

EXTRAPOLATION OF AQUEOUS DISSOLUTION DATA TO DETERMINE COMPARATIVE FREE ENERGIES OF FORMATION (ΔG_f°), AND RELATIVE MINERAL STABILITIES

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Abstract—Analytical data from aqueous dissolution studies of minerals, mineral systems, and naturally equilibrated solutions such as surface waters and groundwaters provide the basic ingredients necessary to calculate comparative solubility (or activity) products (CK_s) and comparative free energies of formation (ΔG_f°) of possible minerals or hypothetical minerals. Using a thermodynamic approach, quasi-thermodynamic values are obtained which can help in understanding the relative stabilities of different but similar materials and changes in reacting systems. Illite equilibrated solutions demonstrated that: 1) there is a 5 kcal spread in comparative free energies of formation of the five illites used, 2) the comparative stabilities remain about the same when highly simplified but similar hypothetical mineral formulas are considered, and 3) some of these illites are probably not the most stable phase in a closed chemical system at standard temperature and pressure.

A “mineral index system” composed of common rock-forming minerals, products of chemical weathering and perhaps hypothetical minerals is proposed, which offers a means of studying naturally equilibrated solutions. Such a system can show changes with respect to ΔG_f° of these minerals at a particular site through time or in relationship to spatial distribution and geologic changes through synchronous sampling at different sites.

Key Words—Dissolution, Energy, Formation, Mineral, Solubility, Stability.

INTRODUCTION

Recent papers by Tardy and Garrels (1974) and Nriagu (1975) provide methods for calculating the appropriate free energies of formation of various layer silicates, including clay minerals based upon “real,” “ideal,” and “average” chemical compositions. These calculated free energies of formation (ΔG_f°) are very close to the ΔG_f° from dissolution and calorimetry techniques for those minerals which have been determined. The methods for approximation of ΔG_f° provide internally consistent results because they are based solely upon chemical composition. Comparative stabilities, however, of polymorphs and minerals with somewhat similar chemical composition cannot be differentiated.

Although the determination of ΔG_f° of minerals by aqueous dissolution methods presents problems, the differentiation of polymorphic stabilities and the determination of comparative stabilities of similar substances are possible by this technique. The need for good approximate values of ΔG_f° for minerals is exceeded by the need for data on the relative stability of polymorphic and chemically similar minerals. This paper explores direct and indirect comparisons of mineral stabilities and the responses of multiphase systems to or toward equilibrium. Analytical data on the dissolution of illites (Reesman, 1974) form the main basis for this study. This is not a rigorous treatment of the physical chemistry of illites, but it will provide information supplementary to the studies by Tardy and Garrels

(1974) and Nriagu (1975) that will aid in distinguishing differences in ΔG_f° polymorphs and the comparative stabilities of minerals that are chemically similar. Extension of this technique to produce quasi-thermodynamic data can supply additional insights into the geochemistry of natural systems.

BACKGROUND

Aqueous solubility data were used by Reesman (1974) to calculate Gibbs free energies of formation (ΔG_f°) of selected illites. The ΔG_f° of four of the illites was based upon the actual chemical compositions (Gaudette et al., 1966) of the specific minerals, except that ferrous iron was replaced with magnesium and ferric iron with aluminum (rationale given in Reesman, 1974). Because no chemical analysis was available for Gage illite, its ΔG_f° or stability was calculated with respect to the dissolution of an ideal muscovite formula. For a comparison with the Gage illite the ΔG_f° of the other four illites also were computed with respect to an ideal muscovite formula. The ΔG_f° of illites based upon chemical formulas that are closer to the “real” chemical formulas of the illites should provide a better means of comparing the relative ΔG_f° for the illites than the corresponding ΔG_f° with respect to ideal muscovite. However, the differences in chemical composition of various illites make it difficult to determine the relative stabilities of these illites. If two illites have identical

chemical formulas (highly unlikely), the illite with the more negative ΔG_f° is the stable phase. In the usual case the two illites could differ in the absolute number of chemical components and more surely in the concentration of those that were common to both. Because the absolute ΔG_f° of an element is unknown and indeterminate, the concept of ΔG_f° assumes by definition that the ΔG_f° of any element in its standard state is 0.0. All ΔG_f° s of substances containing two or more elements or elements in nonstandard states are values of energy relative to the 0.0 standard state values. Although the ΔG_f° of iron and aluminum are both 0.0, there is no way to compare them because of their intrinsic differences. Likewise, when iron and aluminum oxidize to form hematite and corundum, the ΔG_f° of hematite is -177.728 kcal/ Fe_2O_3 and that of corundum is -378.082 kcal/ Al_2O_3 (Robie and Waldbaum, 1968). There are similarities between the two minerals, but even though there are over 200 extra kcal of energy available for work in the formation of corundum, there is no way to compare the relative stabilities of these two minerals because of the elemental differences between iron and aluminum.

The chemical formula for grundite (Gaudette et al., 1966) contained seven chemical components, and 10 components were present in the Fithian, Rock Island, and Marblehead illites. Although the structure of these materials is similar and they contain the same general chemical components, there is considerable variability in the concentration of the various chemical components from sample to sample.

Using an ideal muscovite formula as an arbitrary standard by which to calculate and compare the stability of illites is an oversimplification, but it does eliminate up to six chemical components (Na, Ca, Mg, Fe^{2+} , Fe^{3+} and Ti^{4+}). ΔG_f° for the five illites, calculated by the method used by Reesman (1974) in terms of an ideal muscovite formula is:

Grundite	-1338.0 kcal
Gage illite	-1337.6
Fithian illite	-1334.8
Marblehead illite	-1334.2
Rock Island illites	-1333.2

These values indicate about a 5-kcal variation in the ΔG_f° of these minerals (samples) with respect to ideal muscovite.

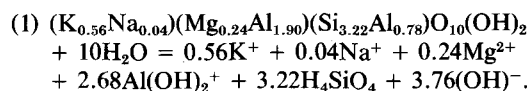
In a closed chemical system aqueous solutions in contact with more than one stable mineral phase eventually should achieve equilibrium with respect to each mineral thereby allowing valid solubility constants to be calculated with respect to each of the minerals in the association. In such associations the rate at which equilibrium is achieved should vary from one phase to another (Helgeson, 1968). Likewise, a multicomponent chemical system should form one or more phases in which the type and amount of the phases are such as

to yield a minimum free energy of formation for the system as a whole.

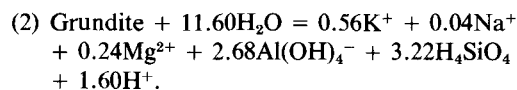
Reesman and Keller (1967) presented the thesis that illites form in response to their chemical environment, tending to form the most stable phase relative to the overall chemical composition of the system as a whole. Or to rephrase it, the chemical composition of illite varies within mineral systems so as to produce the minimum free energy for that system. Thermodynamically, this is the way the system should work. This concept may be tested by using the basic analytical data from the illite equilibrated solutions to form ion-activity products or solubility constants relative to real or hypothetical minerals and calculate ΔG_f° relative to these minerals. Because these free energies are calculated for relative or comparative purposes, they will be denoted as $\text{C}\Delta G_f^\circ$ and the comparative solubility constants (normally, K_s with modifying sub- and superscripts) will be denoted as $\text{C}K_s$.

COMPARATIVE FREE ENERGIES ($\text{C}\Delta G_f^\circ$) OR STABILITIES OF SIMILAR MINERALS

To explore the concept of comparative mineral stabilities a series of direct comparisons was set up among the five illite-equilibrated solutions. Analytical data from each of the five illite-equilibrated solutions were used to calculate $\text{C}K_s$ and corresponding $\text{C}\Delta G_f^\circ$ with respect to the chemical formula of each of the four illites (no formula for Gage illite). Table 1 contains the data used in the calculation of the $\text{C}K_s$. The assumed dissolution of the Grundy illite (grundite) in slightly acid solution is as follows:



For solutions with a pH value above 6.70 (Marblehead illite) the aluminum species was assumed to be $\text{Al}(\text{OH})_4^-$ and the dissolution equation was rewritten to show this change in ionic behavior as follows:



The $\text{C}K_s$ with respect to grundite-, Fithian-, Gage- and Rock Island-equilibrated solutions was calculated based on equation (1) and Marblehead-equilibrated solution using equation (2). The comparative free energy of the reaction ($\text{C}\Delta G_R^\circ$) was calculated from the Nernst equation as follows:

$$\text{C}\Delta G_R^\circ = -RT \ln \text{C}K_s = 1.364\text{Cp}K_s.$$

The $\text{C}\Delta G_f^\circ$ based upon the grundite dissolution was calculated for each illite-equilibrated solution by computing the individual (unique) $\text{C}\Delta G_R^\circ$ and combining it with the $\Sigma\Delta G_f^\circ$ of solution products and ΔG_f° of the water

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 (4.33)	.40 (4.77)	.02 (6.35)	.008 (6.53)	6.6 (3.96)	.094 (5.47)	.02 (6.50)	29.0 (3.57)	--	--	3.70
Gage	.58 (4.84)	.20 (5.07)	--	--	2.2 (4.44)	.047 (5.77)	.014 (6.63)	10. (4.01)	--	--	4.49
Fithian	2.7 (4.17)	.30 (4.89)	.02 (6.17)	.023 (6.04)	1.90 (4.50)	.032 (5.93)	.026 (6.35)	2. (4.70)	3.0 (4.30)	--	5.00
Rock Island	1.80 (4.34)	.13 (5.25)	.13 (5.50)	.056 (5.65)	1.90 (4.50)	.0085 (6.50)	.020 (6.50)	-- (4.09)	5.0 (4.09)	--	5.77
Marblehead	1.65 (4.38)	.12 (5.29)	.36 (5.07)	.64 (4.60)	2.07 (4.46)	.0009 (7.48)	.037 (6.20)	--	15. (3.62)	.56 (5.25)	7.42

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).

utilized in the reaction, or: ΔG_f° Illite = $\Sigma \Delta G_f^\circ$ solution products - ΔG_R° - ΔG_f° water. Dissolution reactions, a sample calculation and the ΔG_f° of solution products were presented in Reesman (1974, pp. 446-7). For this study the methods are of secondary importance to the results. Table 2 contains the resulting ΔG_f° .

If each sample of illite represents the most stable mineral phase compared to its particular chemical composition, then the ΔG_f° , as calculated from the K_s of that mineral-equilibrated solution, should be lower (less negative) than any of the ΔG_f° calculated using solution data of the other mineral-equilibrated solutions and the chemical formula for the particular mineral under consideration. That is, the underlined value in each column of Table 2 is the computed ΔG_f° for that particular mineral. All the other values in that column are ΔG_f° . The hypothesis offered by Reesman and Keller (1967) would predict that the underlined value in each column should have the lowest value in that column. Instead, the Gage and Grundy illites appear to show about the same ΔG_f° with respect to each of the illites or they show about equal relative stability and are apparently

the most stable with respect to all of these substances. The Fithian illite is third, followed by Marblehead and Rock Island illites. The deviation in ΔG_f° from the mean value for the various individual illite formulas is greater than that with respect to the deviation for the ΔG_f° relative to the muscovite formula. This seems to indicate that the use of the muscovite formula may be a good indirect comparator to express the relative stability or ΔG_f° of illites. In addition the muscovite formula reduces the chemical components under consideration (no Ca, Na, or Mg).

EXTRAPOLATION OF ΔG_f° FROM SOLUBILITY DATA

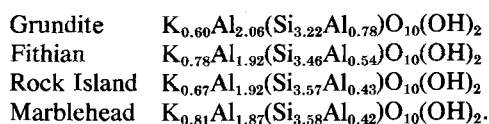
The calculation of a ΔG_f° with respect to a muscovite formula from illite-equilibrated solutions was an extrapolation of activity-product data to consider a possible mineral that may or may not have been present in the sample. Because the use of a muscovite formula reduced the chemical components and still apparently provided a fairly good approximation of the relative stabilities of the illites, let us try another approach. If illite is primarily a potassium-poor dioctahedral mica, then muscovite could be considered the potassium-saturated and pyrophyllite the potassium-depleted end members of this hypothetical series. With additional simplification of the chemical formula of the individual illites they can be made to fit into the system: $K_2O-Al_2O_3-SiO_2-H_2O$ and the illites would fall between the muscovite-pyrophyllite end members. For this transformation the interlayer charge of the illites is considered to be only potassium with charge equivalents of the sodium and calcium being replaced by potassium. Magnesium in a mineral formula of the illite is considered to be present in the octahedral layer, and is replaced on a charge for charge basis with aluminum. The resulting simplified "illite" formulas are as follows:

Table 2. Relative stabilities of illites as calculated from each illite equilibrated solution with respect to each illite formula.

Solutions for ΔG_f°	Formulas for Comparison				
	Muscovite	Grundite	Fithian	Marblehead	Rock Island
Grundite	-1338.0	<u>-1322.73</u>	-1322.08	-1317.25	-1311.90
Gage	-1337.6	-1322.44	-1322.35	-1317.30	-1312.02
Fithian	-1334.8	-1319.85	<u>-1319.76</u>	-1314.29	-1309.35
Marblehead	-1334.2	-1318.09	-1315.45	<u>-1310.83</u>	-1305.95
Rock Island	-1333.2	-1317.99	-1317.33	-1311.94	<u>-1307.29</u>
Mean	-1335.56	-1320.22	-1319.55	-1314.32	-1309.30
	± 2.13	± 2.28	± 3.19	± 2.97	± 2.71

Table 3. Comparative stabilities of modified and simplified illites (in system $K_2O-Al_2O_3-SiO_2-H_2O$) as calculated from ion activities in each illite-equilibrated solution.

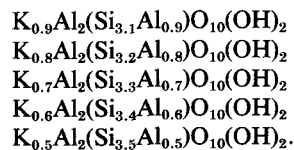
Formula for Comparison	Solutions from which ΔG_f° were Calculated					
	Grundite	Gage	Fithian	Marblehead	Rock Island	Mean
Muscovite	-1338.0	-1337.6	-1334.8	-1334.2	-1333.2	-1335.56 ± 2.13
Grundite	-1313.86	-1313.84	-1311.78	-1312.25	-1310.50	-1312.45 ± 1.43
Fithian	-1308.18	-1308.51	-1306.36	-1305.94	-1305.06	-1306.81 - 1.48
Marblehead	-1303.33	-1303.82	-1301.72	-1301.06	-1300.44	-1302.07 ± 1.45
Rock Island	-1299.11	-1299.62	-1297.72	-1297.52	-1296.54	-1298.10 + 1.25
pyrophyllite	-1255.63	-1256.91	-1256.28	-1257.78	-1255.75	-1256.47 ± 0.89



Using the analytical data in Table 1 for the five illite-equilibrated solutions, the ΔG_f° with respect to the four simplified illite formulas, muscovite, and pyrophyllite was calculated for each of the solutions. The results are shown in Table 3. These extrapolations represent the comparative stability of these samples in the system $K_2O-Al_2O_3-SiO_2-H_2O$. Note that the deviations from the mean ΔG_f° for these simplified formulas are less than those calculated for the more complex formulas shown in Table 2. These smaller deviations do not imply that these data are better than those in Table 2, but that there is a little more "sameness" or less of a chemical individuality from sample to sample which resulted during the process of chemical "simplification." Huang and Keller (1972) would argue that this is the reason that the "real mineral formulas" should be used when possible. This is a sound goal but it would mean that all minerals and each mineral in a system being studied by changes in free energies would have to be evaluated in terms of a somewhat artificial precision related to slight or moderate deviations from "ideal" chemical formulas. One major objective of this paper is to demonstrate that simplification of mineral chemistry can provide useful ΔG_f° data. The precision shown in Table 3 (one hundredth of a kcal) is artificial, if one considers these values as sacred ΔG_f° ; they are not. These are fairly valid numbers in terms of comparative stabilities because the largest portion of the ΔG_f° results from the summation of ΔG_f° of solution products and reactants which are constants for each of the mineral-dissolution equations. The only variable

portions in the ΔG_f° come from the relative activity products.

The numerical relationships in Table 3 are shown graphically in Figure 1. In this figure muscovite and pyrophyllite are the end members plotted on the abscissa and ΔG_f° are on the ordinate. Along the abscissa from muscovite to pyrophyllite there is a decrease in potassium and aluminum and an increase in silicon. The ΔG_f° s with respect to muscovite and pyrophyllite formulas are fixed points from which the diagonal tie-lines are connected. Each tie-line runs from the hypothetical ΔG_f° with respect to muscovite to the ΔG_f° of pyrophyllite for each of the individual solutions. The ΔG_f° s with respect to the simplified illite formulas are plotted on the tie-lines for each solution and points, representing a particular simplified illite, plot very neatly in relationship to some composition. Figure 2 shows how hypothetical potassium-depleted micas with only tetrahedral charge deficiencies would plot on this diagram. The formulas for these hypothetical substances are:



In Figure 2 the 0.9K mica plots exactly 0.9 between muscovite and pyrophyllite, and the 0.8K, 0.7K, 0.6K, and 0.5K micas plot at 0.8, 0.7, 0.6, and 0.5, respectively. This is not magic but a mathematical necessity.

The location of the ΔG_f° with respect to simplified formulas of grundite, Fithian, Marblehead, and Rock Island illites as plotted between the muscovite-pyrophyllite end members shows some deviation from an ideal plot between the end members (Table 4). In ad-

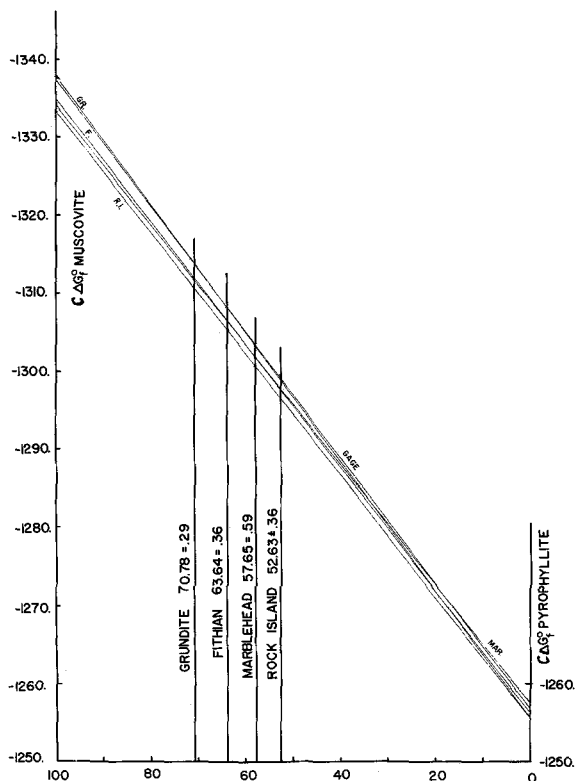


Fig. 1. A graphical representation of the extrapolated $C\Delta G_R^0$ of illite-equilibrated solutions in the muscovite-pyrophyllite system. The diagonal lines represent the extrapolated $C\Delta G_R^0$ from each illite-equilibrated solution. Broad vertical lines are plots of mean positions between the muscovite-pyrophyllite end members for each particular illite formula.

dition, the relationship between the chemical formula of an illite and its location between the end members is obscure. For example, the simplified grundite formula has the least potassium, but it plots closest to the muscovite end member and Marblehead illite with the most potassium (0.81K) plots about 0.58 of the pyrophyllite-muscovite distance.

Table 4. Actual and calculated percentage of distance between the pyrophyllite-muscovite end members as plotted from simplified illite formulas in Figure 1.

	Grundite	Fithian	Marblehead	Rock Island
% of Distance from Pyr - Musc	70.78 ±.29	63.64 ±.36	57.65 ±.59	52.63 ±.37
Tetrahedral Charge	.78	.54	.42	.43
Octahedral Charge	-.18	.24	.39	.24
100 X Tet. Charge	78.	54.	42.	43.
40.1 X Oct. Charge	-7.218	9.624	15.639	9.624
Calculated %	70.78	63.62	57.64	52.62

$$\text{Calculated percentage} = (\text{Tetrahedral Charge}) (100) + .401 (\text{Octahedral Charge}) (100)$$

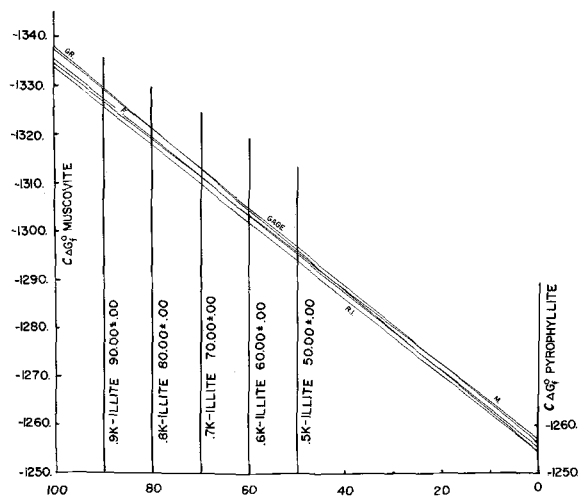


Fig. 2. Extrapolated $C\Delta G_R^0$ of illite-equilibrated solutions in the muscovite-pyrophyllite system showing where hypothetical illites with only tetrahedral charge deficiencies plot relative to the end members.

The approximate position that a particular simplified illite plots in the system $K_2O-Al_2O_3-SiO_2-H_2O$, as shown in Figure 1, is given by the following formula:

$$\% \text{ toward Muscovite} = (\text{Tetrahedral Charge} + 0.40 \times \text{Octahedral Charge}) (100)$$

Although the hypothetical illitelike formulas with only tetrahedral charge deficiencies plotted in Figure 2 at the distance between pyrophyllite and muscovite that is equal to the tetrahedral charge with a deviation from these plotted positions of 0.0, the simplified illite formulas plotted in Figure 1 contain tetrahedral deficiencies and octahedral deficiencies or surpluses. Having both types of deficiencies results in a slight deviation from the ideal relationship that was noted with the tetrahedral charge only, and this is evidenced by the deviations about the ordinate position. These deviations arise from minor variations within the chemistry of the equilibrated solutions, which appear as minor variations in the comparative activity-product constants and thus in the comparative free energies of reaction ($C\Delta G_R^0$). In general these deviations are relatively slight within the system $K_2O-Al_2O_3-SiO_2-H_2O$, and because they are slight it indicates that the extrapolation of data derived from solubility studies can offer an indirect means of comparing the stabilities of similar but different substances.

MINERAL INDEX SYSTEM

In studying a natural solution, be it pore water, stream water, or other, there are two interesting but generally unanswered questions. With what phase or phases is the solution in equilibrium? Is the solution sub- or supersaturated with respect to certain minerals?

Rarely is a solution checked to determine if it is saturated with respect to minerals such as calcite, dolomite, quartz, and/or other relatively simple minerals. In these determinations ion or activity products are either compared to established solubility constants, or more likely the analytical data are plotted on a mysterious graph or "phase" diagram to determine the state of the solution with respect to potential equilibrium with one or more minerals. If the silica concentration in solution is above 6.0 mg/liter, the solution may be supersaturated with respect to quartz, indicating quartz is stable and another source of silica is probably supplying the dissolved silica. Comparing analytical data from solutions with known solubility constants can aid in understanding the chemical reactions that may have contributed to the concentrations of dissolved constituents in the water. Much more information could be gleaned from analytical data if there were sufficient confidence in solubility constants and free energies of formation for more complex and less soluble minerals. A suite of mineral comparators or index minerals should be established and used as a base for comparison between these minerals and unknown CpKs and ΔG_f° . The index minerals should include the common rock-forming minerals and products of chemical weathering and diagenesis. Because many of these minerals are aluminum- and iron-bearing silicates problems are to be expected.

Possible problems of a mineral index system

Problems which could plague the use of a mineral index system are: 1) the poorly understood nature of key ions in solution (especially iron and aluminum), 2) analytical techniques for the analyses of aluminum in the part-per-billion range are not commonly used and the tenuous stability between ferrous and ferric ions in solutions once the solutions have been removed from their natural setting is a problem, and 3) the lack of generally accepted solubility constants for the minerals which should be used for comparison.

Problems in determining many of the potentially useful solubility constants and free energies of formation are interrelated. Low solubilities, slow dissolution, analytical methods, and possible reactions that form secondary minerals create problems in calculating solubility constants and in studying the nature of ions in solution. Studies involving the synthesis of many of these minerals from solution, to determine equilibrium conditions between mineral and solutions, are often plagued with kinetic problems in which less stable polymorphs and/or other minerals that may be favored kinetically often form. Only minor quantities of amorphous material, poorly crystalline material, or relatively unstable polymorphs will result in the calculation of an erroneous solubility constant and ΔG_f° . Even prolonged aging of solutions in contact with a precipitated mineral that contains a very minor amount (undetected)

able) of an unstable phase might not result in equilibrium between the solution and the major solid phase.

A solubility constant as calculated from dissolution data presumes a "pure" mineral or if additional phases are present, all phases will respond toward equilibrium. In dealing with fine-grained products of weathering such as clay minerals, multiphase materials are a fact of life. Solubility studies, using coarse-grained minerals such as feldspars, generally require reduction in grain size to increase the surface area. Grinding or pulverizing minerals to increase surface area requires mechanical energy and results in high-energy lattice disorders, some of which would be considered to be amorphous (Reesman and Keller, 1968). Only minor amounts of disordered mineral can provide enough dissolved constituents to supersaturate such mineral-equilibrated solutions.

Calculation of solubility constants from free energies of formation of minerals which have been determined by calorimetry presumes a knowledge of the solution products and their free energies of formation. Agreement on the nature of aluminum ions in aqueous solution is far from unanimous. It is likely that the type of aluminum ions in solution is controlled partially by kinetic effects in which the slow dissolution of aluminum-bearing minerals yields monomeric aluminum ions. Rapid precipitation of aluminum ions by adding hydroxyls may result in polymerization of aluminum ions along with the precipitation.

Natural solutions in contact with minerals strive toward equilibrium with respect to these minerals. Equilibrium may not be reached between solution and minerals, but at least these minerals have not been ground prior to equilibration. Once separated from the mineral phases, solutions may become diluted or changes in chemical environment of the solutions may cause supersaturation with respect to one or more possible mineral phases.

Lack of universal acceptance of some solubility constants and ΔG_f° of minerals, and the nature and ΔG_f° of solution products will cause problems with the establishment of a mineral index system, but these problems are not insurmountable. If data, both analytical and thermodynamic, are specified, other investigators can make suitable adjustments to determine how the results from other investigators fit into the system that he or she prefers. The use of such a system would stimulate additional investigations into the thermodynamic properties of minerals and solutions and aid in more rapid refinement of the needed data.

Application of index system to natural systems

A high degree of thermodynamic refinement is not necessary to show changes with respect to index minerals if naturally equilibrated solutions from one location are compared to those of another, or to examine

Table 5. Possible index minerals and the response of illite-equilibrated solutions to these index minerals.

	Quartz		Gibbsite		Kaolinite		Pyrophyllite		Microcline		Albite	
	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°
Grundite	3.93	-204.65	15.77	-275.21	39.46	-903.02	47.38	-1255.63	42.27	-900.78	42.72	-896.51
Gage	4.44	-205.31	15.28	-274.54	39.42	-902.97	48.32	-1256.91	42.93	-901.68	43.16	-897.11
Fithian	4.50	-205.39	14.93	-274.06	38.86	-902.21	47.86	-1256.28	41.59	-899.86	42.32	-895.96
Rock Island	4.50	-205.39	14.74	-273.81	38.47	-901.67	47.46	-1255.75	40.80	-898.78	41.71	-895.14
Marblehead	4.46	-205.33	14.90†	-274.92	38.73†	-903.83	47.64†	-1257.78	25.25†	-897.65	26.16†	-893.92
	ΔG_f°	-204.65*	ΔG_f°	-273.49*	ΔG_f°	-902.87*	ΔG_f°	-1261.9‡	ΔG_f°	-892.82*	ΔG_f°	-883.99*
Montmorillonites												
	Beidellites ($M^{+}_{.33}Al_{2.33}Si_{3.67}O_{10}(OH)_2$)						$(M^{+}_{.33}Al_{1.86}Si_4O_{10}(OH)_2$)					
	Ca _{.165} Beid.		Na _{.33} Beid.		K _{.33} Beid.		Ca _{.165} Mont.		Na _{.33} Mont.		K _{.33} Mont.	
Grundite	55.73	-1281.78	56.25	-1281.32	56.11	-1282.83	50.10	-1265.64	50.62	-1265.18	50.48	-1266.69
Gage	—	—	56.70	-1281.93	56.63	-1283.54	—	—	51.45	-1266.31	51.38	-1267.92
Fithian	55.30	-1281.19	55.89	-1280.82	55.66	-1282.22	50.21	-1265.79	50.80	-1265.42	50.57	-1266.82
Rock Island	54.74	-1280.43	55.56	-1280.37	55.26	-1281.67	49.40	-1264.78	50.29	-1264.73	49.99	-1266.03
Marblehead	49.48†	-1281.62	50.31†	-1281.58	50.09†	-1282.99	44.40†	-1265.87	45.23†	-1265.83	45.01†	-1267.24
	ΔG_f°	-1280.8‡	ΔG_f°	-1279.5‡	ΔG_f°	-1282.5‡	ΔG_f°	-1265.0§	ΔG_f°	-1263.5§	ΔG_f°	-1267.5§
Illites												
	.7K "Ideal" Illite (Figure 3)				$K_0Mg_{.25}Al_{2.3}Si_{3.5}O_{10}(OH)_2$							
	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°	CpKs	ΔG_f°				
Grundite	65.88	-1313.15	—	—	65.69	-1309.61	—	—				
Gage	65.93	-1313.20	—	—	—	—	—	—				
Fithian	64.38	-1311.09	—	—	64.00	-1307.31	—	—				
Rock Island	63.43	-1309.80	—	—	63.03	-1305.98	—	—				
Marblehead	52.48†	-1311.15	—	—	45.49†	-1305.13	—	—				
	ΔG_f°	-1298.00§	—	—	ΔG_f°	-1301.5§	—	—				

* From Robie and Waldbaum (1968).

† CpKs₄ was used for Marblehead-equilibrated solutions because Al(OH)₄⁻ was assumed to be the aqueous species of aluminum. All other solubility constants are CpKs₂ values with Al(OH)₂⁺ assumed as the aluminum ion.

‡ From Nriagu (1975).

§ Calculated by Nriagu Method, Nriagu (1975).

changes in index minerals at a particular site with respect to time. Studies using synchronous collection of water at several sampling sites within a basin could show variations, relative to index minerals, of a systematic nature that would provide information of great value. Repeated sampling and analyses at a single site through time and under different rates of flow and temperature could supply data on the rate of reactions in natural systems or other changes that might not be intuitively obvious. These are examples in which an index system could be used with little or no further refinement. It is not necessary to have a full-scale laboratory or to be an analytical chemist because much analytical data for study of natural systems are already available (U.S.G.S. Water-Supply Papers). With one set of analytical data (e.g., one stream analysis) it is possible to produce all sorts of interesting, but mostly useless output.

During the past six years, most analytical data obtained at this laboratory (springs, wells, streams, and mineral equilibrations) have been computer processed to calculate activities of dissolved constituents and to play with real and hypothetical activity products and ΔG_f° s. In addition about a 1000 U.S.G.S. surface water samples also have been processed to study aluminum ions in natural solutions.

For simplicity sake, the number of index minerals should be fairly small for any particular study and the comparator minerals that are chosen would probably differ to reflect differences in terrain, rock type, and climate. A sequence of minerals similar to those proposed by Goldich (1938), Reiche (1943), Jackson and Sherman (1953) and many others could be adopted.

Table 5 contains six possible index minerals and the response of the five illite-equilibrated solutions to these minerals. In addition, eight hypothetical phyllosilicate

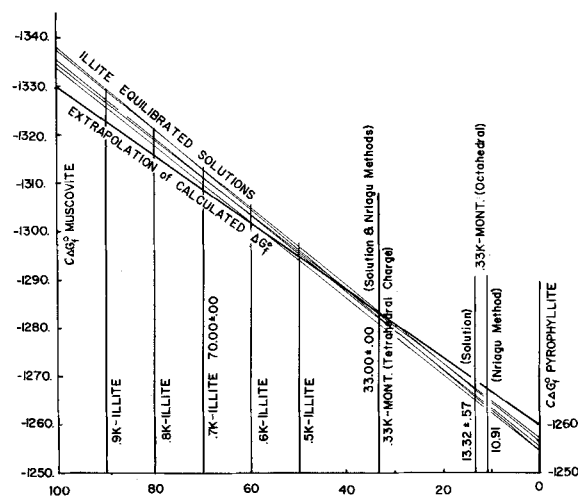


Fig. 3. Extrapolated relationships of illite-equilibrated solutions and calculated ΔG_f^0 from Nriagu (1975). The broader diagonal line, representing the extrapolation of calculated ΔG_f^0 values, crosses the illite-equilibrated lines in the region of the 0.33 K-montmorillonite (beidellite); thus, the good fit between the equilibrated ΔG_f^0 and the calculated ΔG_f^0 values. The octahedral deficient 0.33 K-montmorillonites plot at 10.91% and 13.23% for the calculated and solution equilibrated values. Calculated ΔG_f^0 for the octahedral montmorillonites agrees with the solution derived values if the two "compositional" vertical lines are superimposed. Divergence of calculated and equilibrated ΔG_f^0 is most apparent near the muscovite-pyrophyllite end members.

"minerals" are included. Two of these eight are the 0.7 K-illite as shown in Figures 2 and 3, and the illite from Nriagu (1975, taken from Helgeson, 1969). The remaining six are montmorillonite type minerals, three of which are Ca-, Na-, and K-beidellites with tetrahedral charge deficiencies (Nriagu, 1975) and the equivalent material with octahedral charge deficiencies is included for comparative purposes.

Figure 3 shows how the 0.7 K-illite, the 0.33 K-beidellite, and the 0.33 K-montmorillonite plot on the extrapolated ΔG_f^0 system from muscovite to pyrophyllite. As in Figure 2, the 0.7 K and the 0.33 K tetrahedrally deficient materials plot at 70.00 and 33.00% of the distance toward muscovite for the illite-equilibrated ΔG_f^0 . The calculated ΔG_f^0 for this same material using the method of Nriagu (1975) also plots at this same percentage.

The octahedral equivalent, the 0.33 K-montmorillonite, plots at 13.32(± 0.57)% for the ΔG_f^0 of the illite-equilibrated solutions, which is very close to the predicted value of 13.23% as described in Table 4. However, the calculated ΔG_f^0 of the K-montmorillonite using Nriagu's method plots at 10.91%, which is not very close to the plot of the illite-equilibrated solutions.

Nriagu's (1975) calculated ΔG_f^0 s for the beidellite minerals are very close to the equivalent ΔG_f^0 , as are the octahedral charged montmorillonites (Tables 5 and 6). If octahedral montmorillonites with higher interlay-

Table 6. Mean values of ΔG_f^0 of various hypothetical minerals and calculated ΔG_f^0 from Nriagu (1975).

	$C \Delta G_f^0$	Calc. ΔG_f^0
.7K "ideal" illite	-1311.68 \pm 1.47	-1308.94
Illite	-1307.00 \pm 1.95	-1301.5
Montmorillonite		
Ca-octahedral	-1265.52 \pm .50	-1254.99
Na-octahedral	-1265.49 \pm .61	-1263.5
K-octahedral	1266.94 \pm .70	-1267.46
Ca-tetrahedral	1281.26 \pm .60	-1280.8
Na-tetrahedral	1281.20 \pm .52	-1279.5
K-tetrahedral	1282.65 \pm .72	-1282.5

er charges are considered, the divergence in the ΔG_f^0 as calculated by these two methods becomes greater. It appears that the fairly good agreement in the ΔG_f^0 s of the two systems for the montmorillonites is luck. The ΔG_f^0 calculated from the illite-equilibrated solutions are calculated using constants (the ΔG_f^0 of solution products) that are combined with relative free energies of the reaction, as calculated from CK_s or relative activity products, whereas the Nriagu method utilizes only a set of constants to derive the calculated ΔG_f^0 . The general approach of both Tardy and Garrels (1974) and Nriagu (1975) methods are similar but they differ in that Tardy and Garrels considered energies of silication in contrast to the hydroxylation energies of Nriagu. The two methods give similar results using different energy values. Likewise, in calculating the ΔG_f^0 of minerals by aqueous dissolution techniques different investigators may use different ΔG_f^0 for dissolution products and have different ideas as to these solution products, but in most cases there is fairly good agreement in the calculated ΔG_f^0 for the minerals in question. In any method of determining ΔG_f^0 certain standard compounds or minerals must be used to determine the ΔG_f^0 of other substances. In more practical terms, thermodynamic data have been extrapolated to derive the present set of ΔG_f^0 for most "known" minerals. These ΔG_f^0 s are no better than the assumptions and standard ΔG_f^0 s that are used to determine the ΔG_f^0 of unknown minerals. The more complex the unknown, the greater the probability of large errors because the "purity" of the data degenerates as more and more assumptions and standards must be introduced.

Although developing ΔG_f^0 s for complex minerals is an important goal, it appears that simplification of data could be as justifiable because of the potential for applying the simplified values of ΔG_f^0 or ΔG_f^0 to study naturally equilibrated aqueous solutions. At present

any new system that will encourage the application of thermodynamic or quasi-thermodynamic treatment of analytical data eventually will help in the study of mineral-water interactions, provided the user realizes the possible pitfalls of the system.

CONCLUSION

Raw data from the chemical analyses of natural and equilibrated solutions can be massaged by thermodynamic techniques to produce quasi-thermodynamic results to help answer questions about the geochemistry of a weathering system or the relative stability of similar minerals. Little in the way of extra expense is needed, only the time necessary to consider the potential meaning of the resulting output. Comparative free energies of real, ideal and hypothetical minerals can be calculated by the method. So long as these values are considered in a manner similar to those calculated by the methods of Nriagu (1975) and Tardy and Garrels (1974) all is well. The advantage of starting with real analytical data is that these calculations yield different results in energy values which arise from differences in activities of dissolved constituents. That is, different analytical data yield different CK_s s with respect to a mineral or group of comparator minerals.

The main significance of such a relative free energy system is:

1. In studies of mineral equilibration, the relative stability of one substance versus another (e.g., illites) can be determined by directly or indirectly comparing the values of ΔG_f° s.

2. The technique can be applied to solutions from natural systems in which there is no assurance of equilibrium and little knowledge of the mineralogy of the system. This would be useful when differences with respect to key or index minerals are studied at one site through time, or from place to place within a larger system.

3. Many analytical data are available presently from natural systems and can be used by anyone with access to a computer or calculator.

4. More common usage of thermodynamic techniques in any form will spur the determination of better quality thermodynamic data both for minerals and solution products.

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REFERENCES

- Gaudette, H. E., Eades, J. D. and Grim, R. E. (1966) The nature of illite: *Clays & Clay Minerals* **13**, 33-48.
- Goldich, S. S. (1938) A study in rock weathering: *J. Geol.* **46**, 17-58.
- Helgeson, H. C. (1968) Evolution of irreversible reactions in geochemical processes involving minerals and aqueous solution—I. Thermodynamic relations: *Geochim. Cosmochim. Acta* **32**, 853-877.
- Helgeson, H. C. (1969) Thermodynamics of hydrothermal systems at elevated temperatures and pressures: *Am. J. Sci.* **267**, 729-804.
- Huang, W. H. and Keller, W. D. (1972) Standard free energies of formation calculated from dissolution data using specific mineral analyses: *Am. Mineral.* **57**, 1152-1162.
- Jackson, J. L. and Sherman, G. D. (1953) Chemical weathering of minerals in soils: *Adv. Agron.* **5**, 219-318.
- Nriagu, J. O. (1975) Thermochemical approximations for clay minerals: *Am. Mineral.* **60**, 834-839.
- Reesman, A. L. and Keller, W. D. (1967) Chemical composition of illite: *J. Sediment. Petrol.* **37**, 592-596.
- Reesman, A. L. and Keller, W. D. (1968) Aqueous solubility studies of high alumina and clay minerals: *Am. Mineral.* **53**, 929-942.
- Reesman, A. L. (1974) Aqueous dissolution studies of illite under ambient conditions: *Clays & Clay Minerals* **22**, 443-454.
- Reiche, P. (1943) Graphical representation of chemical weathering: *J. Sediment. Petrol.* **13**, 58-68.
- Robie, R. A. and Waldbaum, D. R. (1968) Thermodynamic properties of minerals and related substances at 298.15°K (25.0°C) and one atmosphere (1.013 Bars) pressure and at higher temperatures: *U.S. Geol. Surv. Bull.* **1259**, 256pp.
- Tardy, Y. and Garrels, R. M. (1974) A method for estimating the Gibbs energies of formation of layer silicates: *Geochim. Cosmochim. Acta* **38**, 1101-1116.

Резюме- Аналитические данные изучения результатов растворения минералов и минеральных систем в воде, а также изучение естественных уравновешенных растворов, таких как поверхностные и подземные воды, обеспечивают основные составляющие, необходимые для вычисления параметров относительной растворимости, или активности, (CK_s) и относительных свободных энергий формирования ($CG^{\circ}f$) возможных минералов или гипотетических минералов. Используя термодинамический подход, могут быть получены квазитермодинамические значения, которые помогают понять относительную стабильность различных, но сходных материалов и изменения в реакционных системах. Иллитовые уравновешенные растворы показали, что: 1) 5 ккал относительно свободной энергии необходимо для формирования пяти иллитов, 2) относительная стабильность остается примерно той же, когда рассматриваются упрощенные, но сходные гипотетические формулы минералов, и 3) некоторые из этих иллитов возможно не являются наиболее стабильной фазой в закрытой химической системе при стандартных температурах и давлении.

Предлагается "минеральная индексная система", состоящая из обычных пороодообразующих минералов, которая может служить средством изучения естественных уравновешенных растворов. Такая система может выявлять изменения, касающиеся $CG^{\circ}f$ этих минералов в отдельных местах с течением времени или по отношению к пространственному распределению и геологическим изменениям при одновременном отборе образцов из различных мест.

Kurzreferat- Analytische Meßdaten, aus Auflösungsversuchen in Wasser von Mineralien, Mineralsystemen und natürlich equilibrierten Lösungen wie Oberflächen- und Grundwasser, stammend, liefern die grundlegenden Bestandteile notwendig für die Berechnung der relativen Löslichkeits- (oder Aktivitäts) produkte und der relativen Freien Bildungsenergien von Mineralien oder hypothetischen Mineralien. Indem eine thermodynamische Methode benutzt wurde, wurden quasi-thermodynamische Werte erhalten, die helfen, die relativen Stabilitäten von verschiedenen aber ähnlichen Materialien und Veränderungen in reagierenden Systemen, zu verstehen. Mit Illiten equilibrierte Lösungen demonstrieren das folgende: 1) es existiert eine 5 kcal Spanne in relativen Freien Bildungsenergien unter den 5 benutzten Illiten, 2) die relativen Stabilitäten bleiben ungefähr die gleichen, wenn sehr simplifizierte aber gleichartige, hypothetische Mineralformeln erwägt werden, 3) einige dieser Illiten sind wahrscheinlich nicht die stabilste Phase in einem geschlossenen, chemischen System bei Standard-Temperatur und Druck.

Résumé- Les données analytiques obtenues d'études de dissolution aqueuse de minéraux, de systèmes minéraux et de solutions naturellement équilibrées telles des eaux de surface et de la nappe phréatique procurent les éléments nécessaires de base pour calculer les produits de solubilité (ou d'activité) comparative (CK) et les énergies libres comparatives de formation ($CAG^{\circ}f$) de minéraux possibles ou de minéraux hypothétiques. Par l'emploi d'une approche thermodynamique, des valeurs quasi-thermodynamiques sont obtenues, valeurs qui aident à comprendre les stabilités relatives de matériaux différents mais similaires, et les changements dans les systèmes réagissants. Les solutions équilibrées à l'illite montrent que 1) il y a un étalage de 5 kcal. dans les énergies libres comparatives de formation des 5 illites utilisées, 2) les stabilités comparatives sont maintenues à peu près égales lorsqu'elles sont fort simplifiées, mais des formules de minéraux hypothétiques semblables sont considérées, 3) certaines de ces illites ne sont probablement pas la phase la plus stable dans un système chimique fermé à température et pression standards. Un "système d'index minéral" composé des minéraux communément formant des roches, les produits d'altération chimique, et peut-être des minéraux hypothétiques est proposé, système qui offre un moyen d'étudier les solutions équilibrées naturellement. Un tel système peut montrer des changements vis à vis du $CAG^{\circ}f$ de ces minéraux à un site particulier pendant un certain laps de temps, ou vis à vis de distribution spatiale et de changements géologiques par des échantillonnages synchroniques à différents sites.