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CALCULATION OF APPARENT STANDARD FREE ENERGIES OF FORMATION OF SIX ROCK-FORMING SILICATE MINERALS FROM SOLUBILITY DATA

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ABSTRACT

Using aqueous solubility data, standard free energies of formation have been calculated for several rock-forming silicate minerals. Because proof of equilibrium solubility conditions has not been unequivocally established, although evidence indicates little deviation from equilibrium, the free energies calculated are conservatively called *apparent* F_f°, or aF_f°. The following values are calculated:

Muscovite	−1328.7 kcal/mole
Nepheline	−476.8
Microcline	−891.3
Enstatite	−350.6
Forsterite	−496.9
Diopside	−725.

INTRODUCTION

Standard free energies of formation of certain rock-forming silicate minerals may be calculated using data obtained from the measured solubility of the minerals in water. In brief, the change in free energy resulting from dissolution of a mineral is calculated primarily from the concentrations of its dissolved products at saturation. This value is added algebraically to the sum of the F_f°'s (obtained from documented measurements) of those dissolved products, yielding a final sum that is the F_f° of the mineral. The procedure will be illustrated in detail with specific examples.

Mandatory to obtaining the solubility product is a condition of equilibrium between the solution and solid mineral. Ideally this condition is realized by approaching equilibrium from both directions, but it is impossible to do so at room temperature with silicates such as feldspars, pyroxenes, etc. Unequivocal proof of saturation, therefore, is not forthcoming from our procedure, but for practical purposes within analytical detection saturation appears to have been reached. For example, no significant change in the dissolved load of water shaken (continuously in a mechanical shaker at room T. and P.) with kaolinite for 18 months as against 3 days could be detected (Keller *et al.* 1964). Likewise, grinding 10g of common, rock-forming silicate minerals under 100 ml of water in a mechanically driven mortar and pestle for one hour apparently produced a steady solute composition (Keller *et al.*, 1963). Even more convincing, concrete confirmation of the adequacy of the experimental conditions, technique, and method, is the fact that our calculated $F_f°$'s are in the same magnitude as those already determined for a few of the minerals by older, time-tested methods. Presumably the other new values for additional minerals are likewise realistic. However, being cognizant that saturation has not been ideally established we shall conservatively term our calculated values as *apparent* standard free energies of formation: "$aF_f°$".

LABORATORY WORK

Data on aqueous solubilities of some common rock-forming minerals useful for these calculations are available from dissolution experiments reported in 1963 (Keller *et al.*). In addition to grinding under distilled water exposed to the air, as described in preceding paragraphs, the process was repeated with CO_2 bubbled into the water against atmospheric pressure. Other details of centrifugation and analysis are described in the 1963 paper.

TREATMENT OF DATA

The first step in the calculation of the $aF_f°$ of a mineral from solubility data is the determination of its equilibrium (solubility) constant from experimentally measured data. The activities of the products conventionally are divided by the activities of the reactants, in which the activity of the relatively pure water, and of solids, are taken as unity. Activity of H^+ in the solution was measured by a glass electrode, and the activities and logs of activities of all other ions were determined from the solution analysis by the Debye-Huckel method on an IBM 1620 computer. The activity of the bicarbonate ion was calculated from the pH of the solution and the partial pressure of atmospheric CO_2 (about $10^{-3.5}$ atmosphere), and the activity of carbonic acid (H_2CO_3) was calculated by its equilibrium to the partial pressure of CO_2 at $10^{-1.5}$—hence, it was taken to be $10^{-5.0}$ moles/liter (Garrels, 1960).

The change in free energy occurring during the dissolution of the mineral to yield dissolved products is next calculated through the following relationship:

$$\Delta F_R° = - RT \ln K_{eq} = - 1.364 \log K_{eq}$$

where $\Delta F_R°$ is the difference in the standard free energy of the reaction, R is the gas constant, T is the absolute temperature, and K_{eq} is the equilibrium constant.

The $F_f°$ of the mineral is then obtained by subtracting $\Delta F_R°$ and $F_f°$ of the other reactants from the sum of the $F_f°$ of the dissolved products.

The standard free energies of the dissolved products resulting from solution of the mineral in water (reaction with water) are known from independent chemical measurements, as shown in Table 1. The F_f° of dissolved silica, referred to in this paper as silicic acid, H_2SiO_4 (following convention), has been re-evaluated in terms of most recent data on quartz. Siever (1957), using solubility data from amorphous silica (glass), determined -300.2 kcal/mole to be the best calculated value. His determination was based on the F_f° of quartz as -192.4 kcal but work by Wise *et al.* (1962) revises F_f° of quartz to -204.75 kcal. By readjusting Siever's determination to the new data, we obtain -312.8 kcal/mole for the F_f° of silicic acid, a value that will be used in our further calculations.

TABLE 1. STANDARD FREE ENERGIES OF FORMATION USED IN DETERMINING aF_f°

H_2O	$-$ 56.72 kcal/mole	(Wicks and Block, 1963)
OH^-	$-$ 37.63	(calc. from above reference)
H_4SiO_4	-312.8	(re-evaluated by authors)
AlO_2^-	-200.7	(Rossini *et al.*, 1952)
K^+	$-$ 67.46	(Rossini *et al.*, 1952)
Mg^{2+}	-108.99	(Rossini *et al.*, 1952)
Ca^{2+}	-132.18	(Rossini *et al.*, 1952)
Na^+	$-$ 62.59	(Rossini *et al.*, 1952)
$MgCO_3$	-246.0	(Rossini *et al.*, 1952)
$CaCO_3$	-269.78	(Rossini *et al.*, 1952)
H_2CO_3	-149.0	(Rossini *et al.*, 1952)

Calculations of Apparent Standard Free Energies of Minerals

Muscovite. Although muscovite is not the simplest of the minerals to be discussed, its aF_f° will be calculated first because an independently obtained F_f°, useful for control, is available for it. Barany (1964) calculated the F_f° of mucsovite to be -1330.1 ± 1.3 kcal/mole.

Our solubility data (Keller *et al.*, 1963) for muscovite from Keystone, So. Dak., yield the following:

Dissolved (open H_2O):

	ppm	moles/liter	act.	coef. act.	log act.
K	20.4	.00052	.9727	.000506	-3.294
Na	4.1	.000178	.9729	.000173	-3.761
Al	.40	.0000148	.9730	.0000144	-4.841
Si	6.90	.0002459	1.0	.000246	-3.609
H^+					-8.0
OH^-					-6.0

Equation and Free energies:

$$\begin{array}{lllllll} KAl_2(AlSi_3O_{10})(OH)_2 + & 6H_2O & = & K^+ & + 3AlO_2^- & + 3H_4SiO_4 & + 2H^+ \\ -X & -340.2 & & -67.46 & -602.1 & -938.4 & 0 \end{array}$$

$$\Sigma F^\circ_{\text{products}} = -1608.0$$

$$\Sigma F^\circ_{\text{reactants}} = -X + (-340.2)$$

$$\Delta F_R^\circ = \Sigma F^\circ_{\text{products}} - \Sigma F^\circ_{\text{reactants}}$$

$$aF_f^\circ(\text{muscovite}) = \Sigma F^\circ_{\text{products}} - \Delta F_R^\circ - F_f^\circ(6H_2O)$$

$$\Delta F_R^\circ = -1.364 \log K_{eq}$$

$$aK_{eq} = [K^+][H^+]^2[AlO_2^-]^3[H_4SiO_4]^3$$

$$\log aK_{eq} = \log [K^+] + 3 \log [AlO_2^-] + 3 \log [H_4SiO_4] - 2pH$$

$$\log aK_{eq} = -3.29 + 3(-4.84) + 3(-3.61) - 2(8.0)$$

$$\log aK_{eq} = -44.64$$

$$\Delta aF_R^\circ = (-1.364)(-44.67) = 60.89 \text{ kcal/mole}$$

$$aF_f^\circ \text{ muscovite} = -1608.0 - (60.9) - (-340.2)$$

$$aF_f^\circ \text{ muscovite} = -1328.7 \text{ kcal/mole}$$

The presence of Na^+ has been neglected in the preceding calculation, but by using log (Na+K) in place of log K, the aF_f° for this muscovite becomes −1328.5. Both of these values are very close to −1330.1 kcal/mole, that calculated by Barany (1964). It should be noted that the calculations of both Barany, and in this report, refer to F_f at 25° C. (ours at ambient room temperature), but not at the temperature of formation of the pegmatite from which our muscovite was collected.

It is of passing interest that an aF_f° was run on Beaver Bend illite, a very well characterized micaceous clay (Mankin and Dodd, 1963), by shaking the clay in water for periods up to 18 months, which yielded −1331.3 kcal/mole (Keller *et al.*, in press).

Nepheline. Nepheline, which is notably simpler than muscovite with respect to components of reaction with water, was studied from material collected from Bancroft (Nephton), Ontario.

$$\begin{array}{llllll} NaAlSiO_4 + & 2H_2O & = & Na^+ & + AlO_2^- & + H_4SiO_4 \\ x & -113.4 & & -62.59 & -200.7 & -312.8 \end{array}$$

$$\Sigma F_f^\circ(\text{products}) = -576.1 \text{ kcal/mole}$$

$$\Sigma F_f^\circ \text{ (reactants)} = x + (-113.4)$$

Dissolved (open H_2O):

	ppm	moles/liter	activity	log. act.
Na	85.7	.00373	.00354	−2.450
Al	2.20	.0000816	.0000774	−4.111
Si	14.8	.000527	.000527	−3.278
H^+				−8.0

$$\log aK_{eq} = -9.84$$

$$\Delta aF_R^\circ = 13.43 \text{ kcal}$$

$$aF_f^\circ(\text{nepheline}) = -576.1 - (-113.4) - (+13.43)$$

$$aF_f^\circ(\text{nepheline}) = -476.1 \text{ kcal/mole}$$

A second dissolution experiment was run by bubbling CO_2 at atmospheric pressure into the water before, and during, the grinding of the nepheline. This lowered the pH below that of the solution exposed only to the atmospheric partial pressure of CO_2. Although the CO_2 buffered the solution, CO_2, per se, does not enter into the equation of the nepheline-water reaction; therefore its presence, although it modifies the solubilities of the components very significantly, should not alter the value for the F_f° of nepheline (except for experimental error). The CO_2 rich system yielded the following.

Dissolved (CO_2-charged water):

	ppm	moles/liter	activity	log act.
Na	114.0	.00496	.00467	−2.331
Al	.20	.00000741	.00000698	−5.155
Si	12.40	.0000442	.000442	−3.355
H^+				−6.3

$$\log aK_{eq} = -10.84$$

$$\Delta aF_R^\circ = 14.78$$

$$aF_f^\circ(\text{nepheline}) = -477.5 \text{ kcal/mole}$$

The two values thus determined for nepheline differ by 1.4 kcal, showing that (1) the effect of the CO_2 is a buffer, and (2) suggesting that the products were close to dynamic equilibrium with the reactants. The mean of the 2 runs is approximately −476.8 kcal/mole. No correction was made for the relatively small amount of K^+ present in the solute.

Microcline. Pink, perthitic cleavage microcline from near Bathurst, Ontario, was processed in distilled water open to the atmosphere, and in water charged with CO_2 before and during grinding of the mineral, yielding the following results.

$$\begin{array}{cccccc} KAlSi_3O_8 + & 6H_2O & = & K^+ & + AlO_2^- & + 3H_4SiO_4 \\ x & -340.2 & & -67.47 & -200.7 & -938.4 \end{array}$$

$$\Sigma F_f^\circ \text{ products} = -1206.57 \text{ kcal}$$

$$\Sigma F_f^\circ \text{ reactants} = x + (-340.2)$$

Dissolved (open H_2O):

	ppm	moles/liter	act.	log act.
K	38.8	.000993	.000955	−3.020
Na	17.4	.000757	.000728	−3.138
Al	.86	.0000319	.0000307	−4.513
Si	7.4	.000264	.000264	−3.578
H^+				−8.0

$$aK_{eq} = [K^+][AlO_2^-][H_4SiO_4]^3$$

$$\log aK_{eq} = \log [K^+] + \log [AlO_2^-] + 3 \log [H_4SiO_4]$$

$$\log aK_{eq} = -3.02 + (-4.51) + (3x - 3.58) = -18.27$$

$$\Delta aF_R = +24.92 \text{ kcal}$$

$$aF_f^\circ(\text{microcline}) = -1206.6 - (-340.2) - (24.92) = -891.3 \text{ kcal/mole}$$

If K and Na are taken together:

$$\log [K + Na] = -2.77$$

$$\log aK_{eq} = -18.02$$

$$aF_f^\circ(\text{microcline, K + Na}) = -891.0 \text{ kcal/mole}$$

Dissolved (CO_2-charged water):

	ppm	mol/liter	act.	log act.
K	69.3	.00177	.00169	−2.771
Na	26.9	.00117	.00112	−2.952
Al	1.00	.0000371	.0000354	−4.450
Si	6.20	.00022	.000221	−3.656
H^+				−6.2

$$\log aK_{eq} = -2.77 + (-4.45) + (3\times - 3.66) = -18.20$$

$$aF_R^\circ = +24.82 \text{ kcal}$$

$$aF_f^\circ(\text{microcline}) = -891.2 \text{ kcal/mole}$$

$$\log [K + Na] = -2.55$$

$$aK_{eq} = -17.98$$

$$aF_f^\circ(\text{microcline, K + Na}) = -890.9 \text{ kcal/mole}$$

Very close agreement (0.1 kcal) exists between the aF_f° values determined for microcline dissolved in open water and CO_2-charged water, indicating that equilibrium conditions were probably attained during grinding. The CO_2 present acted as a buffer, as it did in the nepheline experiment.

Enstatite. Enstatite from near Brewster, New York, was dissolved first in water open to the air, and later in CO_2-charged water. Data from open-water dissolution follow.

$$\begin{array}{ccccc} MgSiO_3 + & 3H_2O & = \quad Mg^{2+} & + H_4SiO_4 & + 2(OH^-) \\ x & -170.1 & -108.99 & -312.8 & -75.2 \end{array}$$

$$\Sigma F^\circ_{Products} = -497.0 \text{ kcal}$$

$$\Sigma F^\circ_{Reactants} = x + (-170.1)$$

Dissolved (open water):

	ppm	moles/liter	act.	log act.
Mg	12.0	.000494	.000471	−3.327
Si	16.5	.000588	.000588	−3.230
OH^-				−5.4

$$K_{eq} = [Mg][H_4SiO_4][OH]^2$$

$$\log aK_{eq} = (-3.33) + (-3.23) + (-10.8) = -17.36$$

$$\Delta aF_R^\circ = -1.364 \log aK_{eq} = 23.72 \text{ kcal}$$

$$aF_f^\circ(\text{enstatite}) = -497.0 - (-170.1) - (23.72) = -350.6 \text{ kcal/mole}$$

When CO_2 is charged against atmospheric pressure into the water before, and during, grinding of the mineral, the concentration of HCO_3^- increases and OH^- decreases. After standing in the air for several days after grinding the solution returns, or tends to return, to equilibrium with the partial pressure of CO_2 in the air. The pH is less, HCO_3^- is higher, and more Mg^{2+} ions are dissolved than in the solution never charged with CO_2. To maintain the K_{eq} the activities of Mg^{2+} and/or silicic acid must change in response to substitution of HCO_3^- for OH^-. For this system the aF_f° will be calculated using the same procedure as before.

Dissolved (CO_2-charged water):

	ppm	act.	log act.
Mg	72.0	.00274	−2.562
Si	17.4	.000620	−3.208
OH^-			−7.1
HCO_3^-		.0000316	−4.5

$$\log aK_{eq} = -19.97$$

$$\Delta aF_R^\circ = 27.24 \text{ kcal}$$

$$aF_f^\circ(\text{enstatite}) = -354.14 \text{ kcal/mole}$$

A disparity of 3.5 kcal (354.1 − 350.6) exists between the aF_f° values from open-water and CO_2-charged water determinations of enstatite, which is beyond permissible experimental error. The possibility that reaction of CO_2 with water and Mg^{2+} formed $MgCO_3$ and affected the reaction will be explored. Simultaneously the aF_f° value (−350.6 kcal) of enstatite determined in open water will be tested by using it in the following calculation of enstatite with water and CO_2:

$$\begin{array}{ccccc} MgSiO_3 + & H_2CO_3 + & H_2O & = MgCO_3 + & H_4SiO_4 \\ -350.6 & -149.0 & -56.7 & -246.0 & -312.8 \end{array}$$

Summing both sides of the reaction, yields

$$-558.8 - (-556.3) = -2.5$$

Therefore, $\Delta F_R°$ for the preceding reaction is -2.5 kcal.

This reaction was carried out, as previously stated, by charging in CO_2 and then allowing it to stand for several days in open air, which presumably allowed the solution to return to equilibrium with the normal partial pressure of CO_2 in the atmosphere. Under those conditions carbonic and silicic acids in solution tend to come to equilibrium as follows:

$$aK_{eq} = \frac{[H_4SiO_4]}{[H_2CO_3]}$$

The ΔF accompanying the reaction of enstatite with carbonated water will be calculated and compared with that observed. First, the activity of the H_2CO_3 must be evaluated for this reaction. At the partial pressure of CO_2, about $10^{-3.5}$ atmosphere, the activity of carbonic acid (H_2CO_3) calculated from equilibrium constant of carbonic acid and atmospheric CO_2, $10^{-1.5}$, is $10^{-5.0}$ moles/liter carbonic acid (Garrels, 1960).

Substituting in the expression for the apparent equilibrium constant:

$$aK_{eq} = \frac{10^{-3.21}}{10^{-5}} = 10^{1.79}$$

$$\log aK_{eq} = 1.79$$

$$\Delta aK_R° = -2.44 \text{ kcal}$$

Thus the calculated $\Delta aF_R°$ is within .06 kcal of the value (-2.5 kcal) that was determined from the solubility reaction when the $aF_f°$ reported for enstatite, -350.6 kcal/mole (determined in the solution open to the air), was used in the computation for the $MgCO_3$ reaction. Such agreement lends confidence that the value for enstatite is reasonably good.

Forsterite. Forsterite ($Mg_{1.86}Fe_{.14}SiO_4$) from Jackson County, North Carolina, was processed, and calculated by the same procedure used for enstatite (but omitting Fe which does not enter into, or modify, the solubility of Mg.)

$$\begin{array}{ccccccccc} Mg_2SiO_4 & + & 4H_2O & = & 2Mg^{2+} & + & H_4SiO_4 & + & 4(OH) \\ x & & -226.8 & & -217.98 & & -312.8 & & -150.4 \end{array}$$

$$\Sigma F° \text{ products} = -681.2 \text{ kcal/mole}$$

$$\Sigma F° \text{ reactants} = x + (-226.8)$$

Dissolved (open water)

	ppm	moles/liter	act.	log act.
Mg	12.0	.000494	.000470	−3.328
Si	6.0	.000214	.000214	−3.670
OH_				−5.2

$$K_{eq} = [Mg^{2+}]^2[H_4SiO_4][OH]^4$$

$$\log aK = (2x - 3.33) + (3.67) + (4x - 5.2) = -31.13$$

$$\Delta aF_R^\circ = -1.364 \log k = 42.46 \text{ kcal}$$

$$aF_f^\circ \text{ forsterite} = -681.2 - (42.46) - (-226.8) = -496.9 \text{ kcal/mole}$$

Pulverizing in CO_2-charged water, the solute from olivine yields:
Dissolved (CO_2-charged water)

	ppm	moles/liter	act.	log act.
Mg	150.0	.006172	.005579	−2.253
Si	13.6	.0004847	.00004847	−3.315
OH^-				−7.4
HCO_3^-			.0000158	−4.8

From these solubility data, aF_f° for forsterite is calculated to be −505.4 kcal/mole, which differs by about −8.5 kcal from that calculated when run in water open to the air. As with enstatite the value obtained in the open-water run is tested by comparing the $\Delta a\ F_R^\circ$ of the Mg silicate-carbonate reaction as found by solubility with that calculated from the equilibrium constant.

$$\begin{array}{cccc} Mg_2SiO_4 + & 2H_2CO_3 = & 2MgCO_3 + & H_4SiO_4 \\ -496.9 & -298 & -492 & -312.8 \end{array}$$

$$\Delta F_R^\circ = \Sigma F^\circ_{\text{Products}} - \Sigma F^\circ_{\text{Reactants}}$$

$$\Delta aF_R^\circ = -804.8 - (-794.9) = -9.9 \text{ kcal}$$

The equilibrium constant for the above reaction is:

$$K_{eq} = \frac{[H_4SiO_4]}{[H_2CO_3]^2}, \quad \text{or} \quad \log K_{eq} = \log [H_4SiO_4] - 2 \log [H_2CO_3]$$

$$\log aK = (-3.32) - (-10.0) = 6.68$$

$$\Delta aF_R^\circ = -1.364 \log k = -9.11 \text{ kcal}$$

Agreement between measured ΔaF_R°, −9.9 kcal, and calculated, −9.11 kcal, is fair, indicating that aF_f° for forsterite is not far from −496.9 kcal/mole.

Diopside. Diopside $(Ca_{.45}Mg_{.46}Fe_{.047}Al_{.03})_2(Si_{.92}Al_{.08})O_6$, from near Cascadeville, New York, was pulverized in water open to the air, and in CO_2-charged water. The presence of both Ca and Mg adds complexity to the system.

$$\begin{array}{cccccc} CaMg(SiO_3)_2 + & 6H_2O = & Ca^{2+} + & Mg^{2+} & + 2H_4SiO_4 + & 4(OH)^- \\ x & -340.2 & -132.18 & -108.99 & -625.6 & -150.4 \end{array}$$

$$\Sigma F_f^\circ \text{ products} = -1017.17$$

$$\Sigma F_f^\circ \text{ reactants} = x + (-340.2)$$

$$K_{eq} = [Ca^{2+}][Mg^{2+}][H_4SiO_4]^2[OH]^4$$

Dissolved (water open to air)

	ppm	moles/liter	act.	log act.
Ca	3.7	.0000923	.0000876	−4.057
Mg	1.2	.0000494	.0000469	−4.328
Si	23.0	.000830	.000830	−3.091
OH^-				−5.0

$$\log aK_{eq} = (-4.06) + (-4.33) + (-6.18) + (-20.0) = -34.57$$

$$\Delta aF_R^\circ = 47.15$$

$$aF_f^\circ \text{ diopside} = -1017.17 - (-340.2) - (47.15) = -724.12$$

$$aF_f^\circ \text{ diopside} = -724.1 \text{ kcal/mole}$$

Calculated aF_f° from the CO_2-charged solution diverges considerably from that calculated from the open water solution, but testing the "open-water" value, −724.1 kcal/mole, in the silicic acid-carbonic acid equilibrium yields the following:

$$\begin{array}{cccccc} CaMg(SiO_3)_2 + & 2H_2CO_3 + & 2H_2O & = CaCO_3 & + MgCO_3 & + 2H_4SiO_4 \\ -724.1 & -298.0 & -113.4 & -269.78 & -246.0 & -625.6 \end{array}$$

$$\Delta aF_R^\circ = -5.88 \text{ kcal}$$

$$\text{Calculated from } K_{eq} = \frac{[H_4SiO_4]^2}{[H_2CO_3]^2}$$

$$\Delta aF_R^\circ = -4.47$$

Agreement is fairly close, 1.41 kcal, suggesting that −725 kcal instead of 724.1, as calculated, may be closer to the true aF_f° for diopside. With the possible presence of both Ca and Mg carbonates and bicarbonates, including complexing by them, in the solution, the usefulness of the solution method of calculation F_f° deteriorates. Complexities further increase as Fe, usually divided in oxidation state, comes into minerals such as hornblende, augite, and biotite, on which we have solution data, but which are beyond our ability to handle at this time.

In appraisal of the mineral-solubility approach to calculation of free energies of formation, its simplicity and the need for only ordinary laboratory equipment make it generally useful. On the debit side, there is the possible uncertainty of attainment of equilibrium, as has been pointed out. Other possible difficulties in the method include variable distribution of Al between Al^{3+} and AlO_2^- dependent upon pH, the presence of "amorphous" surface films on mineral particles, non-uniformity or mixed-layering in minerals, rates of reaction of dissolution, polymerization of silica after dissolution, and possible continued pick-up of CO_2 by the solution from the air.

Cognizance of these factors, some of which do not affect other methods of determination of F_f°, does not necessarily invalidate this method, anymore than similar or other weaknesses that affect other methods invalidate them. Indeed, the rate at which values of some earlier determined "standard" $F_f°$'s have been changing (e.g., of silica) raises doubt as to the finality of many of them. We are investigating effects of pH, reaction rates, and polymerization of silica in selected mineral dissolutions. Despite the shortcomings of the dissolution methods, we believe results from it are applicable except possibly when small differences of $F_f°$ separate potentially interacting minerals.

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