some crude data on rates of dissolution; however, delays in laboratory construction and other problems resulted in little useful information on this aspect of the project. However, in this study only a single continuous equilibration was made and there was sufficient reservoir of solution so that analyses could be repeated if necessary. The occasional spurious analysis is easily found, and, thus there is more confidence in the data.

ANALYTICAL PROCEDURE

Solutions were analyzed periodically for pH, potassium, sodium, silica, and aluminum. Less frequent
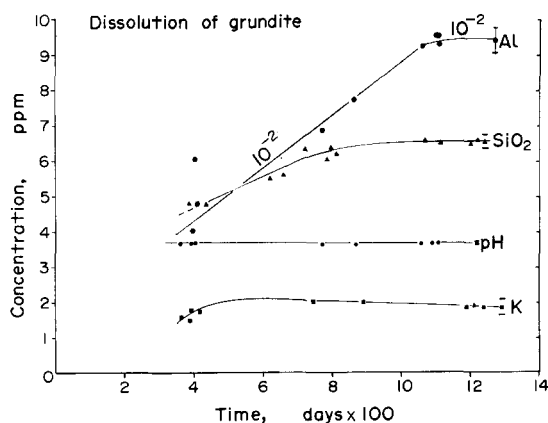

Fig. 1. This diagram shows the concentrations of four major components from solutions equilibrated with grundite as a function of time. These rate data are crude because construction delays resulted in no analyses during the first year of equilibration and with the exception of potassium analyses the analytical data up to about 1000 days were determined by student assistants learning these analytical procedures. The author collected the data thereafter. Horizontal bars above and below the final analyses indicate analytical precision.

analyses were made for additional solution products. Analyses of these solutions were begun in June 1968 and terminated in early 1972. During this time 68 separate analyses were run on each solution. These were broken down as follows: pH 14, SiO$_2$ 20, Al 7, K 9, Na 5, Ca 3, Mg 2, Fe 2, SO$_4$ 2, PO$_4$ 2, Cl 1, and conductivity 1. Most of the data represent repetition that were collected as riders with other samples being analyzed. Although several analysts were involved in the overall collection of data, the data presented herein were determined by the author.

Sodium, potassium and calcium were determined by flame photometry, magnesium by atomic absorption and silica, phosphate, and iron by colorimetry. Aluminum was determined fluorimetrically as the 8-hydroxyquinoline complex extracted into chloroform (Goon, 1953). Chloride and bicarbonate were determined by titration and sulfate by absorption of barium sulfate suspension. The pH was run on an expanded scale pH meter.

Aliquots for analyses were pipetted from the sample containers just prior to analyses. Centrifugation did not precede most analyses because at the beginning of the study a centrifuge was not available. After the first aliquot was taken the mineral–water systems were not subjected to unnecessary agitation; however, the final sample aliquots were centrifuged for one hour at 14,000 rpm in a Sorvall SS-4 prior to analyses.

ANALYTICAL RESULTS

Final analyses of the solutions that had been equilibrated for over three and a half years are given in Table 1. The results are reported in parts per million (ppm); the negative logarithms of the activities (p values) are given below the concentrations in parenthesis. The activities were computed from the ionic strength of the solutions by the Debye–Hückel method.
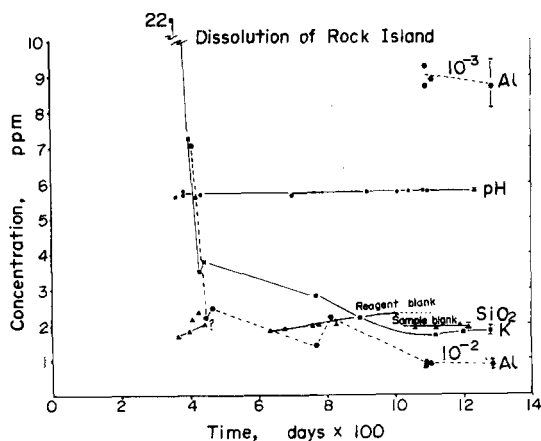
Fig. 2. This diagram shows the concentrations of four major components from solutions equilibrated with Rock Island illite as a function of time. Note the high results in the initial potassium analysis and the discontinuity in the SiO$_2$ plot at about 1000 days. Potassium enhancement was related to unremoved colloidal particles and the silica discontinuity resulted when slight organic coloration in equilibration solution was corrected by using a solution blank rather than a reagent blank (solution had an absorbance of about 0·010 at 650 μm).

Throughout the analytical phase of the study the major 'real' increases that were noted in concentrations were slow, steady increases in silica and aluminum from the solution in contact with the grundite sample (see Fig. 1). The silica in this sample increased from 4·75 ppm at 1 yr equilibration to 6·6 ppm at the end of 3½ yr. During this period of time the solution volume decreased from about 2 l. to about 250 ml. Because of the increase of the mineral to solution ratio as solution aliquots were removed, the effective equilibration between the results of the initial and final determinations of silica was much longer than the 2½ calendar yr. Slight increases of about 0·2 ppm were noted in silica between the first and second year of equilibration with the other samples (see Fig. 2).

Values of pH remained essentially constant during the analytical phase, but slight variations in pH were recorded. These variations resulted from improper electrode equilibration in the solutions. Solutions with very low electrolyte content (buffer capacity?) produce meter drift which can be corrected by using two or three aliquots (one to get the electrode responding, one to bring it to its senses, and one to determine the pH). This method required 15–20 min per sample but it provided very reproducible results.

Both potassium and aluminum showed a general decrease in concentration with time for all samples except the Gage and Grundy illites. This decrease is apparently related to the colloidal nature of the minerals rather than true dissolution phenomena. The

presence of colloidal particles in a sample aliquot yields analytical enhancement of both potassium and aluminum values. During the early stages of analyses a centrifuge was not available, but as settling times increased the corresponding analytical values of both decreased. After about a year of relatively little disturbance of sample bottles the analytical values of both potassium and aluminum reached the same analytical level as they did after centrifugation. The centrifugation was theoretically equivalent to about 2 yr of ideal Stokes settling. The convergence in analytical values of potassium and aluminum between aliquots removed after natural sedimentation for about 1 yr and those following centrifugation are the best evidence for removal of the suspended material prior to analysis (see Figs. 1 and 2).

Table 2 shows both the initial uncentrifuged and the final centrifuged values of potassium and aluminum from these solutions. The Grundy and Gage samples either contained larger particles or were somewhat self-flocculating, and thus showed little difference. Although both Marblehead and Rock Island illites showed about the same degree of initial enhancement, the rate of settling was slower for the Rock Island illite than for the Marblehead.

CALCULATION OF SOLUBILITY PRODUCTS AND STANDARD FREE ENERGIES OF FORMATION

From the analytical results given in Table 1 it is possible to calculate the solubility constants with respect to the minerals undergoing dissolution. The 'p' values or negative logarithms of the activities are used for this calculation.

To form a solubility constant it is necessary that equilibrium or near equilibrium conditions exist between the mineral and the solution and that a valid equation can be written for the formation of the solution products. Figures 1 and 2 show the changes in concentration of aluminum, silicon, and potassium with time for Grundy and Rock Island illites. Although no chemical analysis was available for the Gage illite and its solubility constant was calculated with respect

Table 2. Analytical changes in potassium and aluminum between initial and final analyses (probably related to partial settling)

Sample	K		Al		Solution pH
	First	Last	First	Last	
Grundite	1·6	1·9	0·060	0·094	3·70
Fithian	6·7	2·7	0·078	0·032	5·00
Gage	0·56	0·58	0·030	0·047	4·49
Rock Island	22·0	1·80	0·071	0·0085	5·77
Marblehead	24·0	1·65	0·022	0·0009	7·42

to ideal muscovite, chemical analyses of such chemically complex minerals as illites are desirable.

The illite formulas used in this study were taken from Reesman and Keller (1967); these in turn were modified from the analyses supplied by Gaudette et al. (1966), to remove iron and titanium from the structure. Titanium was removed because of the difficulty in analyzing for the titanium and the uncertainty that the minor amounts of titanium that were reported were actually in the illite structure. Iron was removed by Reesman and Keller (1967) because there was some uncertainty that all of the iron was contained within the mineral structure.

During 13 equilibrations of the Grundy and Fithian illites for the earlier paper (Reesman and Keller, 1967), the pH values of the solutions equilibrated with grundite ranged from 2·68 to 4·0 (mean about 3·2) and the Fithian ranged from 3·4 to 4·8 (mean about 4·3). The low values of pH indicated the probable presence of a ferrous sulfide phase in the system. In addition, the problems associated with the determination of ferrous and ferric iron and working with the Eh of the reacting system was a problem in the earlier study by Reesman and Keller (1967) because mineral equilibrations and sample aliquots were taken in one laboratory and sample analyses were generally started the next day in a laboratory that was several blocks away. In this study iron was omitted so that the results would parallel the earlier study, and the number of chemical components in the system would be reduced. The concentration of total iron in solution at about 1200 days is given in Table 1 for the current work. The activity

of total iron exceeded the activity of aluminum only in the solution equilibrated with Marblehead illite. The molar distribution of ferrous and ferric iron in the structure of the illites originally reported by Gaudette et al. (1966) was as follows:

Grundy	$0·00 Fe^{2+}$	$0·40 Fe^{3+}$
Fithian	$0·22 Fe^{2+}$	$0·45 Fe^{3+}$
Rock Island	$0·08 Fe^{2+}$	$0·07 Fe^{3+}$
Marblehead	$0·07 Fe^{2+}$	$0·04 Fe^{3+}$.

Thus, Marblehead illite, which supposedly contained the least iron, yielded the highest iron concentrations in solution and did so at a nearly neutral pH of 7·42. The substitution of magnesium for ferrous and aluminum for ferric iron has very little effect on the relative Gibbs free energies of formation when the activity of iron in solution is roughly equivalent to that of magnesium and aluminum. In the case of Fithian illite which contains the most iron, the substitution of magnesium for ferrous and aluminum for ferric iron would have the following effect on the solubility constant:

Replace $0·22 Fe^{2+}$ (pFe 6·35) with
$0·22 Mg$ (pMg 6·04) $= (0·31)(0·22) = 0·068$
Replace $0·45 Fe^{3+}$ (pFe 6·35) with
$0·45 Al$ (pAl 5·93) $= (0·42)(0·45) = \underline{0·189}$
Difference in pKs $= \overline{0·257}$.

Thus, the substitutions that were made for iron caused a 0·257 decrease in the pKs for Fithian from the 68·17–68·43. Then of course one would have to differentiate ferrous and ferric activities in solution and consider the

Table 3. Dissolution reactions used to calculate solubility constants grundite

$(K_{0·56}Na_{0·04})(Mg_{0·24}Al_{1·90})(Si_{3·22}Al_{0·78})O_{10}(OH)_2 + 10H_2O$
$= 0·56K^+ + 0·04Na^+ + 0·24Mg^{2+} + 2·68Al(OH)_2^+ + 3·22H_4SiO_4 + 3·76(OH)^-$
$pKs_2 = 0·56pK + 0·04pNa + 0·24pMg + 2·68pAl + 3·22pSi + 3·76pOH$

Fithian

$(K_{0·60}Na_{0·05}Ca_{0·07})(Mg_{0·40}Al_{1·65})(Si_{3·46}Al_{0·54})O_{10}(OH)_2 + 10H_2O$
$= 0·60K^+ + 0·05Na^+ + 0·07Ca^{2+} + 0·40Mg^{2+} + 2·19Al(OH)_2^+ + 3·46H_4SiO_4 + 3·78(OH)^-$
$pKs_2 = 0·60pK + 0·05pNa + 0·07pCa + 0·40pMg + 2·19pAl + 3·46pSi + 3·78pOH$

Rock Island

$(K_{0·59}Na_{0·03}Ca_{0·03})(Mg_{0·34}Al_{1·69})(Si_{3·57}Al_{0·43})O_{10}(OH)_2 + 10H_2O$
$= 0·59K^+ + 0·03Na^+ + 0·03Ca^{2+} + 0·34Mg^{2+} + 2·12Al(OH)_2^+ + 3·57H_4SiO_4 + 3·48(OH)^-$
$pKs_2 = 0·59pK + 0·03pNa + 0·03pCa + 0·34pMg + 2·12pAl + 3·57pSi + 3·48pOH$

Marblehead

$(K_{0·69}Na_{0·03}Ca_{0·05})(Mg_{0·40}Al_{1·60})(Si_{3·58}Al_{0·42})O_{10}(OH)_2 + 10·40H_2O$
$= 0·69K^+ + 0·03Na^+ + 0·05Ca^{2+} + 0·40Mg^{2+} + 2·02Al(OH)_4^- + 3·58H_4SiO_4 + 0·40H^+$
$pKs_4 = 0·69pK + 0·03pNa + 0·05pCa + 0·40pMg + 2·02pAl + 3·58pSi + 0·40pH$

Muscovite

$KAl_3Si_3O_{10}(OH)_2 + 10H_2O = K^+ + 3Al(OH)_2^+ + 3H_4SiO_4 + 4(OH)^-$
$pKs_2 = pK + 3pAl + 3pSi + 4pOH$
for $pKs_4 = pK + 3pAl + 3pSi + 2pH$

Table 4. Standard free energies of formation used in this study

Substance	ΔG_f^0	Source
$Al(OH)_2^+$	$-216 \cdot 1$ kcal/fw	Reesman *et al.* (1969)
$Al(OH)_4^-$	$-311 \cdot 3$	Reesman *et al.* (1969)
$Al_2Si_2O_5(OH)_4$ (kaolinite)	$-903 \cdot 0$	Barany and Kelley (1961)
Ca^{2+}	$-132 \cdot 1$	Robie and Waldbaum (1968)
H^+	$0 \cdot 0$	Robie and Waldbaum (1968)
H_2O (water)	$-56 \cdot 7$	Robie and Waldbaum (1968)
H_4SiO_4	$-312 \cdot 65$	Reesman and Keller (1968)
K^+	$-67 \cdot 7$	Robie and Waldbaum (1968)
$KAl_3Si_3O_{10}(OH)_2$	$-1330 \cdot 1$	Barany (1964)
Mg^{2+}	$-108 \cdot 9$	Robie and Waldbaum (1968)
Na^+	$-62 \cdot 5$	Robie and Waldbaum (1968)
OH^-	$-37 \cdot 6$	Robie and Waldbaum (1968)

partial molar free energies of formation of the ferrous and ferric ions in the structure. The result would lead to the addition of two chemical components and make it more difficult to try to determine the relative chemical stabilities of these different clays.

The nature of the dissolution products are fairly well established except for aluminum. The alkali and alkaline earths are considered to be present as singly and doubly charged cations. Silicon is assumed to be present as un-ionized silicic acid under the conditions of this study. Because of previous and continued studies of the nature of aluminum ions in aqueous solution (Reesman, Pickett and Keller, 1968), the author assumes that below a pH of 6·70 the dominant alu-

minum ion in solution was the monovalent cation $Al(OH)_2^+$ and that above this pH the singly charged anion $Al(OH)_4^-$ dominates. Table 3 shows the dissolution reactions used in this study.

Solubility product constants (Ks) are formed by multiplying the activities of each of the individual dissolved ions, raised to the power of its molar concentration in the mineral. By using logarithms of the individual ion activities, either the logarithm of the solubility constant (log Ks) which is generally negative, or the pKs (where p symbolizes the negative logarithm) can be used to great advantage. Table 3 shows the pKs for each dissolution reaction. By multiplying the corresponding p values of the individual ions in Table 1 by

Table 5. Sample calculation of ΔG_f^0 of grundite from solubility data general thermodynamic equations

ΔG_f^0 of products $= \Delta G_f^0$ of reactants $+ \Delta G_R^0$

$\Delta G_R^0 =$ free energy of reaction $= -RT \ln K = -1 \cdot 364 \log K$

ΔG_f^0 of products $=$ sum of partial molar free energies of solution products (see Table 3 for dissolution equation and Table 4 for molar free energies)

Component	(Molar coef.) $(\Delta G_f^0/\text{mol})$		ΔG_f^0 of component
$0 \cdot 56$ K$^+$	$(0 \cdot 56)(-67 \cdot 7)$	$=$	$-37 \cdot 91$ kcal
$0 \cdot 04$ Na$^+$	$(0 \cdot 04)(-62 \cdot 5)$	$=$	$-2 \cdot 50$ kcal
$0 \cdot 24$ Mg^{2+}	$(0 \cdot 24)(-108 \cdot 9)$	$=$	$-26 \cdot 14$ kcal
$2 \cdot 68$ Al(OH)$_2^+$	$(2 \cdot 68)(-216 \cdot 1)$	$=$	$-579 \cdot 15$ kcal
$3 \cdot 22$ H$_4$SiO$_4$	$(3 \cdot 22)(-312 \cdot 65)$	$=$	$-1006 \cdot 73$ kcal
$3 \cdot 76$ (OH)$^-$	$(3 \cdot 76)(-37 \cdot 6)$	$=$	$-141 \cdot 38$ kcal
	ΔG_f^0 of solution products $=$		$-1793 \cdot 81$ kcal
	ΔG_f^0 of 10 moles of H$_2$O (reactant) $=$		$-567 \cdot 0$ kcal

Ks_2	$= [K^+]^{0 \cdot 56}[Na^+]^{0 \cdot 04}[Mg^{2+}]^{0 \cdot 24}[Al(OH)_2^+]^{2 \cdot 68}[H_4SiO_4]^{3 \cdot 22}[(OH)^-]^{3 \cdot 76}$
$\log Ks_2$	$= -pKs_2$
pKs_2	$= 0 \cdot 56pK + 0 \cdot 04pNa + 0 \cdot 24pMg + 2 \cdot 68pAl + 3 \cdot 22pSi + 3 \cdot 76pOH$
	$= (0 \cdot 56)(4 \cdot 33) + (0 \cdot 04)(4 \cdot 77) + (0 \cdot 24)(6 \cdot 53) + (2 \cdot 68)(5 \cdot 47) + (3 \cdot 22)(3 \cdot 96) + (3 \cdot 76)(10 \cdot 30)$
	$= 70 \cdot 32$
ΔG_R^0	$= -1 \cdot 364 \log K = 1 \cdot 364 \, pK$
	$= 95 \cdot 92$ kcal
ΔG_f^0 (Grundite)	$= \Delta G_f^0$ (solution products) $- \Delta G_f^0$ (10·0 waters) $- \Delta G_R^0$
	$= -1793 \cdot 81 - (-567 \cdot 0) - (-95 \cdot 92)$
	$= -1322 \cdot 73$ kcal/fw

Table 6. Standard free energies calculated with respect to 'ideal' illite formulas and ideal muscovite (Table 3)

| Sample | 'Ideal' illite formula | | Muscovite formula | |
	Previous	This Paper	Previous	This Paper
Fithian	−1318·0	−1319·7	−1334·4	−1334·8
Grundite	−1317·6	−1322·7	−1335·4	−1338·0
Rock Island	−1298·9	−1307·3	−1323·7	−1333·2
Marblehead	−1307·2	−1310·8	−1336·1*	−1334·2
Gage			−1334·7	−1337·6

* Previous value was in error and should have been reported as −1332·2.

the coefficients for the particular reaction as given in Table 3, the solubility constant for each mineral is obtained. For comparison, the solubility constants are also computed with respect to ideal muscovite.

The standard free energy of the reaction ΔG_R^0 can be calculated from the Nernst equation as follows:

$$\Delta G_R^0 = -RT \ln K_s = 1·364 \, pK_s.$$

By utilizing the ΔG_R^0 for the dissolution reaction and the standard free energies of formation ΔG_f^0 of the dissolution products and water, the ΔG_f^0 for the illites can be determined as the difference in free energy between the $\sum \Delta G_f^0$ (products of solution) and the ΔG_R^0 and the ΔG_f^0 (water utilized in the reaction), or:

ΔG_f^0 Illite $= \sum \Delta G_f^0$ solution products $- \Delta G_R^0 - \Delta G_f^0$ water.

The ΔG_f^0 for the solution products and water are given in Table 4. Calculations of ΔG_f^0 for the Grundy illite are shown in Table 5.

Table 6 summarizes the ΔG_f^0 for the minerals with respect to both the ideal illite formula and ideal muscovite. In all cases the free energies with respect to the ideal illite formulas were lower in this study than reported by Reesman and Keller (1967); however, the Marblehead solution increased with respect to the muscovite formula because the previous value was in error. The extreme change in the free energy for Rock Island illite can be related to unremoved suspended material in the sample solutions of the previous study.

X-ray diffractograms of the illites (Fig. 3) showed that all of the samples contained a measurable amount of 7 Å material except the Marblehead illite. This material was originally present in the sample. Gaudette (personal communication) believes that at least part of these 7 Å peaks represent the 002 spacings of chlorite. In any event, it is interesting to note that if the solubility constant and corresponding ΔG_f^0 are calculated with respect to kaolinite (Table 7), only Marblehead solution with a calculated ΔG_f^0 at −903·8 kcal/fw would be unsaturated with respect to kaolinite. The generally accepted ΔG_f^0 for kaolinite is −903·0 kcal/fw.
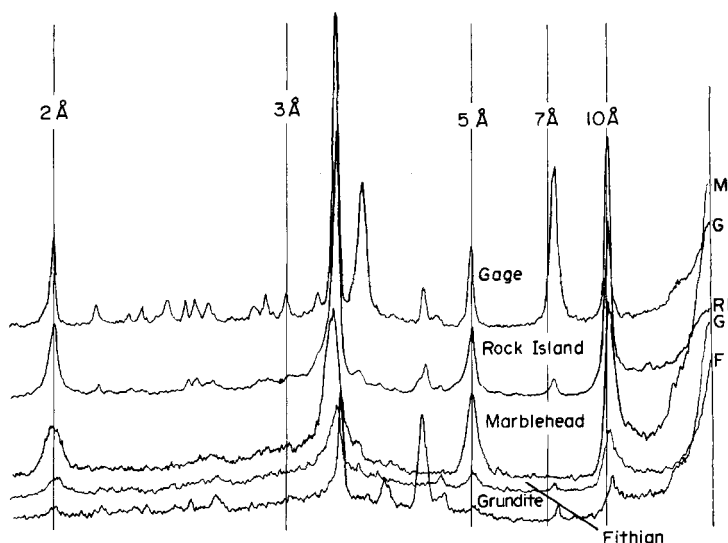

Fig. 3. X-ray diffractograms of thin-glycolated films of illites mounted on microporous filters.

Table 7. Dissolution reations for kaolin minerals with pKs and ΔG_f^0 relative to kaolin as determined from illite equilibrated solutions

$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al(OH)_2^+ + 2H_4SiO_4 + 2(OH)^-$
$pKs_2 = 2pAl + 2pSi + 2p(OH)$
$Al_2Si_2O_5(OH)_4 + 7H_2O = 2Al(OH)_4^- + 2H_4SiO_4 + 2H^+$
$p^*Ks_4 = 2pAl + 2pSi + 2pH$

	p^*Ks_4	pKs_2	ΔG_f^0 Kaolin
Marblehead	38·73		−903·8
Fithian		38·86	−902·2
Rock Island		38·47	−901·7
Grundite		39·46	−903·0
Gage		39·42	−903·0

Thus, it appears as though equilibrium was established between the illite and kaolinite (?) phases in those samples that contained both minerals.

ESTIMATION OF ERRORS AND THEIR EFFECT ON ΔG_f^0

Random errors related to analytical precision (equilibrium assumed)

Errors related to analytical precision add relatively minor variability to the calculation of the solubility

constant and to the ΔG_R^0. The calculated errors in pKs and ΔG_R^0 for grundite are shown in Table 8. The analytical precision was estimated at two standard errors. These confidence limits are shown for the final series of analyses in Figs. 1 and 2 by horizontal bars above and below the analysis. Because the analytical values of sodium and magnesium were rather low (below optimum analytical values) an error of ten times the potassium error was used. The net errors in the pKs for grundite would have been ± 0.17 which corresponds to a ΔG_R^0 of ± 0.23 kcal.

Uncertainites in ΔG_f^0 assuming equilibrium

Estimation of two standard errors in the calculation of the ΔG_f^0 of grundite is given in Table 9. Errors for water and all aqueous species except aluminum were taken from Robie and Waldbaum (1968). In the calculation of the ΔG_f^0 the largest contributors to the calculated uncertainties of ± 3.23 kcal result primarily from the high estimated value in the error for the aluminum ion and secondly from the silicic acid.

Non-random error: non-equilibrium

To assume true equilibrium in these mineral–solu-

Table 8. Estimation of uncertainty associated with the calculation of pKs of grundite assuming equilibration

Constituent	Precision	Effect on pValue	Molar Coef.	Total $\mathscr{S}$	$\mathscr{S}^2$
pH	± 0.03 pH	± 0.03	3·76	± 0.113	0·0128
H_4SiO_4	$\pm 5\%$	± 0.02	3·22	± 0.064	0·0041
Al	$\pm 8\%$	± 0.04	2·68	± 0.107	0·0114
K^+	$\pm 3\%$	± 0.01	0·56	± 0.006	0·0000
Na^+	Low value	± 0.1 (high est.)	0·04	± 0.004	0·0000
Mg^{2+}	Low value	± 0.1 (high est.)	0·24	± 0.024	0·0006

$\mathscr{S}^2 pKs = \mathscr{S}_1^2 + \mathscr{S}_2^2 + \mathscr{S}_3^2 - \mathscr{S}_6^2$
$= 0.0128 + 0.0041 + 0.0114 + 0.0000 + 0.0000 + 0.0006$
$\mathscr{S} pKs = \pm 0.17$
$pKs = 70.32 \pm 0.17$ or $\Delta G_R^0 = 95.92 \pm 0.23$ kcal

Table 9. Estimation of uncertainties in calculation of ΔG_f^0 on grundite

Soure of error	Error in (kcal/mole)	Moles	Total error	Error^2	
Ksp			± 0.23	0·0529	
K^+	$\pm 0.10^*$	0·6	± 0.06	0·0036	
Na^+	$\pm 0.05^*$	0·04	± 0.00	0·0000	
Mg^{2+}	$\pm 0.20^*$	0·24	± 0.04	0·0016	
$(OH)^-$	$\pm 0.02^*$	3·76	± 0.07	0·0049	
H_2O	$\pm 0.05^*$	10·0	± 0.50	0·2500	
H_4SiO_4	$\pm 0.41^*$	3·22	± 1.71	2·9241	(Ksp of quartz assumed to be $10^{-4.0}$)
$Al(OH)_2^+$	± 1.0	2·68	± 2.68	7·1824	(Estimated)
			$\mathscr{S}^2 =$	10·4195	

ΔG_f^0 Grundite $= -1322.7 \pm 3.2$ kcal $\quad \mathscr{S} = 3.23$ kcal

* Errors from Robie and Waldbaum (1968).

Table 10. Calculated pKs for grundite, assuming all components but hydrogen ion were in error by about 20 per cent

Component	Observed value	Upgraded value	Upgraded pvalue	Molar conc.	Contribution to pKs
K^+	1·9 ppm	2·5 ppm	4·21 (X)	0·56	2·36
Na^+	0·4	0·5	4·67	0·04	0·19
Mg^{2+}	0·008	0·08 (10X)	5·53	0·24	1·33
Al	0·094	0·11	5·40	2·68	14·47
SiO_2	6·6	8·0	3·88	3·22	12·49
pH	3·70	3·70	10·30	3·76	38·73
					69·57

Upgraded value of pKs = 69·57

Analytical value of pKs = 70·32.

tion systems is folly. No such condition has been proven, nor can it be. From Figs. 1 and 2 a reasonable assumption is that equilibrium is being approached. If we assume that the pH of grundite solution remained at 3·70 (which it did after 400 days) and all other components were allowed to increase by 20 per cent, what affect would this have on the calculation of the solubility constant? To imagine this one would double the height of the upper confidence limit bar on aluminum, increase the upper bar on silica by a factor of four, and increase potassium 6 times. Table 10 shows the observed analytical values, an upgraded value, and the net results of these upgraded values on the calculation of the solubility constant. Increasing the analytical values results in a decrease in the pKs from 70·32 to 69·57. The author believes that a more reasonable estimation of undersaturation might be the upper confidence level of the analytical precision. From Table 8 the total change would be:

$$pKs = -0.064 - 0.107 - 0.006$$
$$- 0.004 - 0.024 = -0.203.$$

This would result in a change in pKs from 70·32 to 70·12. Thus, the pKs values reported for the illites have much smaller uncertainties than the ΔG_f^0. The uncertainties in the pKs and ΔG_f^0 for the other illites are equivalent to those for grundite. The estimated errors in ΔG_f^0 are greater than would be calculated from solution calorimetry (if it were available). The uncertainty in the muscovite equivalent of the illites would show about the same ± 3.2 kcal that was calculated in Table 9. A value of ± 1.32 kcal is reported in the uncertainty of muscovite by Barany (1964). If the uncertainty in $Al(OH)_2^+$ was reduced to the level of that of silica, the associated error would be reduced to ± 2.1 kcal/fw.

In view of the relative uncertainty of over 3 kcal, one might conclude that the data presented herein are almost meaningless. Such is not the case. Let us consider the muscovite equivalent ΔG_f^0 of the illites shown in Table 6. All of the reported values fall within 4·8 kcal

and the standard errors on each value would be greater than 3·0 kcal. Almost all of this error is a constant error for each calculation, the variable portion between samples arises from the standard error in calculating the individual solubility constants which would amount to about ± 0.2 kcal if equilibrium had been achieved.

GEOLOGIC IMPLICATIONS

The ΔG_f^0 of the individual illites with respect to the illite formula has very little practical value because of the variations in the chemical composition from one illite to another. Thus, direct comparisons of relative stability of illites of differing chemical composition cannot be made. Indirect methods for such comparisons will be covered in a later paper; however, if we assume that illite is similar to muscovite and that an
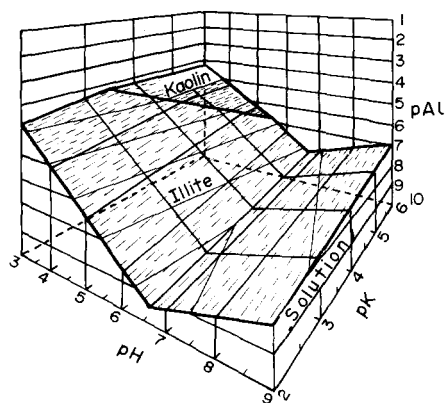

Fig. 4. pH–pK–pAl diagram showing the relative stabilities of kaolin (ΔG_f^0 −903·0 kcal) and the muscovite equivalent of illite (grundite, ΔG_f^0 −1338·0 kcal). Silica assumed to be present at a pSi of 4·0 (6·0 ppm SiO_2), which is close to the measured value of 3·96 for grundite. The muscovite equivalent is labeled 'illite' on the diagram because the chemical conditions more nearly reflect those of illite than those of muscovite.

Table 11. Equations for Fig. 4

ΔG_f^0 for kaolinite $= -903 \cdot 0$ kcal/fw or using data in Tables 4 and 7.

This is equivalent to pKs_2 of $39 \cdot 4$ and a $p*Ks_4$ of $38 \cdot 2$

ΔG_f^0 of muscovite equivalent of illite $= -1338 \cdot 0$ kcal/fw.

This is equivalent to pKs_2 of $73 \cdot 8$ and a $p*Ks_4$ of $57 \cdot 8$

Equations for kaolinite pKs_2 and $p*Ks_4$:

$$pKs_2 = 2pAl(OH)_2^+ + 2pH_4SiO_4 + 2p(OH) = 39 \cdot 4 \qquad (1)$$
$$p*Ks_4 = 2pAl(OH)_4^- + 2pH_4SiO_4 + 2pH = 38 \cdot 2 \qquad (2)$$

Equations for muscovite pKs_2 and $p*Ks_4$:

$$pKs_2 = pK + 3pH_4SiO_4 + 3pAl(OH)_2^+ + 4p(OH) = 73 \cdot 8 \qquad (3)$$
$$p*Ks_4 = pK + 3pH_4SiO_4 + 3pAl(OH)_4^- + 2pH = 57 \cdot 8 \qquad (4)$$

If $pH_4SiO_4 = 4 \cdot 0$ as assumed in Fig. 4.

Equations for kaolinite lines in Fig. 4:

$$pAl(OH)_2^+ + p(OH) = 31 \cdot 4/2 = 15 \cdot 7 \quad \text{From equation (1)} \qquad (5)$$
$$pAl(OH)_4^- + pH = 30 \cdot 2/2 = 15 \cdot 1 \quad \text{From equation (2)} \qquad (6)$$

Equations for muscovite equivalent lines in Fig. 4:

$$pK + 3pAl(OH)_2^+ + 4p(OH) = 61 \cdot 8 \quad \text{From equation (3)} \qquad (7)$$
$$pK + 3pAl(OH)_4^- + 2pH = 45 \cdot 8 \quad \text{From equation (4)} \qquad (8)$$

Equation	pK	pH	p(OH)	pAl	Comments
(5)	—	3·0	11·0	4·7	Independent of pK
(5)	—	6·0	8·0	7·7	
(6)	—	9·0	5·0	6·1	Independent of pK
(6)	—	7·0	7·0	8·1	
(7)	2·0	3·0	11·0	5·27	
(7)	6·0	3·0	11·0	3·93	
(7)	2·0	6·0	8·0	9·27	
(7)	6·0	6·0	8·0	7·93	
(8)	2·0	9·0	5·0	8·60	
(8)	6·0	9·0	5·0	7·27	
(8)	2·0	7·0	7·0	9·93	
(8)	6·0	7·0	7·0	8·60	

indirect comparison with ideal muscovite formula will provide meaningful information, it is possible to reduce the number of chemical components of these five illites from seven to four, and to provide a common reference base for comparison. This reduction in components makes it possible to present phase diagrams relative to kaolinite and to the muscovite equivalent of illite.

Figure 4 is a phase diagram showing the relationships between the muscovite equivalent of grundite $(\Delta G_f^0 - 1338 \cdot 0 \text{ kcal})$ and the kaolinite equivalent $(\Delta G_f^0 - 903 \cdot 0)$. In order to compress the four components into three dimensions, the value of silica was held constant at a pSi (same as $pSiO_2$ or pH_4SiO_4) of $4 \cdot 0$. The region of kaolinite stability of this diagram is at low pH and low potassium with grundite being the more stable of the minerals over most of the region of the diagram. Equations for plotting Fig. 4 are shown in Table 11.

In Fig. 5 the diagram has been cluttered by plotting two muscovite equivalents of illite and two kaolins. The lower muscovite equivalent boundary represents the most stable of the illites (grundite) and the upper muscovite equivalent boundary the least stable (Rock Island). The two kaolin surfaces also show a possible range in kaolin stability with the lower surface plotted at a ΔG_f^0 of $-903 \cdot 0$ and the upper kaolin surface plotted at $-901 \cdot 7$ kcal (Rock Island equivalent of a kaolin stability).

Because the ranges in ΔG_f^0 of both muscovite equivalents of illite and kaolins are the maximum and minimum values for the five samples, Fig. 5 provides insights into stability relationships between kaolin minerals and illites. The pSi of this diagram is $4 \cdot 5$
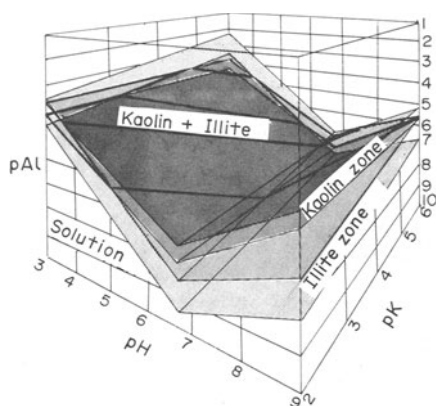
Fig. 5. pH–pK–pAl diagram showing maximum and minimum range in muscovite and kaolin equivalents of the illite equilibrated solutions. Dark diagonal lines are intersections between the two sets of illite and kaolin planes. The pSi for this diagram is 4·5, about 1·9 ppm SiO_2, which was near the silica value of all illites except grundite.

(1·9 ppm SiO_2), which is near the value of dissolved silica for all of the illites except grundite. This diagram could be redrawn with any value for the pSi without changing the pH–pK geometry of the diagram, or the (001) plane of the diagram. Changing the pSi results in either upward or downward displacement on the aluminum or pAl axis of the diagram. The vertical view of Fig. 5 is shown in Fig. 6. In this diagram the pH–pK region of sea water appears to be well within the illite stability field, as are both normal ground waters from limestones shown in area II (Reesman and Godfrey,
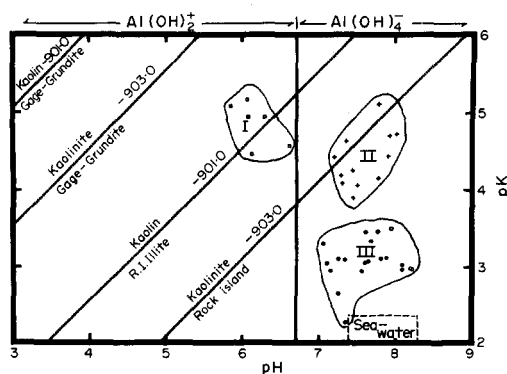

Fig. 6. Top view of Fig. 5. Dashed lines show the (001) projection of the intersections of the four sets of planes shown in Fig. 3. Areas I, II, and III show the pH–pK relationships for groundwaters from cherty residuum of Ft. Payne Fm. (I), shallow limestone wells (II), and deep mineralized artesian water from the Knox Fm. (III). This diagram shows the mineral phase that is in equilibrium with the solution at the minimum concentration of aluminum in solution.

1970) and deep mineralized waters in carbonates in area III (Fischer and Hoagland, 1970, and Fischer, personal communication). Ground waters from cherty residuum that formed from the Fort Payne Formation are shown in area I (Stearns and Wilson, 1971). The pH–pK conditions represented within area I correspond to the kaolinite–illite transition zone and to a region of chemical weathering.

SUMMARY

Revised ΔG_f^0 for five of the six illites reported by Reesman and Keller (1967) indicate that these minerals are more stable than previously reported. Because of the inherent chemical variability of the different illites, relative stabilites of the samples cannot be determined by direct comparisons of the calculated ΔG_f^0 based upon the illite formula. Current studies indicate that the use of an indirect comparator, such as the muscovite formula, provides a very good means of predicting the relative stabilities of these complex samples and also reduces the number of chemical components under consideration. The revised ΔG_f^0 for these illites are:

	ΔG_f^0 illite formula	ΔG_f^0 muscovite formula
Fithian illite	−1319·7 kcal/fw	−1334·8 kcal/fw
Grundy illite	−1322·7	−1338·0
Rock Island	−1307·3	−1333·2
Marblehead	−1310·8	−1334·2
Gage	(no formula)	−1337·6

Solutions equilibrated with illites that contained a sufficient amount of 7 Å mineral phase to be detected by X-ray diffraction appear to have established near equilibrium conditions with the illite, kaolin and solution phases. Thus, an apparently valid ΔG_f^0 for kaolin was also determined. Marblehead illite did not contain any detectable 7 Å phase and the Marblehead equilibrated solutions appeared to be undersaturated with respect to kaolinite. Using the ranges in ΔG_f^0 of the illites with respect to ideal muscovite and the apparent kaolin equivalent of the solutions, the ranges in pH–pK conditions along the 'illite–kaolin' join showed a very large graphical spread which was related to the differences in relative stabilities of the illites and kaolin minerals. In carbonate rich rocks where solution pH values are generally around 8, illites are stable. Normal marine conditions are well within the illite stability field.

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Résumé—Les résultats de la dissolution de six illites donnés par Reesman et Keller (1968) indiquent que ces illites sont plus stables qu'on ne le pensait. Les énergies libres de formation (ΔG_f°) recalculées par rapport aux formules de l'illite 'idéale' et de la musconite sont les suivantes:

Echantillon	ΔG_f° 'formule illite'	ΔG_f° 'formule muscovite'
Illite de Fithian	$-1319{,}7$ kcal/fw	$-1334{,}8$ kcal/fw
Illite grundite	-1322	$-1338{,}0$
Illite de Rock Island	$-1307{,}3$	$-1333{,}2$
Illite de Marblehead	$-1310{,}8$	$-1334{,}2$
Illite de Gage	(pas de formule)	$-1337{,}6$

L'utilisation de la formule de la muscovite comme un test de comparaison indirecte donne le moyen de prédire les stabilités relatives de ces matériaux chimiquement complexes.

La réponse de la solution équilibrée pour l'illite au ΔG_f° du Kaolin a été mise en évidence dans tous les échantillons où une phase à 7 Å est détectée par diffraction X. Les diagrammes de sélectivité basés sur le ΔG_f° se rapportant aux formules de la muscovite idéale et du kaolin révèlent un domaine assez étendu de conditions chimiques dans lequel des illites et des minéraux du type kaolin de ΔG_f° différents seraient stables. Cependant, dans les roches carbonatées et dans l'eau de mer, l'illite est stable par rapport au kaolin. Pendant l'altération des carbonates, les zones de plus bas pH dans le résiduum riche en argile situé au-dessus des carbonates favorisent la transformation de l'illite en minéraux du type kaolin.

Kurzreferat—Löslichkeitswerte von 5 der 6 von Reesman und Keller (1968) beschriebenen Illite zeigen, daß diese stabiler sind als angenommen wurde. Die revidierten Gibbs'schen freien Bildungsenergien (ΔG_f^0) bezogen auf die "ideale" Illitformel und auf die Muskovitformel sind:

Probe	ΔG_f^0 Illitformel	ΔG_f^0 Muskovitformel
Fithian-Illit	$-1319{,}7$ Kcal/F.G.	$-1334{,}8$ kcal/F.G.
Grundy-Illit	$-1322{,}7$	$-1338{,}0$
Rock Island-Illit	$-1307{,}3$	$-1333{,}2$
Marblehead	$-1310{,}8$	$-1334{,}2$
Gage	(keine Formel)	$-1337{,}6$

Die Benutzung der Muskovitformel als eines indirekten Vergleichsmaßstabes ermöglicht die Voraussage der relativen Stabilitäten dieser chemisch komplexen Substanzen.

Die Beeinflussung einer mit Illit ins Gleichgewicht gesetzten Lösung durch ΔG_f^0 des Kaolins wurde in allen Proben gefunden, in denen eine 7 Å Mineralphase durch Röntgenbeugung nachgewiesen wurde. Stabilitätsdiagramme, die auf dem auf ideale Muskovit- und Kaolinformeln bezogenen ΔG_f^0 beruhen, zeigen einen ziemlich weiten Bereich chemischer Bedingungen an, innerhalb dessen Illit- und Kaolinminerale mit unterschiedlichem ΔG_f^0 stabil wären. In Carbonatgestein und Seewasser ist dagegen Illit gegenüber Kaolin stabil. Während der Verwitterung von Carbonaten begünstigen die Zonen mit niedrigeren pH-Werten im tonreichen Verwitterungsrückstand oberhalb der Carbonate die Umwandlung von Illit in Kaolinminerale.

Резюме—Данные по растворению пяти иллитов из шести в сообшении **Рисмана и Келлера** (1968 г.) указывают, что зти иллиты являются более устойчивыми, чем думали ранее. Уточненное Гиббсоном образование свободной знергии (ΔG_f^o) по отношению к идеальному иллиту и к мусковиту выражается в следующих формулах:

Образец	''Формула ΔG_f^o, иллита	Формула ΔG_f^o, мусковита
Иллит Фифиана	—1319,7 ккал-пресн. вода	—1334,8 ккал-пресн. вода
Иллит Грунда	—1322,7	—1338,0
Иллит Рок айланд	—1307,3	—1333,2
Иллит Марбелхзд	—1310,8	—1334,2
Иллит Геджа	(Формулы не имеется)	—1337,6

Использование формулы мусковита в качестве косвенного компаратора предоставляет способ предсказания сравнительной устойчивости зтих химически сложных материалов.

Во всех образцах в которых минеральная фаза 7 А была обнаружена рентгенографией была найдена реакция раствора, уравновешенного иллитом, с ΔG_f^o, каолином. Графики устойчивости базированные на ΔG_f^o, по отношению к идеальному мусковиту и каолину охватывают довольно широкий ряд химических усповий при которых иллиты и каолины с различными ΔG_f^o, будут устойчивыми. Однако в карбонатной горной породе и моской воде иллит по сравнению с каолином является устойчивым. Во время выветривания карбонатов нижние зоны pH в коре выветривания богатой глиной, находящиеся выше карбонатов, способствуют превращению иллита в каолиновые минералы.