

FREE ENERGIES OF FORMATION OF ILLITE SOLID SOLUTIONS AND THEIR COMPOSITIONAL DEPENDENCE

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Abstract—Electron probe analyses of diagenetic illites in Eocene sandstones from Kettleman North Dome, California, along with analyses of coexisting interstitial waters were used to calculate apparent molal free energies of formation of the illites at the *in situ* conditions of 100°C and 150 bars. Various triangular and rectangular compositional plots, once contoured for free energy, crudely indicate that the free energy decreases as the potassium content increases, decreases as the Al-for-Si substitution increases, and appears to be a minimum along a narrow composition valley having ~3% Fe₂O₃ of octahedral cations. Qualitatively, the shape of the free energy surface suggests only small departures from ideality.

The illites and water samples used in the calculations were chosen as close to each other as possible and are in equilibrium. The waters contain mainly Cl⁻, SO₄²⁻, Na⁺, and Ca²⁺ and have a total salinity of ~10,000 ppm. The illites, which coexist in the sandstones with diagenetic quartz, albite, and K-feldspar, are phenogitic and contain 5–9% K₂O, 1–3% total FeO, 1% MgO, and minor Na₂O, MnO, and TiO₂. The Fe₂O₃/FeO ratio has been set arbitrarily to 7 by comparison with published analyses.

Log *K* (100°C) was first calculated for the equilibrium illite \rightleftharpoons ions from the ionic activities obtained through speciation calculations for each water sample. The apparent free energies of formation of illites at 100°C were then calculated. The effect of instrumental uncertainty on the values of ΔG_f was assessed by accepting a 2.5 or 3.5% error in the probe analyses and by using a Monte Carlo method of error propagation. The free energies of formation obtained (on the basis of O₁₆(OH₂)) range from -1280 to -1320 kcal/mole at 100°C and 150 bars, and their Monte-Carlo uncertainties are less than ± 2 kcal/mole. Combining the compositions of natural, coexisting aqueous solutions and mineral solid solutions through thermodynamic equations constitutes a fast method to determine, at least crudely, the free energy-composition surface for the solid solution. This is in contrast to experimental methods such as calorimetry or hydrothermal equilibrium, which are very time-consuming and difficult.

Key Words—Formation, Free energy of formation, Illite, Interstitial water, Solid solution, Thermodynamics.

INTRODUCTION

Illite is a complex solid solution mainly of the components muscovite, pyrophyllite, and celadonite, plus smaller amounts of one or more of the following: paragonite, margarite, phlogopite, annite, proton-deficient oxyannite, and talc. Its composition may vary considerably (e.g., Hower and Mowatt, 1966; Weaver and Pollard, 1973; Velde, 1977; Bailey *et al.*, 1979 and references therein), but illite typically contains less K⁺ and Al^{IV} than muscovite and significant Mg²⁺ and Fe³⁺. The interpretation of occurrences of illite and closely related minerals such as hydromuscovite, phengite, sericite, and to a lesser extent celadonite and glauconite, in terms of the physical and chemical features of the environment of crystallization requires knowing the compositional dependence of the thermodynamic properties of the illite solid solution. To this end, Stoessel (1979, 1980), Helgeson and Aagaard (1981), and Aagaard *et al.* (1981) presented theoretical crystalline solution models for illites, Tardy and Garrels (1974) proposed a useful empirical method to calculate free energies of formation of illites and other layer silicates

of any composition, and Routson and Kittrick (1971) and Reesman (1974) measured by solubility in water the free energies (reproduced in Table 3) of several well-known illites. All three approaches—theoretical, empirical, and experimental—are commendable and needed. The purpose of the present paper is to add another source of thermodynamic/compositional data that might be called experimental/natural. As shown below, we have calculated the free energies of formation of many diagenetic illites from the Eocene McAdams Sandstone in Kettleman North Dome, California, by combining their microprobe analyses with the chemical analyses of the associated interstitial waters, with which they are probably in equilibrium. This approach is essentially identical to that used on the results of many solubility studies and of many hydrothermal-equilibrium studies at high temperature and pressure, except that we have applied it here to natural occurrences. When more thermodynamic/compositional data are assembled for illites it will become possible (1) to determine accurately their free energy vs. composition functions and (2) to compare those functions with the ones predicted by the theoretical models cited above. In this contribution we attempt to solve the first of these two goals by means of compositional diagrams contoured for the free energy of formation of illite.

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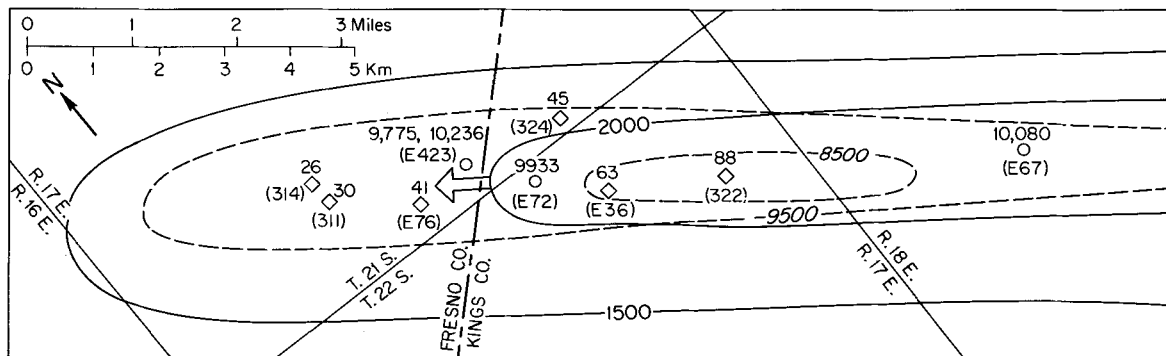


Figure 1. Location of Kettleman North Dome wells referred to in this study. The circles represent wells from which illite samples have been probed (see Table 1); the number below each circle is the well number, and the number above it is the depth in feet of the illite samples. The diamonds represent wells from which interstitial water samples from the McAdams Sandstone were used in calculating free energies of illite solid solutions. The number below each diamond is the well number (Table 2), and the number above it is the water sample number (Table 2, and Merino 1975b, Table 1). The solid contours (labelled in feet and taken from Berry, 1973) describe the potentiometric surface for fluids in the Eocene McAdams Sandstone. The large hollow arrow indicates the direction of flow. The dashed contours (labelled in feet below sea level) are structural contours on top of the McAdams Sandstone (Sullivan, 1966).

GEOLOGICAL, HYDRODYNAMIC, AND HYDROCHEMICAL SETTING AT KETTLEMAN NORTH DOME

Kettleman North Dome is a narrow anticline in the western San Joaquin Valley, California. Details on location, geology, and detrital and diagenetic mineralogies are given by Merino (1975a). The formation of interest here is the Eocene McAdams Sandstone, which consists of fine to coarse quartzose or feldspathic arenites that contain diagenetic quartz, albite, K-feldspar, kaolinite, illite, calcite, dolomite, pyrite, and glauconite pellets. The sandstones were buried to pre-folding depths of about 4200 m and, at the measured local geothermal gradient of 26°C/km, have been subjected to $\leq 110^\circ\text{C}$.

The diagenetic illite of interest occurs sparsely as tiny flakes (≤ 0.05 mm but mostly ~ 0.01 mm long) and as much larger ones up to 0.5 mm across. The tiny flakes are commonly associated with kaolinite cement and may themselves be a cement or a replacement of the kaolinite; the large flakes are *in situ* replacements of biotite, kaolinite, or quartz clasts (see textures in Table 1).

The interstitial aqueous solutions in the McAdams Sandstone have total salinities of the order of 10,000 ppm and consist mainly of Na and Cl with subordinate amounts of HCO_3^- , SiO_2 , Ca, K, Br, I, and B (Kharaka and Berry, 1976). Merino (1975b) calculated the distribution of aqueous species for the McAdams waters at the *in situ* conditions of $\sim 100^\circ\text{C}$ and 150 bars ensuring internal consistency for each analysis, and showed by means of logarithmic activity diagrams that the interstitial waters are in equilibrium with the illite and other diagenetic minerals. The regional flow of interstitial

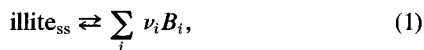
waters is to the northeast, but in the Upper McAdams Sandstone at Kettleman North Dome the water flows to the northwest along the crest of the anticline (see Figure 1 and Berry, 1973). In spite of this movement, the chemical composition of the interstitial waters appears to be in equilibrium with the diagenetic minerals in the rocks (Merino, 1975b). By plotting the Upper McAdams Sandstone waters on various activity diagrams (see Figure 2), a chemical trend results that is fairly well correlated with the geographic alignment of the samples themselves (see Figure 1). This trend indicates that the water flow is slow enough relative to the diagenetic reactions for the diagenetic minerals to be able to buffer the compositions of the waters. Furthermore, the chemical-geographic correlation suggests to us that the most appropriate way to calculate the free energy of an illite occurrence is to pair it with its nearest available *down-flow* water sample, which is the procedure followed below (see Table 1, bottom row, and Figure 1).

METHODS

Computation of apparent free energy of formation of illites

When Kettleman North Dome interstitial waters are plotted on activity diagrams, they fall on or very close to phase boundaries or saturation lines of quartz, albite, K-feldspar, mica, and smectite, which crystallized *in situ* in the sandstone (Merino, 1975b, Figures 3–5; 1975a). This strongly suggests that the waters are in equilibrium with those minerals and constitutes the basis of the $\Delta G_r^{\text{app}}(\text{illite})$ calculations presented here. All thermodynamic quantities below refer to 100°C and 150 bars, the *in situ* conditions. The calculation begins by

writing a balanced equilibrium reaction among a given illite solid solution and aqueous ions in the nearest available down-flow water sample:



where B_i represents the aqueous species Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Fe^{2+} , Fe^{3+} , Al^{3+} , H^+ , SiO_2 , and H_2O , and ν_i is the stoichiometric coefficient of species i . The equilibrium constant for Eq. (1) is

$$K = \prod_i a_i^{\nu_i}, \quad (2)$$

where the standard state for H_2O is pure H_2O_{liq} at the temperature and pressure of interest, that for the ions is a hypothetical one-molal solution referenced to infinite dilution at the temperature and pressure of interest, and that for the illite solid solution is the actual composition under consideration at the temperature and pressure of interest. With these choices, $a_{\text{H}_2\text{O}} \sim 1$ because the interstitial solutions have low total salinities (~10,000 ppm), and $a_{\text{illite}} = 1$ at any temperature, any pressure, and any illite composition.

By inserting the values of all activities of the aqueous ions into Eq. (2), we calculated the equilibrium constant K for each specific illite considered in Eq. (1). The activities of all aqueous species except Al^{3+} were obtained previously by carrying out the speciation for all interstitial aqueous solutions at the *in situ* conditions of 100°C and 150 bars (Merino, 1975b). The activity of Al^{3+} was calculated here from the mass-action law equation for the equilibrium between the aqueous solutions and albite, which is one of the diagenetic minerals present in the sandstones along with illite and quartz. The equilibrium constant for the reaction albite \rightleftharpoons ions was calculated with the program SUPCRT (Helgeson *et al.*, 1978, p. 202), which incorporates equations for the temperature and pressure dependence of the partial molal volume and heat capacity of aqueous ions (Walther and Helgeson, 1977, Eqs. (19) and (23); Helgeson *et al.*, 1981), as well as internally consistent thermodynamic data for minerals and aqueous species.

Once K for the Eq. (1) is known at 100°C and 150 bars, the standard free energy of reaction at these conditions can be calculated with the equation

$$\Delta G_r^{\circ*} = -RT \ln K, \quad (3)$$

and finally $\Delta G_f^{\text{app}}(\text{illite})$ can be obtained from

$$\Delta G_r^{\circ*} = \sum_i (\nu_i \Delta G_{f,i}^{\text{app}*}) - \Delta G_f^{\text{app}*}(\text{illite}). \quad (4)$$

The use of apparent free energies and enthalpies was introduced by Benson (1968) and Helgeson and Kirkham (1974, p. 1097 and Eqs. (6) and (8)) to remove from calculations of the thermodynamics of reactions the contributions by the elements, which cancel out any-

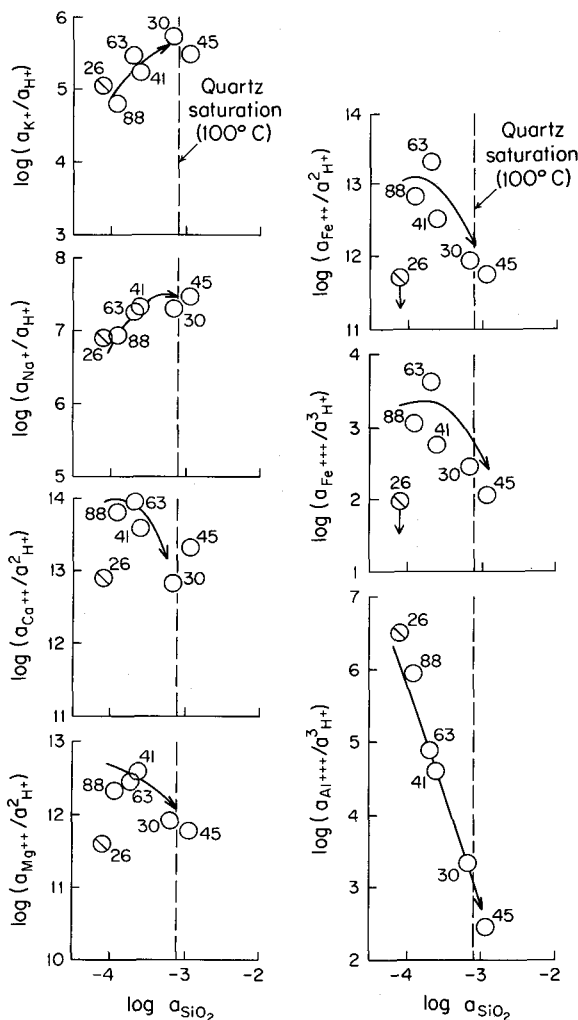


Figure 2. Plots of seven log activity ratios vs. the logarithm of the activity of aqueous silica for the six interstitial solutions from the Eocene McAdams Sandstone at Kettleman North Dome that have been used in this study to calculate the free energy of illite solid solutions. The rough chemical trends indicated by arrows correspond to the geographic alignment of samples 88, 63, 41, 30, and 45 (see Figure 1), all of which are waters from the Upper McAdams Sandstone. Sample 26 (indicated by a different symbol) does not conform to the geographic trend probably because it is from the Lower McAdams Sandstone. Note that all the waters except sample 45 are undersaturated with respect to quartz at the *in situ* conditions of 100°C and 150 bars.

way. Note that in the calculation of K for each illite by Eq. (2), each K refers to a different composition of illite.

Electron microprobe analyses

About 150 illites were analyzed for total FeO, SiO_2 , TiO_2 , Al_2O_3 , MnO, MgO, CaO, Na_2O , and K_2O with a three-spectrometer Etec Autoprobe. The operating

Table 1. Selected microprobe analyses, calculated formulae, and calculated free energies of formation of Kettleman North Dome diagenetic illites.¹

Well ² Depth Spot ³ Texture ⁴	E67-17Q 10,080 B1' (2) II	E67-17Q 10,080 A1' I or II	E67-17Q 10,080 FS1' IV	E67-17Q 10,080 FS1' (2) IV	E67-17Q 10,080 FS4' IV	E67-17Q 10,080 FNWW1' IV	E67-17Q 10,080 FNWW2' IV	E67-17Q 10,080 FNWW3' I or II	E67-17Q 10,080 FN1' I or II	E67-17Q 10,080 FN3' I or II	E72-3P 9933 D2' I	E72-3P 9933 D3' I
SiO ₂	50.04	53.40	46.22	46.17	53.64	50.18	48.94	48.31	48.08	46.80	46.32	46.39
TiO ₂	0.08	0.99	0.00	0.00	0.16	0.20	0.01	0.23	0.13	0.23	0.22	0.12
Al ₂ O ₃	34.78	26.97	29.34	28.09	19.03	31.20	31.71	32.49	31.89	32.30	34.14	36.21
FeO ⁵	2.27	0.565	5.81	5.02	9.65	3.31	3.67	1.81	1.66	1.99	0.86	0.74
MnO	0.09	0.09	0.08	0.07	0.15	0.10	0.00	0.00	0.07	0.02	0.00	0.066
MgO	0.89	0.99	3.23	3.22	3.52	1.50	1.62	1.30	1.48	1.21	0.53	0.35
CaO	0.09	0.045	0.00	0.00	0.11	0.14	0.12	0.09	0.14	0.00	0.00	0.00
Na ₂ O	0.00	0.21	0.00	0.03	0.14	0.00	0.00	0.29	0.04	0.065	0.70	0.20
K ₂ O	1.92	7.36	9.41	9.27	7.15	3.46	3.27	6.89	7.91	9.58	7.38	4.77
Total	90.15	90.63	94.11	91.89	93.57	90.09	89.33	91.42	91.39	92.20	90.14	88.82
Numbers of ions per O ₁₀ (OH) ₂												
Si	3.30	3.635	3.14	3.20	3.63	3.36	3.30	3.26	3.265	3.20	3.18	3.16
Al ^{IV}	0.70	0.365	0.86	0.80	0.37	0.64	0.70	0.74	0.835	0.80	0.82	0.84
Al	2.00	1.80	1.49	1.49	1.15	1.83	1.82	1.85	1.72	1.80	1.94	2.07
Fe(III) ⁶	0.11	0.03	0.29	0.25	0.48	0.16	0.18	0.09	0.08	0.10	0.043	0.037
Fe(II) ⁶	0.016	0.004	0.04	0.04	0.07	0.02	0.03	0.01	0.01	0.01	0.006	0.005
Mg	0.09	0.10	0.33	0.33	0.355	0.15	0.16	0.13	0.15	0.12	0.05	0.035
Ca	0.01	0.003	0.00	0.00	0.008	0.01	0.01	0.007	0.01	0.00	0.00	0.00
Na	0.00	0.03	0.00	0.005	0.02	0.00	0.00	0.04	0.005	0.01	0.09	0.03
K	0.16	0.64	0.81	0.82	0.62	0.30	0.28	0.59	0.685	0.83	0.65	0.41
$\Delta G_f^{\text{app}7}$	-1286.9	-1295.4	-1294.2	-1295.9	-1244.9	-1282.4	-1282.6	-1304.3	-1307.3	-1311.6	-1318.4	-1312.7
Std. dev. ⁸	1.14	1.17	1.20	1.19	1.03	1.11	1.12	1.19	1.21	1.24	1.33	1.31
Water ⁹	88	88	88	88	88	88	88	88	88	88	41	41
Well ² Depth Spot ³ Texture ⁴	E72-3P 9933 D5 I	E72-3P 9933 D6 I	E72-3P 9933 D7 I	E72-3P 9933 G1' II or IV	E72-3P 9933 G2' II or IV	E72-3P 9933 G3' II or IV	423-34J 9775 G4' II or IV	423-34J 9775 G1' I	423-34J 9775 F1' VI(?)	423-34J 9775 F4' II or IV	423-34J 9775 F5' II or IV	
SiO ₂	45.20	44.70	43.89	49.47	50.29	50.55	48.61	49.27	48.80	50.95	51.52	
TiO ₂	0.21	0.32	0.24	0.00	0.09	0.004	0.00	0.00	0.00	0.00	0.04	
Al ₂ O ₃	36.05	33.49	34.94	35.39	34.70	33.74	34.14	38.40	37.28	30.72	29.27	
FeO ⁵	1.10	1.58	1.16	1.99	1.71	2.62	1.42	0.52	0.62	2.31	2.76	
MnO	0.03	0.00	0.06	0.00	0.075	0.00	0.00	0.05	0.10	0.06	0.03	
MgO	0.53	0.62	0.48	0.58	0.59	0.71	0.96	0.16	0.36	1.08	1.06	
CaO	0.02	0.02	0.00	0.12	0.056	0.17	0.02	0.05	0.06	0.76	0.37	
Na ₂ O	0.67	0.39	0.50	0.28	0.00	0.005	0.27	0.03	0.05	0.00	0.13	
K ₂ O	7.05	8.61	6.97	3.04	2.61	3.26	4.23	1.04	0.965	5.73	6.27	
Total	90.91	89.77	88.29	90.85	90.10	91.05	89.64	89.49	88.20	91.61	91.46	
Numbers of ions per O ₁₀ (OH) ₂												
Si	3.06	3.125	3.08	3.26	3.32	3.325	3.27	3.225	3.24	3.395	3.45	
Al ^{IV}	0.94	0.875	0.92	0.74	0.68	0.675	0.73	0.775	0.76	0.605	0.55	
Al	1.94	1.885	1.97	2.01	2.02	1.94	1.97	2.19	2.16	1.808	1.76	
Fe(III) ⁶	0.055	0.08	0.06	0.10	0.08	0.13	0.07	0.025	0.03	0.11	0.135	
Fe(II) ⁶	0.008	0.01	0.009	0.01	0.01	0.02	0.01	0.003	0.004	0.016	0.02	
Mg	0.13	0.065	0.05	0.06	0.06	0.07	0.10	0.015	0.04	0.11	0.11	
Ca	0.001	0.00	0.00	0.01	0.004	0.01	0.001	0.003	0.004	0.05	0.03	
Na	0.095	0.05	0.07	0.04	0.00	0.001	0.035	0.004	0.007	0.00	0.017	
K	0.61	0.77	0.62	0.26	0.22	0.27	0.36	0.09	0.08	0.49	0.54	
$\Delta G_f^{\text{app}7}$	-1320.9	-1319.2	-1320.0	-1297.5	-1294.4	-1290.8	-1306.7	-1306.0	—	-1299.3	-1293.9	
Std. dev. ⁸	1.32	1.33	1.32	1.25	1.25	1.19	1.34	1.37	—	1.30	1.28	
Water ⁹	41	41	41	41	41	41	30	30	30	30	30	

¹ *In situ* conditions of 100°C and 150 bars. For lack of space, only half of the reliable analyses are given here, though all have been used in Figure 3. The analyses not included here can be obtained from the senior author on request.

² Well number (for location, see Figure 1 and Table 3 in Merino, 1975a).

³ Spot analyzed with probe.

⁴ I = illite replaces kaolinite cement. II = illite replaces, in whole or in part, kaolinite that has replaced a clastic mica. III = illite replaces quartz. IV = illite replaces detrital mica. V = illite cement. VI = squashed, partly recrystallized phyllosilicate clast.

⁵ FeO is total iron.

Table 2. Thermodynamic activities of Kettleman North Dome water samples.¹

Water sample no. ²	88	63	41	30	45	26
Well ²	322-1P	E36-2P	E76-33J	311-33J	324-35J	314-28J
$\log(a_{\text{SiO}_2})$	-3.911	-3.679	-3.597	-3.171	-2.931	-4.09
$\log(a_{\text{Na}^+}/a_{\text{H}^+})$	6.896	7.245	7.299	7.294	7.457	6.856
$\log(a_{\text{K}^+}/a_{\text{H}^+})$	4.805	5.451	5.22	5.723	5.455	5.033
$\log(a_{\text{Ca}^{2+}}/a_{\text{H}^+}{}^2)$	13.79	13.928	13.562	12.823	13.294	12.876
$\log(a_{\text{Mg}^{2+}}/a_{\text{H}^+}{}^2)$	12.306	12.425	12.577	11.922	11.761	11.581
$\log(a_{\text{Fe}^{2+}}/a_{\text{H}^+}{}^2)$	12.85	13.33	12.55	11.98	11.79	9.45
$\log(a_{\text{Fe}^{3+}}/a_{\text{H}^+}{}^3)$	3.07	3.64	2.77	2.47	2.07	0.225
$\log(a_{\text{Al}^{3+}}/a_{\text{H}^+}{}^3)$	5.926	4.881	4.581	3.308	2.425	6.503

¹ All activity ratios except $\log(a_{\text{Al}^{3+}}/a_{\text{H}^+}{}^3)$ were obtained from the distribution of aqueous species for each brine at 100°C and are taken from Merino (1975b); this reference also gives details of the speciation calculations. The values of $\log(a_{\text{Al}^{3+}}/a_{\text{H}^+}{}^3)$ have been calculated by assuming that the brines are in equilibrium with albite at 100°C, 150 bars. This assumption is strongly supported by the fact that Kettleman North Dome waters plot on or near the phase boundaries for quartz, albite, and K-feldspar on activity diagrams in terms of $\log(a_{\text{SiO}_2})$, $\log(a_{\text{K}^+}/a_{\text{H}^+})$, and $\log(a_{\text{Na}^+}/a_{\text{H}^+})$. See Merino (1975b) Figures 3-5. See also text.

² For location of water samples and wells, see Figure 1.

conditions were 15 kV accelerating voltage and 0.0084 μA sample current. This low current (much smaller than the usual 0.02 μA or the 0.01 μA used by Boles and Franks [1979]), a relatively large electron beam size of $\sim 3\text{--}6\ \mu\text{m}$, and 10-sec counts were used to reduce volatilization of the illite. The standards used were orthoclase, kyanite, diopside, eulite, rhodonite, and albite. Data reduction was carried out as outlined by Klein (1974). (Cf. the procedures of Bodine and Standaert, 1977; Boles and Franks, 1979; and Buckley *et al.*, 1978.) All the H_2O — was assumed to have been driven off by the electron beam.

Each analysis was assessed critically by inspecting the percentages obtained and relating them to the position of the spot(s) probed in relation to cracks, cleavages, grain sizes, and neighbors. This and our decision to select only analyses yielding totals $>88\%$ left only 56 acceptable analyses of the ~ 150 made. In Table 1 only half of the acceptable analyses are given to save space, though all are used in Figure 3. At a few spots, several 10-sec counts were performed consecutively; often (but not always) the totals obtained were increasingly larger than the first one, although the ratios among individual oxides did not vary appreciably. In these cases only the first analysis was used in the $\Delta G_f(\text{illite})$ calculation. In other cases, colorless crystals having high refractive index, parallel extinction and birefrin-

gence of ~ 0.020 —a combination that, coupled to the texture and general composition, identifies illite positively—turned out to contain too little potassium to be regarded as typical illite. Based on their distinctive optical and textural properties, we tentatively regard such grains as illites² and have included them in our calculations. If these low K_2O analyses are correct (and in spite of our precautions the volume analyzed by the microprobe could have included some quartz along with the illite), the actual extent of the illite compositional field is larger than it is presently held to be. A larger illite field would not be too surprising, considering that most of the relatively few published analyses (e.g., Hower and Mowatt, 1966; Weaver and Pollard, 1973; Velde, 1977) belong to illites from argillaceous rocks and include no illites from other rock types and environments.

Transmission of instrumental errors in $\Delta G_f^{\text{app}}(\text{illite})$ calculations

We have assumed that the instrumental uncertainty in the electron probe analyses of the illites was $\pm 2.5\%$

² Because the sandstone contains (along with abundant kaolinite and glauconite pellets) very little diagenetic illite, our diffractograms show very small 10- and 5-Å peaks, which do not shift upon glycolation.

⁶ Distribution of total iron has been made assuming $\text{Fe}_2\text{O}_3/\text{FeO} = 7$. See text.

⁷ Apparent free energy of formation of illite solid solution from elements at 100°C and 150 bars, in kcal/mole.

⁸ Monte-Carlo calculated uncertainty (kcal/mole) in the $\Delta G_f^{\text{app}}(\text{illite})$ values. See text. This uncertainty arises solely on account of the estimated uncertainty in the probe analyses.

⁹ Sample number of the Kettleman North Dome aqueous solution with which illite analysis has been paired to calculate $\Delta G_f^{\text{app}}(\text{illite})$. See Figure 1 for location. Chemical compositions are given in Merino (1975b) and thermodynamic activities in Table 2.

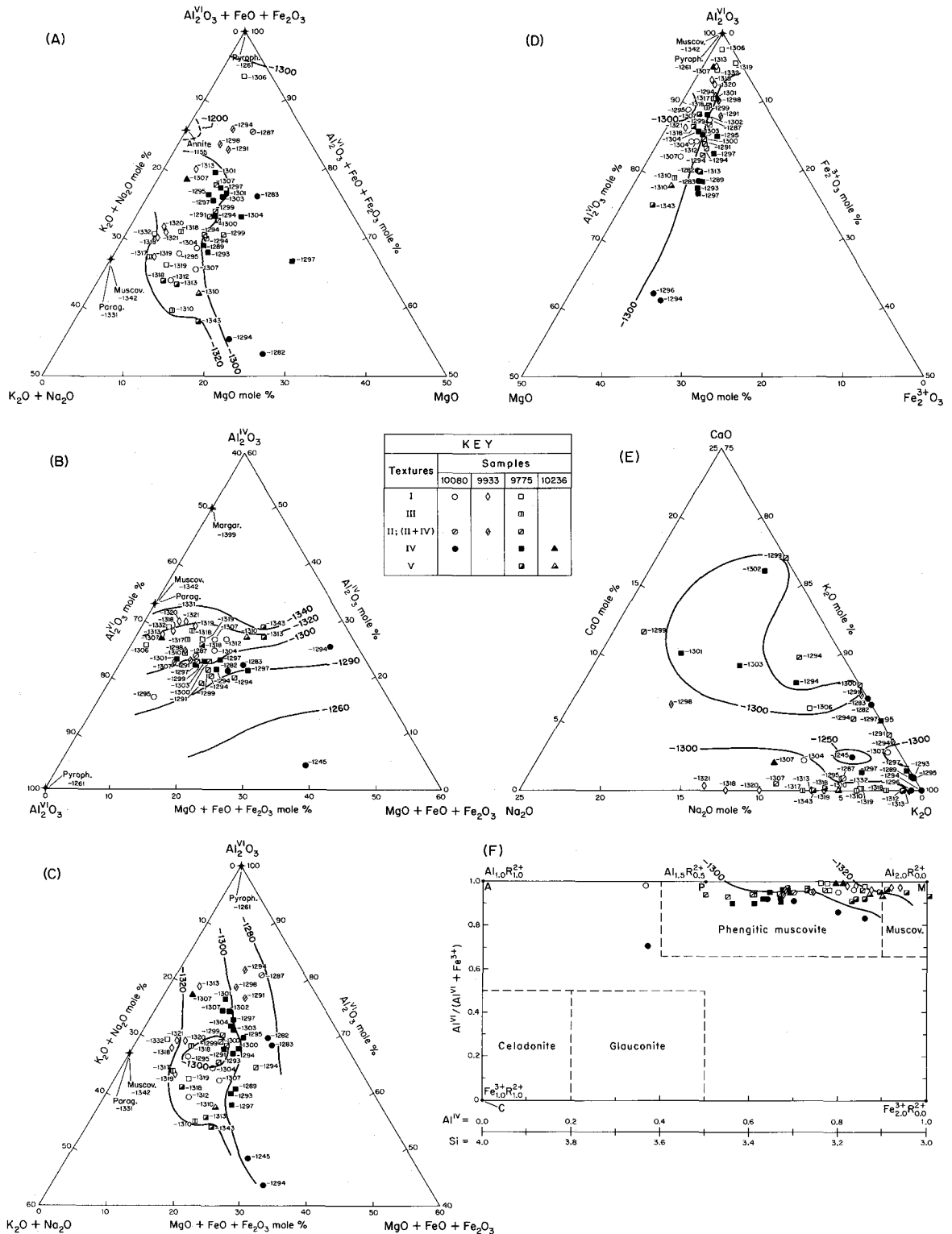


Figure 3. Plots of apparent free energy (in kcal/mole) vs. composition for Kettleman North Dome illites. The rectangular diagram is from Bailey *et al.* (1979). The different symbols represent different authigenic illite textures, also given in Table 1. The compositions and free energies in all diagrams are from Table 1; a few points have been suppressed to avoid too much superposition.

Table 3. Numbers of ions per $O_{10}(\text{OH})_2$ and free energies of formation of some layer silicates.

	Si	Al ^{IV}	Al	Fe ³⁺	Fe ²⁺	Mg	Ca	Na	K	$\Delta G_{f,25,1}$ (kcal/mole)	$\Delta G_{f,100,150}^{\text{app}}$ (kcal/mole)
Muscovite ¹	3	1	2	0	0	0	0	0	1	-1336.3	-1341.7
Phlogopite ¹	3	1	0	0	0	3	0	0	1	-1396.2	-1402.1
Annite ¹	3	1	0	0	3	0	0	0	1	-1147.2	-1154.6
Pyrophyllite ¹	4	0	2	0	0	0	0	0	0	-1256.0	-1260.5
Paragonite ¹	3	1	2	0	0	0	0	1	0	-1326.0	-1331.2
Margarite ¹	2	2	2	0	0	0	1	0	0	-1394.4	-1399.4
Illites											
Beavers Bend, Oklahoma ²	3.62	0.39	1.66	0.20		0.13	0	0	0.53	-1267.6	—
										(-1274.7 ^a)	
Fithian, Illinois ²	3.51	0.49	1.54	0.29		0.19	0	0	0.64	-1270.6	—
										(-1277.7 ^a)	
Goose Lake, Illinois ²	3.65	0.35	1.58	0.24		0.15	0	0	0.59	-1265.3	—
										(-1272.1 ^a)	
Fithian, Illinois ³	3.46	0.54	1.65	0	0	0.40	0.07	0.05	0.60	-1319.7	—
Grundy, Illinois ³	3.22	0.78	1.90	0	0	0.24	0	0.04	0.56	-1322.7	—
Rock Island, Illinois ³	3.57	0.43	1.69	0	0	0.34	0.03	0.03	0.59	-1307.3	—
Marblehead, Wisconsin ³	3.58	0.42	1.60	0	0	0.40	0.05	0.03	0.69	-1310.8	—
"End member" ^{3b}	3.43	0.57	1.5	0.17	0.04	0.34	0	0	0.80	-1299.0 ^b	—

¹ End-member compositions. The values of ΔG_f (25°C, 1 bar) are from Helgeson *et al.* (1978); those of ΔG_f^{app} (100°C, 150 bars) have been calculated with the program SUPCRT (Helgeson *et al.*, 1978, p. 202).

² Values of ΔG_f (25°C, 1 bar) determined experimentally by Routson and Kittrick (1971).

³ Values of ΔG_f (25°C, 1 bar) determined experimentally by Reesman (1974).

⁴ Values recalculated by Tardy and Garrels (1974, Table 4) by subtracting 3.5 kcal/(Al atom) from the experimental values.

⁵ ΔG_f (25°C, 1 bar) estimated by Tardy and Garrels (1974, Table 7) using an empirical method.

of the actual oxide weight percent for oxides present in amounts >1% and $\pm 3.5\%$ of the actual oxide weight percent for oxides present in amounts <1%. These errors bring about an uncertainty in the $\Delta G_f^{\text{app}}(\text{illite})$ values that were calculated from the chemical analyses of the illites and their associated formation waters. We have estimated the uncertainty in $\Delta G_f^{\text{app}}(\text{illite})$ by a Monte Carlo method of error propagation that "... is based on repeated calculations of a result, each time having each input datum changed by a random selection from its probability distribution ... The accumulated answers define a distribution which can be regarded as an uncertainty distribution" (Anderson, 1976, p. 1534). This method of calculating error propagation is simple, realistic, and easily programmable for use by a computer. Some applications of it are given by Anderson (1976) and Merino (1979). In the present study, $\Delta G_f^{\text{app}}(\text{illite})$ was calculated at least 500 times for a given illite-water composition pair; each time, the value of each of the nine input weight percentages that make up the illite analysis was chosen randomly within its bracket of uncertainty. For example, an illite with 46.0% SiO_2 has an uncertainty bracket for SiO_2 of $46.0 \pm 0.025 \times 46.0 = 47.15\%$ and 44.85%. The calculation was carried out with a simple computer program that propagates uncertainties in the data through any function provided by the user. For each particular problem, the minimum number of times that the calculation has to be repeated is simply the number needed for the cumulative mean

and standard deviation to start to approach constancy (see Merino, 1979, Figure 1 and p. 1535). The random choice of input values from within the bracket of uncertainty of each variable was carried out with the standard random-number generator RANF at the CDC 6600 of the Wrubel Computer Center of Indiana University. RANF was subjected to rigorous tests for the distribution of random numbers and for the randomness of occurrences of pairs and passed them both well. Also, because the CDC 6600 computer has 60-bit words, a much higher word length than in IBM computers, the cycle of randomness for a random number generator is extremely long.

Structural formulae

In constructing the structural formulae of the illites analyzed (see Table 1), all of the Si was assigned to the tetrahedral sheet; the number of tetrahedral atoms per formula was then brought to 4 with Al; and the remainder of the Al was assigned to the octahedral sheet, as was all of the Mg, Fe²⁺, and Fe³⁺. All of the K and Na was assigned to the interlayer. Because the activities of Mn²⁺ (aq) and Ti⁴⁺ (aq) in the Kettleman North Dome waters were not available (the waters were not analyzed for Mn and Ti) and because the concentrations of these two components are likely to be negligibly small anyway, Mn and Ti were excluded from the illite formulae. The formulae were then corrected to re-es-

Table 4. Free energies of formation of aqueous species used in this study.

Aqueous species	ΔG_f (25°C, 1 bar) (cal/mole)	ΔG_f^{app} (100°C, 150 bar) ¹ (cal/mole)
H ⁺	0	0
Na ⁺	-62,593	-63,749
K ⁺	-67,700	-69,522
Mg ²⁺	-108,700	-106,352
Ca ²⁺	-132,300	-131,425
Fe ²⁺	-18,850	-16,544
Fe ³⁺	-1100	4402
Al ³⁺	-116,970	-111,650
SiO ₂	-100,190	-200,172
H ₂ O	-56,687	-58,030

¹ Calculated with the program SUPCRT (Helgeson *et al.*, 1978, p. 202).

establish electrical neutrality by modifying proportionally all other cations.

Seven of the illites in Table 1 have an octahedral cation content slightly greater than 2. McDowell and Elders (1980, p. 298) and Weaver and Pollard (1973, p. 10) also obtained octahedral occupancies greater than 2, even for illites in which the ferric iron content was known. In our illites, the >2 value may result simply from our arbitrary decision to set the mole ratio Fe₂O₃/FeO = 7, or it may mean that indeed slightly more than 2 of every 3 octahedral sites are on the average occupied. It need not indicate that part of the Mg or other cations should have been assigned to the interlayer instead of the octahedral sheet. At any rate, the assumptions made here to construct the structural formulae of the Kettleman North Dome illites have *no* effect on the calculations of free energy of formation explained above and shown in Table 1 and Figure 3.

RESULTS

The apparent free energies of formation from the elements at 100°C and 150 bars have been calculated for about 50 Kettleman North Dome illites. For lack of space, only half are reported in Table 1 along with their compositions, formulae, locations, and textures, although all are plotted on Figures 3A through 3F, where free energies have been contoured on several triangular and rectangular compositional diagrams to determine the shape of the free energy-composition surface for illite solid solutions.

More diagrams could be constructed with different choices of components at the corners. The free energies calculated here from data on natural mineral and water samples are validated by their relative proximity (see Table 3) to those measured experimentally by Routson and Kittrick (1971) and Reesman (1974) and to the free energies calculated independently from data in Helgeson *et al.* (1978) of the end members muscovite, paragonite, pyrophyllite, phlogopite, and margarite.

Some stability trends are apparent in the triangular diagrams. Figures 3A and 3C show that the free energy of illite decreases with increasing K₂O + Na₂O but is essentially independent of the ratio Al₂^{VI}O₃/(MgO + FeO total). Figure 3B indicates that the free energy decreases with increasing Al substitution for Si, at least within the range indicated in the figure. Figure 3D suggests that the free energy goes through a minimum along a valley at about 3% Fe₂O₃ of the octahedral cations. Figure 3E shows two free energy minima (one along the Na₂O–K₂O join; the other, broader and smaller, over the center of the diagram) separated by a maximum along a crest between ~94 and 100% K₂O. These trends are tentative but appear to be real because the contours are 20 or more kcal/mole apart, an order of magnitude greater than the free energy uncertainties (Table 1) brought about by the probable errors in the probe analyses.

DISCUSSION

Our calculations of free energies of formation of illites of various compositions relate water flow, water chemistry, and diagenetic water/mineral reactions and are based upon the following assumptions: (1) The mole ratio Fe₂O₃/FeO has been arbitrarily fixed at 7, the average value for many illites (Weaver and Pollack, 1973, Table III, p. 9); (2) The MnO and TiO₂ contents in the Kettleman North Dome illites, which vary respectively between 0 and 0.18% and between 0 and 1%, have been neglected; (3) The electron probe analyses are considered precise to within ±2.5% (or ±3.5%—see section on analyses) of the weight percentages measured; (4) On the basis of conclusions reached earlier (Merino, 1975b), the waters and K-feldspar, albite, illite and quartz are assumed to be in equilibrium; and (5) All illites from one rock sample, despite their different compositions, are assumed to be in equilibrium with the same nearest down-flow aqueous interstitial solution.

Assumption (1) introduces slight changes in the stoichiometric coefficients of the reaction illite \rightleftharpoons ions with respect to the case where all the iron determined with the microprobe is regarded as ferrous. These changes in the stoichiometric coefficients, plus those caused by neglecting MnO and TiO₂ (assumption 2), can bring about changes of as much as 4 or 5 kcal in the computed values of $\Delta G_f^{app}(illite)$. Assumption (4) is based on the fact that the Kettleman North Dome waters, when plotted on several activity diagrams for the *in situ* temperature, fall on or near the phase boundaries for the minerals mentioned. This assumption has been used in calculating illite free energies and the activity of the Al³⁺ ion of the waters from their equilibrium with albite, as the waters were not analyzed for aluminum (Kharaka and Berry, 1976). Because $\Delta G_f(Al^{3+}, 25^\circ C) = -116$ kcal/mole, an error of 0.01 in the number of aluminum ions in the formula of an illite causes an error of 1.16 kcal in the calculated value of $\Delta G_f(illite)$; the same is

true for errors in the numbers of the other ions. Nevertheless, because all such ions satisfy stoichiometric and electrostatic-neutrality requirements, the errors in $\Delta G_f(\text{illite})$ caused by reasonable uncertainties in the probe analyses (assumption 3) tend to cancel each other, leading to the surprisingly small uncertainties listed in Table 1 (<2 kcal/mole, calculated by the Monte Carlo method explained above).

Assumption (5) cannot be strictly true, as each solid solution can be in equilibrium with only one aqueous solution; it was made, however, because we noted empirically that the calculated ΔG_f^{app} of each illite at Kettleman North Dome depends to a much higher degree on the chemical composition of the illite itself than on that of the formation water with which it is paired in the calculation. At any rate, by being consistent in the choice of water-illite pairs internal consistency was preserved among the ΔG_f^{app} values obtained (Table 1), so that the qualitative shape of the free energy-composition surfaces (Figures 3A–3E) should not change appreciably on account of assumption (5). In summary, all of the approximations and assumptions affect the illite apparent free energies at 100°C and 150 bars listed in Table 1. In absolute terms the ΔG_f^{app} values can be trusted only to within about ± 7 kcal/mole (which allows also for errors in the water analyses), but they are probably consistent with each other to within less than that amount, e.g., ± 4 kcal/mole. The $\Delta G_f^{\text{app}}(\text{illite})$ values obtained are therefore only estimates.

Before the free energy-composition data given in Table 1 can be used to test theoretical models (e.g., Stoessell, 1978, 1980) which predict the variation of the free energy of mixing (ΔG_{mixing}) with composition, it is necessary to compute the ΔG_{mixing} values of the Kettleman North Dome illites by the equation:

$$\Delta G_{\text{mixing}} = \Delta G_f^{\text{app}}(\text{illite}) - \sum_j x_j \Delta G_{f,j}, \quad (5)$$

where x_j and $\Delta G_{f,j}$ are the mole fraction and apparent free energy of formation of the pure component j . To do this an appropriate set of components must be chosen, their mole fractions in each illite must be calculated, and all of their free energies of formation must be known. This calculation was not made because no thermodynamic data are available for the celadonite end member, $\text{KFe}^{3+}\text{MgSi}_4\text{O}_{10}(\text{OH})_2$. A final drawback to the calculation of the free energies of mixing could be that one would be computing very small numbers (the ΔG_{mixing} values are of the order of 1 or 2 kcal/mole) by difference of very large ones (~ 1300 kcal/mole) in Eq. (1), a calculation with very large uncertainty.

In conclusion, the molar free energy of the illite solid solution becomes more negative with increasing potassium content and with increasing Al-for-Si substitution and appears to go through a minimum for a small amount of ferric iron. In general, compositional data of both interstitial aqueous solutions and minerals precip-

itated in nature in contact with them appear to be useful to determine the composition dependence of the free energy of a crystalline solid solution. The values obtained here for illite are probably only crude, but in exchange many free energy-composition pairs can be obtained quickly and easily. Obtaining a similar number of data points by either hydrothermal or calorimetric experimental methods would be enormously time consuming and difficult.

ACKNOWLEDGMENTS

We are greatly indebted to Abhijit Basu and Martin Gole for their careful microprobe analyses of the illites. Thanks also to R. F. Blakely, C. Klein, J. A. Kittrick, W. Moran, J. Tolen, G. Ringer, B. Velde, R. Stoessell, K. Walker, and Robert Wintsch for their help at many stages of this work. The manuscript has benefited much from fast and meticulous reviews by Cornelis Klein, Bruce Velde, D. D. Eberl, H. C. Helgeson, and the editor. The Wrubel Computer Center at Indiana University generously provided computing time on its CDC 6600 computer. The work reported here was supported in part by NSF grant EAR 76-24082. Acknowledgement is also made with thanks to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research under grant PRF #9542-AC2.

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(Received 16 December 1980; accepted 17 April 1981)

Резюме—Анализы структурной зависимости диагенетических иллитов в эоценовых песчаниках из Кеттлеманного Северного Доума, Калифорния, посредством электронного зонда вместе с анализами существования межщелевых вод были использованы для расчета мнимых молярных свободных энергий образования иллитов в локальных условиях 100°C и 150 бар. Различные треугольные и прямоугольные структурные графики, представленные для свободной энергии, указывают, с грубым приближением, что свободная энергия уменьшается при увеличении содержания калия, при увеличении замены кремния алюминием и, как кажется, имеет минимум в узком пределе по составу, имеющим ~3% Fe₂O₃ октаэдрических катионов. Качественно форма поверхности свободной энергии указывает на только небольшие отклонения от идеала.

Образцы иллитов и воды, использованные при расчетах, были выбраны как можно ближе друг к другу и в равновесии. Воды содержат в основном Cl⁻, SO₄²⁻, Na⁺, и Ca²⁺ и их общая соленость ~10 000 миллионных. Иллиты, которые существуют в песчаниках с диагенетическим кварцем, альбитом и К-фельдшпатом, являются фенгитическими и содержат 5–9% K₂O, 1–3% целого FeO, 1% MgO, а также немного Na₂O, MnO, и TiO₂. Отношение Fe₂O₃/FeO было установлено примерно на 7 путем сравнения с опубликованными анализами.

Величина Log K (100°C) была первоначально рассчитана для равновесия иллит ⇌ ионы, используя ионные активности, полученные путем специальных расчетов для каждого образца воды. Затем рассчитывались мнимые свободные энергии образования иллитов при 100°C. Эффект неточности, вызванной измерительными приборами на величины ΔG_f, был оценен, учитывая 2,5 или 3,5% погрешности зондового анализа и используя метод Монте-Карло распространения погрешности. Полученные (на основе O₁₀(OH)₂) свободные энергии образования находились в пределах от -1280 до -1320 ккал/моль при 100°C и 150 бар и их монте-карловские неточности были меньше ±2 ккал/моль. Связывая составы натуральных существующих водных растворов и растворов твердых минералов посредством термодинамических уравнений можно разработать быстрый метод для определения, по крайней мере грубо, поверхности свободной энергии—состав для твердых растворов. Этот метод можно противопоставить экспериментальным методам, таким как калориметрия либо гидротермальное равновесие, которые являются трудными и требующими большого количества времени. [E.C.]

Resümee—Mikrosondenuntersuchungen von diagenetischen Illiten aus eoänen Sandsteinen von Kettleman North Dome, Kalifornien, zusammen mit Analysen von koexistierenden Porenwässern wurden verwendet, um die molaren freien Bildungsenergien der Illite bei *in situ*-Bedingungen von 100°C und 150 bar zu berechnen. Verschiedene dreieckige und rechteckige Darstellungen, die bereits für freie Energien aufgestellt wurden, zeigen grob an, daß die freie Energie abnimmt, wenn der Kaliumgehalt ansteigt und abnimmt, wenn die Substitution von Aluminium für Silizium zunimmt. Außerdem zeigt sich, daß die freie Energie ein Minimum erreicht, wenn sich etwa 3% Fe₂O₃ auf den oktaedrisch-koordinierten Plätzen befindet. Qualitativ deutet die Form der freien Energie-Fläche nur auf geringe Abweichungen vom Idealzustand hin.

Die Illite und Wasserproben, die für die Berechnungen verwendet wurden, wurden so nahe wie möglich beieinander gezogen und sind somit im Gleichgewicht. Die Wässer enthalten hauptsächlich Cl⁻, SO₄²⁻, Na⁺, und Ca²⁺ und haben einen Gesamtsalzgehalt von etwa 10 000 ppm. Die Illite, die in den Sandsteinen mit diagenetischem Quarz, Albit, und Kalifeldspat koexistieren, sind phengitisch und enthalten 5–9% K₂O, 1–3% Gesamt-FeO, 1% MgO und geringe Mengen an Na₂O, MnO, und TiO₂. Das Fe₂O₃/FeO-Verhältnis wurde mit ungefähr 7 angenommen aus dem Vergleich mit bereits publizierten Analysen.

Der log *K* (100°C) wurde zuerst für das Gleichgewicht Illit ⇌ Ionen aus den Ionenaktivitäten berechnet, die durch Rechnungen für jede Wasserprobe einzeln berechnet wurden. Die freien Bildungsenergien für die Illite bei 100°C wurden anschließend berechnet. Die Auswirkung des instrumentellen Fehlers auf die Δ*G*_f^o-Werte wurden ermittelt, indem ein 2,5 bzw. 3,5% Fehler in den Analysen angenommen wurde, und eine Monte Carlo-Methode für die Fehlerfortpflanzung verwendet wurde. Die erhaltenen freien Bildungsenergien (auf der Basis von O₁₀(OH)₂) reichen von –1280 bis –1320 kKcal/Mol bei 100°C und 150 bar; ihre Monte-Carlo-Fehlergrößen betragen weniger als ±2 kKcal/Mol. Vergleicht man die Zusammensetzungen von natürlichen koexistierenden wässrigen Lösungen und Mineralmischkristallen mit Hilfe thermodynamischer Gleichungen, so ergibt dies eine schnelle Methode für eine zumindest grobe Bestimmung der freien Energie als Funktion der Zusammensetzung der Mischkristalle. Experimentelle Methoden, wie z.B. kalorimetrische oder hydrothermale Gleichgewichte, sind im Gegensatz dazu sehr zeitaufwendig und schwierig. [U.W.]

Résumé—Des analyses, faites à la microsonde électronique, d'illites diagénétiques dans des grès éocènes de Kettleman North Dome, Californie, ainsi que des analyses d'eaux interstitiales coexistantes ont été utilisées pour calculer des énergies libres molales apparentes de formation des illites sous les conditions *in situ* de 100°C et 150 barres. Des diagrammes variés de composition, triangulaires et rectangulaires, contournés pour l'énergie libre, indiquent grossièrement que l'énergie libre décroît proportionnellement à une augmentation du contenu en potassium, décroît également au fur et à mesure que la substitution d'Al pour Si se produit, et semble être à un minimum le long d'une étroite vallée de composition ayant 3% Fe₂O₃ de cations octaédriques. Qualitativement, la forme de la surface de l'énergie libre suggère seulement de petits écarts de l'idéal.

Les illites et les échantillons d'eau employés dans les calculs ont été choisis aussi proches les uns des autres que possible, et sont en équilibre. Les eaux contiennent principalement Cl⁻, SO₄²⁻, Na⁺, et Ca²⁺, et ont une salinité totale de ~10 000 ppm. Les illites, qui coexistent dans les grès avec du quartz, de l'albite et du feldspar-K diagénétiques, sont phengitiques et contiennent 5–9% K₂O, 1–3% FeO total, 1% MgO, et des quantités moindres de Na₂O, MnO, et TiO₂. La proportion Fe₂O₃/FeO a été arbitrairement fixée à 7 par comparaison avec des analyses publiées.

Log *K* (100°C) a d'abord été calculé pour l'équilibre illite ⇌ ions, à partir des activités ioniques obtenues par les calculs de spéciation pour chaque échantillon d'eau. Les énergies libres apparentes de formation des illites à 100°C ont ensuite été calculées. L'effet des incertitudes instrumentales sur les valeurs des Δ*G*_f^o a été estimé en acceptant une erreur de 2,5 à 3,5% dans les analyses de probe et en utilisant une méthode de Monte Carlo de propagation d'erreurs. Les énergies libres de formation obtenues (basées sur O₁₀(OH)₂) s'étagent de –1280 à –1320 kcal/mole à 100°C et 150 barres, et leurs incertitudes de Monte Carlo sont moins que ±2 kcal/mole. La combinaison de compositions de solutions aqueuses naturelles coexistantes et de solutions solides minérales au moyen d'équations thermodynamiques constitue une méthode rapide pour déterminer, de manière grossière au moins, la surface de composition/énergie libre pour la solution solide. Ceci est en contraste avec les méthodes expérimentales telles que la calorimétrie ou l'équilibre hydrothermal, qui prennent beaucoup de temps, et qui sont difficiles à effectuer. [D.J.]