Gibbs Free Energies of Formation Calculated from Dissolution Data Using Specific Mineral Analyses. II. Plagioclase Feldspars

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Abstract

Gibbs free energies of formation ($\Delta G°_f$) for plagioclase feldspars, albite, oligoclase, labradorite, bytownite, and anorthite were calculated from the dissolution in aqueous solutions, using (a) the actual mineral formulas derived from the chemical analyses of the specific mineral samples, and (b) the ideal structural formulas of the minerals. Results with $\Delta G°_f$ in kcal/mole were: albite, $Ab_{95}An_1Or_4$, −897.1; albite, $Ab_{99}An_1$, −894.7; oligoclase, $Ab_{75}An_{18}Or_7$, −910.3; oligoclase, $Ab_{80}An_{20}$, −906.8; labradorite, $Ab_{50}An_{46}Or_4$, −930.9; labradorite, $Ab_{52}An_{48}$, −928.5; bytownite, $Ab_{30}An_{67}Or_3$, −948.5; bytownite, $Ab_{31}An_{69}$, −942.7; anorthite, $Ab_{12}An_{86}Or_2$, −959.4, and anorthite, $Ab_{12}An_{88}$, −957.7.

The Gibbs free energy of formation for a high K-plagioclase ($Ab_{44}Or_{56}$) was also calculated to be −896.4 kcal/mole.

Introduction

Supplementing the calculation of Gibbs free energies of formation ($\Delta G°_f$) for primary rock-forming silicate minerals (Huang and Keller, 1972), this paper presents the calculation of $\Delta G°_f$ for a series of plagioclase minerals from aqueous dissolution data.

Laboratory Work

Three grams (3.00 gm) each of freshly fractured albite, oligoclase, labradorite, bytownite, anorthite, and a high-K variety of plagioclase in particle size between 44 μm and 150 μm were equilibrated at room temperature in deionized water for periods up to 24 days. The detailed experimental procedure and analytical results have been published in a paper by Huang and Kiang (1972). The results of the laboratory dissolution show that the dissolution of major cations (Si, Al, Ca, and Na) from the plagioclase minerals increased very rapidly within the first 24 hours, slowed down between the period of one day and six days, and then reached near saturation after 24 days. Although complete equilibrium cannot be established, the cation concentrations at 24 days dissolution may be taken as "apparently" equilibrated concentrations, and the solubilities (K_s) calculated from these concentrations then represent "apparent" solubilities.

Methods of Calculation

The detailed steps and assumptions for the calculation of $\Delta G°_f$ from the laboratory dissolution data were given in a paper by Huang and Keller (1972). These include the following:

(1) *Species in the Equilibrium Solution.* It is possible to calculate, if chemical equilibrium is assumed, the proportion of each dissolved species of a specific element in the system, where certain species are assumed more likely to be present in the system. The equilibrium concentration (Huang and Keller, 1972) of each species in the systems was calculated (1) from the pH of the solution; (2) from the concentration of each cation in the solution in which Si, Al, Fe, Mg, Ca, K, and Na were determined and reported as moles/liter as in an earlier paper (Huang and Kiang, 1972); and (3) using the constants of hydrolysis and dissociation obtained from Sillén and Martell (1964). The validity of the calculation is based on the law of mass action (Butler, 1964). The results of the calculation of each Al, Fe, Mg, Ca species from the dissolution of plagioclase are shown in Table 2.

(2) *Activities.* Using the Debye-Hückel method, ions in the solution were computed on an IBM 360/65 electronic computer.

(3) *Mineral formulas.* The actual mineral for-

mulas, as determined for each plagioclase feldspar from bulk analyses published earlier (Table 1, Huang and Kiang, 1972), were used in calculation of $\Delta G^{\circ}{}_f$. For comparison, ideal structural formulas were also used in calculation of $\Delta G^{\circ}{}_f$.

(4) *Solubility constants (K_s) and Gibbs free energies of formation ($\Delta G^{\circ}{}_f$).* Assuming "apparent" equilibrium in the systems, the solubility constants (K_s) from aqueous dissolution of plagioclase minerals could be calculated from the most probable chemical reactions of the minerals in water. Then, Gibbs free energies of formation for the minerals ($\Delta G^{\circ}{}_f$) can be calculated from the following two relationships: (1) $\Delta G^{\circ}{}_r$ (Gibbs free energies of reaction) $= -1.364 \log K_s$ (Nernst equation), and (2) $\Delta G^{\circ}{}_r = \Sigma \Delta G^{\circ}{}_f$ (products) $- \Sigma \Delta G^{\circ}{}_f$ (reactants), using known Gibbs free energies of formation for other species in equation (2) (Table 1).

Results

(A) $\Delta G^{\circ}{}_f$ based on aqueous solubility data

The analytical data and calculated activities for the dissolution of the plagioclase minerals are listed in Table 2. Table 3 summarizes the reactants and the assumed products of dissolution calculated for both specific and ideal mineral formulas. Points worthy of note are as follows:

TABLE 1. Gibbs Free Energies of Formation Used in Calculation of $\Delta G^{\circ}{}_f$

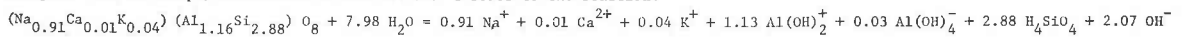| Species	G°_f kcal/mole	Source
H_4SiO_4	-312.8	Reesman and Keller (1965)
Al^{3+}	-115.0	Rossini et al (1952)
$Al(OH)^{2+}$	-164.9	Raupach (1963)
$Al(OH)_2^+$	-216.1	Reesman et al (1969)
$Al(OH)_4^-$	-311.3	Reesman et al (1952)
Fe^{2+}	-20.30	Rossini et al (1952)
$Fe(OH)^+$	-52.58	Huang and Keller (1972)
$Fe(OH)^{2+}$	-55.91	Rossini et al (1952)
$Fe(OH)_2^+$	-106.2	Rossini et al (1952)
Mg^{2+}	-108.76	Langmuir (1968)
$Mg(OH)^+$	-149.76	Berner (1971)
Ca^{2+}	-132.35	Langmuir (1968)
Na^+	-62.59	Rossini et al (1952)
K^+	-67.47	Rossini et al (1952)
OH^-	-37.63	Reesman and Keller (1965)
H_2O	-56.72	Wicks and Block (1963)

TABLE 2. Analytical Data and Activities of Dissolved Species in the Dissolution of Plagioclase Minerals

Species	Moles/liter	Activity	Log act.
(I) ALBITE pH = 5.81; ionic strength = 1.25×10^{-4}			
Na^+	0.231×10^{-4}	0.228×10^{-4}	-4.64
K^+	0.332×10^{-6}	0.328×10^{-6}	-6.48
Ca^{2+}	0.548×10^{-4}	0.521×10^{-4}	-4.28
$Al(OH)_2^+$	0.518×10^{-5}	0.511×10^{-5}	-5.29
$Al(OH)_4^-$	0.121×10^{-6}	0.119×10^{-6}	-6.92
H_4SiO_4	0.166×10^{-4}	0.166×10^{-4}	-4.78
OH^-		$10^{-8.19}$	-8.19
(II) OLIGOCLASE pH = 5.83; ionic strength = 1.73×10^{-4}			
Na^+	0.199×10^{-4}	0.196×10^{-4}	-4.71
K^+	0.703×10^{-5}	0.693×10^{-5}	-5.16
Ca^{2+}	0.758×10^{-4}	0.714×10^{-4}	-4.15
$Al(OH)_2^+$	0.385×10^{-5}	0.379×10^{-5}	-5.42
$Al(OH)_4^-$	0.126×10^{-6}	0.124×10^{-6}	-6.91
H_4SiO_4	0.436×10^{-4}	0.436×10^{-4}	-4.36
OH^-		$10^{-8.17}$	-8.17
(III) LABRADORITE pH = 6.05; ionic strength = 2.86×10^{-5}			
Na^+	0.892×10^{-5}	0.886×10^{-5}	-5.05
K^+	0.271×10^{-5}	0.269×10^{-5}	-5.57
Ca^{2+}	0.103×10^{-4}	0.101×10^{-4}	-4.99
$Al(OH)_2^+$	0.116×10^{-5}	0.115×10^{-5}	-5.94
$Al(OH)_4^-$	0.208×10^{-6}	0.207×10^{-6}	-6.68
H_4SiO_4	0.229×10^{-4}	0.229×10^{-4}	-4.64
OH^-		$10^{-7.95}$	-7.95
(IV) BYTOWNITE pH = 5.95; ionic strength = 5.74×10^{-5}			
Na^+	0.163×10^{-4}	0.161×10^{-4}	-4.79
K^+	0.332×10^{-6}	0.330×10^{-6}	-6.48
Ca^{2+}	0.169×10^{-4}	0.163×10^{-4}	-4.79
$Al(OH)_2^+$	0.168×10^{-5}	0.167×10^{-5}	-5.78
$Al(OH)_4^-$	0.163×10^{-6}	0.162×10^{-6}	-6.79
H_4SiO_4	0.393×10^{-4}	0.393×10^{-4}	-4.41
OH^-		$10^{-8.05}$	-8.05
(V) ANORTHITE pH = 5.91; ionic strength = 3.71×10^{-5}			
Na^+	0.196×10^{-5}	0.194×10^{-5}	-5.71
K^+	0.102×10^{-6}	0.102×10^{-6}	-6.99
Ca^{2+}	0.116×10^{-4}	0.162×10^{-4}	-4.79
$Al(OH)_2^+$	0.885×10^{-6}	0.887×10^{-6}	-6.06
$Al(OH)_4^-$	0.149×10^{-6}	0.148×10^{-6}	-6.83
H_4SiO_4	0.280×10^{-4}	0.280×10^{-4}	-4.55
OH^-		$10^{-8.09}$	-8.09
(VI) HIGH-K PLAGIOCLASE pH = 5.97; ionic strength = 3.05×10^{-5}			
Na^+	0.124×10^{-4}	0.123×10^{-4}	-4.91
K^+	0.187×10^{-4}	0.186×10^{-4}	-4.73
Ca^{2+}	0.474×10^{-5}	0.462×10^{-5}	-5.34
$Al(OH)_2^+$	0.229×10^{-5}	0.214×10^{-5}	-5.67
$Al(OH)_4^-$	0.171×10^{-6}	0.170×10^{-6}	-6.77
H_4SiO_4	0.180×10^{-4}	0.180×10^{-4}	-4.74
OH^-		$10^{-8.03}$	-8.03

TABLE 3. The Subscripts* (and/or Coefficients) and Calculated $\Delta G°_f$ and log K_s Values for Laboratory Dissolutions of Several Plagioclase Minerals

	Reactants Mineral Formula							⇌	Products Assumed for Dissolution							$\Delta G°_f$ (kcal/mole)	log K_s**
	(Na	Ca	K)	(Al	Si)	O	+H₂O		Na⁺ +	Ca²⁺ +	K⁺	+ Al(OH)₂⁺	+ Al(OH)₄⁻	+ H₄SiO₄	+ OH⁻		
Albite																	
Specific, Ab₉₅An₁Or₄	0.91	0.01	0.04	1.16	2.88	8	7.98	⇌	0.91	0.01	0.04	1.13	0.03	2.88	2.07	−897.1	−41.43
Ideal, Ab₉₉An₁	0.99	0.01	--	1.01	2.99	8	8	⇌	0.99	0.01	--	0.98	0.03	2.99	1.96	−894.7	−40.36
Oligoclase																	
Specific, Ab₇₅An₁₈Or₇	0.70	0.17	0.06	1.44	2.64	8	7.99	⇌	0.70	0.17	0.06	1.39	0.05	2.64	2.44	−910.3	−43.64
Ideal, Ab₈₀An₂₀	0.80	0.20	--	1.20	2.80	8	8	⇌	0.80	0.20	--	1.15	0.05	2.80	2.30	−906.8	−42.18
Labradorite																	
Specific, Ab₅₀An₄₆Or₄	0.47	0.43	0.04	1.74	2.34	8	7.97	⇌	0.47	0.43	0.04	1.48	0.26	2.34	2.59	−930.9	−46.72
Ideal, Ab₅₂An₄₈	0.52	0.48	--	1.48	2.52	8	8	⇌	0.52	0.48	--	1.26	0.22	2.52	2.52	−928.5	−45.70
Bytownite																	
Specific, Ab₃₀An₆₇Or₃	0.31	0.70	0.03	1.87	2.15	8	7.97	⇌	0.31	0.70	0.03	1.70	0.17	2.15	3.27	−948.5	−51.80
Ideal, Ab₃₁An₆₉	0.31	0.69	--	1.69	2.31	8	8	⇌	0.31	0.69	--	1.54	0.15	2.31	3.08	−942.7	−49.69
Anorthite																	
Specific, Ab₁₂An₈₆Or₂	0.12	0.85	0.02	2.07	1.97	8	7.96	⇌	0.12	0.85	0.02	1.76	0.31	1.97	3.29	−959.4	−53.27
Ideal, Ab₁₂An₈₈	0.12	0.88	--	1.88	2.12	8	8	⇌	0.12	0.88	--	1.60	0.28	2.12	3.20	−957.7	−52.06
High-K plagioclase*																	
Specific, Ab₄₄Or₅₆	0.42	--	0.53	1.11	2.92	8	7.98	⇌	0.42	--	0.53	1.03	0.08	2.92	1.90	−896.4	−40.05
Ideal, Ab₄₄Or₅₆	0.44	--	0.56	1	3	8	8	⇌	0.44	--	0.56	0.93	0.07	3	1.86	−896.9	−39.71

* Example: The subscript/coefficient numbers of line 1 refer to the reaction:

$(Na_{0.91}Ca_{0.01}K_{0.04})(Al_{1.16}Si_{2.88})O_8 + 7.98 H_2O = 0.91 Na^+ + 0.01 Ca^{2+} + 0.04 K^+ + 1.13 Al(OH)_2^+ + 0.03 Al(OH)_4^- + 2.88 H_4SiO_4 + 2.07 OH^-$

** Example of calculation: for albite $(Ab_{95}An_1Or_4)$ $K_s = [Na^+]^{0.91}[Ca^{2+}]^{0.01}[K^+]^{0.04}[Al(OH)_2^+]^{1.13}[Al(OH)_4^-]^{0.03}[H_4SiO_4]^{2.88}[OH^-]^{2.07}$

Then, log $K_s = -41.43$ $\Delta G°_f$ (products) $- \Sigma \Delta G°_f$ (reactants) $= -840.63 - \Delta G°_f$ (albite)

$\Delta G°_r = -1.364$ log K_s $\Delta G°_f$ (albite, $Ab_{95}An_1Or_4$) $= -840.63 + 1.364$ log $K_s = -897.1$ kcal/mole

*** A specimen purchased as and labelled "andesine" proved to be a high-K variety of plagioclase by bulk chemical analyses. Laboratory dissolution data (Huang and Keller, 1972) are in accord with this composition.

(1) The difference in $\Delta G°_f$ for albite by the two calculations (Table 3) is 2.4 kcal/mole. The $\Delta G°_f$ (−894.7 kcal/mole) for albite (Ab₉₉An₁) in terms of the ideal structural formula, however, is smaller than the value obtained by Waldbaum (1966) for low albite (Ab₁₀₀) ($\Delta G°_f = -884.0$ kcal/mole). The presence of one mole percent of $CaAl_2Si_2O_8$ in our albite sample could significantly affect the $\Delta G°_f$.

(2) Our data on $\Delta G°_f$ for labradorite in terms of the specific mineral formula or the ideal structural formula (Table 3) lie just between the values for oligoclase and the labradorite (Ab₄₀An₅₉Or₁ = −932.4 kcal/mole, or Ab₄₀An₆₀ = −932.1 kcal/mole) reported by Huang and Keller (1972). This adds confidence to the validity of the dissolution method used for the calculation of $\Delta G°_f$.

(3) The difference in $\Delta G°_f$ for the two bytownite calculations is 5.8 kcal/mole, which might become significant in determining stabilities of minerals in some geologic systems.

(4) Our data on $\Delta G°_f$ for anorthite is lower than the reported data of −955.6 kcal/mole for anorthite (An₁₀₀) by Barany (1962).

(5) The value for high-K plagioclase (−896.4 or −896.9 kcal/mole) lies just between the value for albite (Ab₉₅An₁Or₄, or −887.3 kcal/mole, this study) and that for microcline (Ab₂₅Or₆₈An₇, −887.3 kcal/mole, or Or₁₀₀, ideal, −892.6 kcal/mole, Huang and Keller, 1972). Our $\Delta G°_f$ for this "high-K plagioglase" specimen indicates that the mineral is not andesine; if the sample were andesine, its $\Delta G°_f$ should lie between −910.3 for oligoclase and −930.9 kcal/mole for labradorite.

(B) $\Delta G°_f$ based on equilibrium with secondary phase

The results of analyses in Table 2 show that the concentration of Al in the solution is less than that

TABLE 4. Summary of $\Delta G°_f$ Calculated on the Basis of Equilibrium with Secondary Phase

	Reactants Mineral Formula								Products Assumed for Dissolution								$\Delta G°_f$** (kcal/mole)
	(Na	Ca	K)	(Al	Si)	O	+ H$_2$O	$\rightleftharpoons$	Na$^+$ + Ca^{2+} + K$^+$			+ Al(OH)$_2^+$	+ Al(OH)$_4^-$	+ H$_4$SiO$_4$	+ OH$^-$	+ Al(OH)$_3$	
Albite																	
Specific, Ab$_{95}$An$_1$Or$_4$	0.91	0.01	0.04	1.16	2.88	8	7.98	$\rightleftharpoons$	0.91	0.01	0.04	0.89	0.02	2.88	1.84	0.25	−897.0*
Ideal, Ab$_{99}$An$_1$	0.99	0.01	--	1.01	2.99	8	8	$\rightleftharpoons$	0.99	0.01	--	0.91	0.03	2.99	1.89	0.07	−894.7
Oligoclase																	
Specific, Ab$_{75}$An$_{18}$Or$_7$	0.70	0.17	0.06	1.44	2.64	8	7.99	$\rightleftharpoons$	0.70	0.17	0.06	0.23	0.01	2.64	1.32	1.20	−909.1
Ideal, Ab$_{80}$An$_{20}$	0.80	0.20	--	1.20	2.80	8	8	$\rightleftharpoons$	0.80	0.20	--	0.24	0.01	2.80	1.43	0.95	−905.9
Labradorite																	
Specific, Ab$_{50}$An$_{46}$Or$_4$	0.47	0.43	0.04	1.74	2.34	8	7.97	$\rightleftharpoons$	0.47	0.43	0.04	0.12	0.02	2.34	1.47	1.60	−928.9
Ideal, Ab$_{52}$An$_{48}$	0.52	0.48	--	1.48	2.52	8	8	$\rightleftharpoons$	0.52	0.48	--	0.13	0.02	2.52	1.59	1.33	−926.8
Bytownite																	
Specific, Ab$_{30}$An$_{67}$Or$_3$	0.31	0.70	0.03	1.87	2.15	8	7.97	$\rightleftharpoons$	0.31	0.70	0.03	0.09	0.01	2.15	1.82	1.77	−946.4
Ideal, Ab$_{31}$An$_{69}$	0.31	0.69	--	1.69	2.31	8	8	$\rightleftharpoons$	0.31	0.69	--	0.10	0.01	2.31	1.78	1.58	−940.8
Anorthite																	
Specific, Ab$_{12}$An$_{86}$Or$_2$	0.12	0.85	0.02	2.07	1.97	8	7.96	$\rightleftharpoons$	0.12	0.85	0.02	0.06	0.01	1.97	1.89	2.00	−956.2
Ideal, Ab$_{12}$An$_{88}$	0.12	0.88	--	1.88	2.12	8	8	$\rightleftharpoons$	0.12	0.88	--	0.07	0.01	2.12	1.94	1.80	−956.6
High-K plagioclase																	
Specific, Ab$_{44}$Or$_{56}$	0.42	--	0.53	1.11	2.92	8	7.98	$\rightleftharpoons$	0.42	--	0.53	0.34	0.03	2.92	1.26	0.74	−895.6
Ideal, Ab$_{44}$Or$_{56}$	0.44	--	0.56	1	3	8	8	$\rightleftharpoons$	0.44	--	0.56	0.35	0.03	3	1.32	0.62	−896.2

*Example of calculation: for albite (Ab$_{95}$An$_1$Or$_4$) K$_s$ = [Na$^+$]$^{0.91}$ [Ca^{2+}]$^{0.01}$ [K$^+$]$^{0.04}$ [Al(OH)$_2^+$]$^{0.89}$ [Al(OH)$_4^-$]$^{0.02}$ [H$_4$SiO$_4$]$^{2.88}$ [OH$^-$]$^{1.84}$

Then, log K$_s$ = −38.21 $\Delta G°_f$ (products) − $\Sigma\Delta G°_f$ (reactants) = −844.84 − $\Delta G°_f$ (albite)

$\Delta G°_r$ = −1.364 log K$_s$ $\Delta G°_f$ (albite, Ab$_{95}$An$_1$Or$_4$) = −844.84 + 1.364 log K$_s$ = −897.0 kcal/mole.

**$\Delta G°_f$ calculated on the basis of equilibrium with secondary amorphous aluminum hydroxide ($\Delta G°_f$ = −271.3 kcal/mole).

TABLE 5. Comparison of $\Delta G°_f$ Obtained from Different Calculations

	$\Delta G°_f$ based on aqueous solubility data	$\Delta G°_f$ based on equilibrium with secondary phase*			
		A	B	C	D
Albite					
Specific, Ab$_{95}$An$_1$Or$_4$	−897.1	−897.0	−897.2	−897.6	−897.9
Ideal, Ab$_{99}$An$_1$	−894.7	−894.7	−894.7	−894.8	−894.9
Oligoclase					
Specific, Ab$_{75}$An$_{18}$Or$_6$	−910.3	−909.1	−910.3	−912.2	−913.9
Ideal, Ab$_{80}$An$_{20}$	−906.8	−905.9	−906.8	−908.3	−909.7
Labradorite					
Specific, Ab$_{50}$An$_{46}$Or$_4$	−930.9	−928.9	−930.5	−933.0	−935.3
Ideal, Ab$_{52}$An$_{48}$	−928.5	−926.8	−928.2	−930.3	−932.1
Bytownite					
Specific, Ab$_{30}$An$_{67}$Or$_3$	−948.5	−946.4	−948.1	−951.0	−953.4
Ideal, Ab$_{31}$An$_{69}$	−942.7	−940.8	−942.3	−944.9	−947.1
Anorthite					
Specific, Ab$_{12}$An$_{86}$Or$_6$	−959.4	−956.2	−958.2	−961.4	−964.2
Ideal, Ab$_{12}$An$_{88}$	−957.7	−956.6	−958.4	−961.3	−963.8
High-K plagioclase					
Specific, Ab$_{44}$Or$_{56}$	−896.4	−895.6	−896.4	−897.5	−898.6
Ideal, Ab$_{44}$Or$_{56}$	−896.9	−896.2	−896.8	−897.8	−898.7

* A: equilibrium with amorphous Al(OH)$_3$
  B: equilibrium with microcrystalline gibbsite
  C: equilibrium with gibbsite ($\Delta G°_f$ =−273.9 kcal/mole)
  D: equilibrium with gibbsite ($\Delta G°_f$ =−275.3 kcal/mole)

a = −897.1; b = −910.3; c = −930.9; d = −932.4
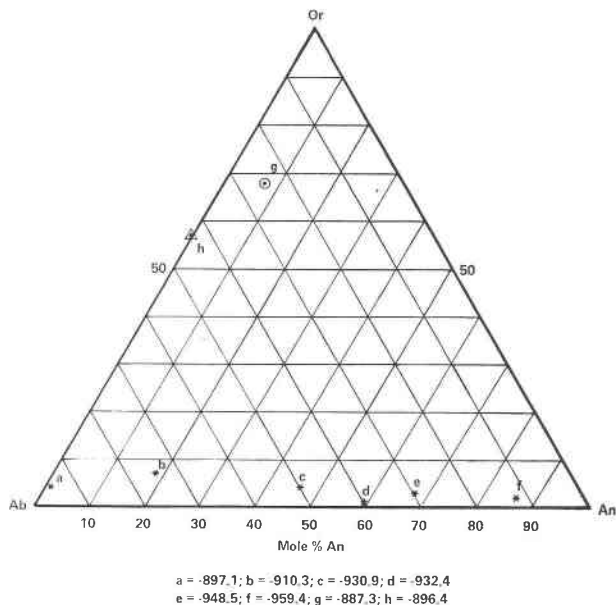e = −948.5; f = −959.4; g = −887.3; h = −896.4

FIG. 1. Triangular diagram showing the $\Delta G°_f$ (kcal/mole) for the plagioclases and K-feldspars. The value, −887.3 kcal/mole, for microcline (g) is obtained from Huang and Keller (1972).
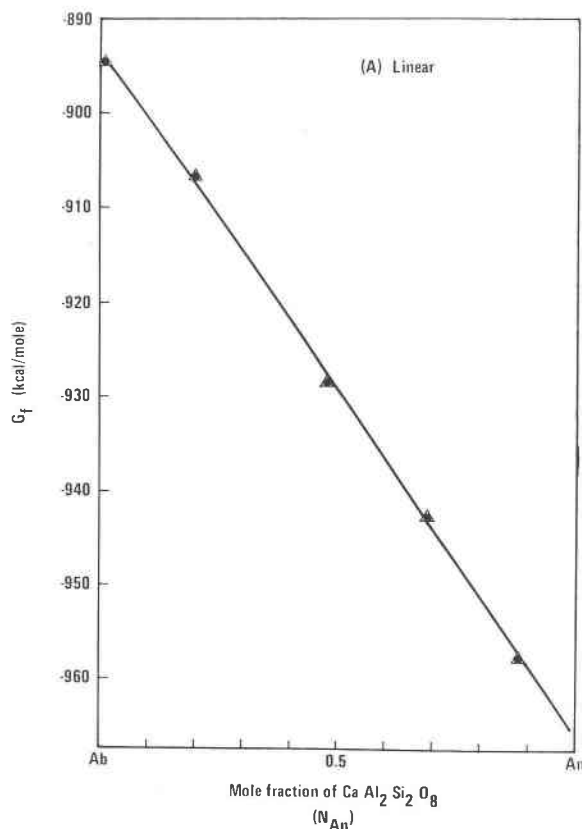
FIG. 2a. The best linear curve for five experimentally determined ΔG°_f as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The linear equation is $\Delta G^\circ_f = -893.24 - 0.726\ N_{An}$.

Discussion and Conclusions

1) In Figure 1 are plotted the Gibbs free energies of formation for plagioclase minerals of specific mineral formulas (data taken from Table 3) in terms of Ab (albite), An (anorthite), and Or (microcline). There is a consistent decrease of ΔG°_f from Na-rich (albite) to Ca-rich (anorthite) plagioclase minerals. Specific values in the trend are subject to solid-solution and other compositional effects.

2) The Gibbs free energies of formation (ΔG°_f) of ideal mineral formulas (data taken from Table 3) are also plotted against mole fraction of $CaAl_2Si_2O_8$ (N_{An}) in linear, quadratic, and cubic equations in Figures 2 (a), (b), and (c) respectively. Statistical analyses of polynomial regression of ΔG°_f, Table 6, shows that at the 1 percent level, the linear or quadratic relationship between ΔG°_f and N_{An} is highly significant. The cubic relationship, however, is not significant at the 1 percent level, but is significant at the 5 percent level.

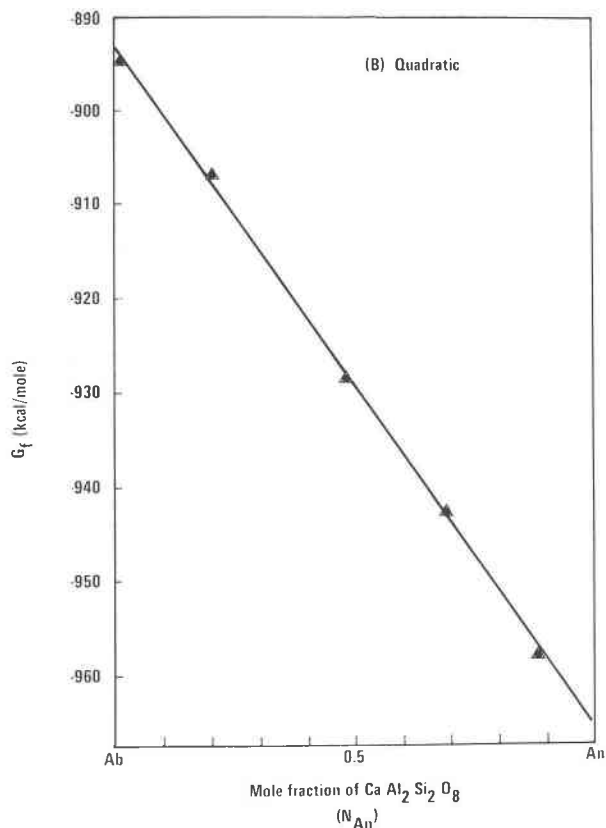3) The Gibbs free energy of formation for a

of Si with respect to its mineral formula, suggesting that secondary Al-phase could be formed during the dissolution of plagioclase feldspar. Thus, secondary phase, such as amorphous aluminum hydroxide ($\Delta G^\circ_f = -271.3$ kcal/mole, Feitknecht and Schindler, 1963), microcrystalline gibbsite ($\Delta G^\circ_f = -272.3$ kcal/mole, Hem and Roberson, 1967), or gibbsite ($\Delta G^\circ_f = -273.9$ kcal/mole, Latimer, 1952; $\Delta G^\circ_f = -275.9$ kcal/mole, Parks, 1972), may be assumed in the equilibrium equation from which ΔG°_f for plagioclase is calculated. The results of ΔG°_f from such calculations are shown in Table 4.

As shown in Table 5, ΔG°_f calculated on the basis of equilibrium with secondary phase (amorphous $Al(OH)_3$, microcrystalline gibbsite, or gibbsite) are somewhat different from ΔG°_f calculated from aqueous solubility data.

FIG. 2b. The best quadratic curve for five experimentally determined ΔG°_f as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The quadratic equation is $\Delta G^\circ_f = -893.70 - 0.683\ N_{An} - 0.00048\ (N_{An})^2$.
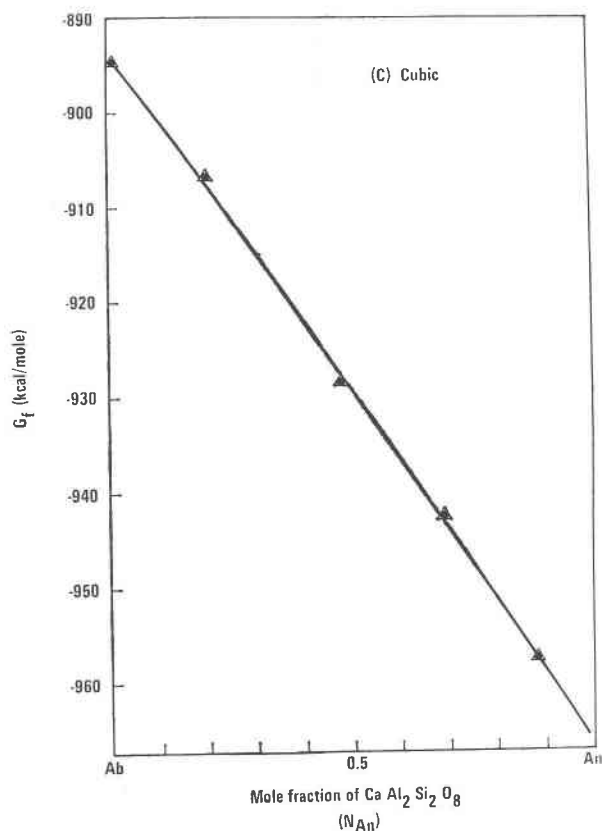
Fig. 2c. The best cubic curve for five experimentally determined $\Delta G°_f$ as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The cubic equation is $\Delta G°_f = -893.88 - 0.640\ N_{An} - 0.00179\ (N_{An})^2 + 0.00001\ (N_{An})^3$.

plagioclase mineral of specific mineral formula is always a smaller negative quantity of $\Delta G°_f$ than for that of an ideal structural formula, as shown in Table 7.

4) The values of $\Delta G°_f$ calculated from dissolution data of specific mineral samples are subject to *uncertainties* and possible sources of error in (a) bulk chemical analysis of the mineral sample from which the specific mineral formula is calculated; (b) the solution analysis; (c) the $\Delta G°_f$ of ions used in the calculation; (d) the computed specific mineral formula used in calculation of $\Delta G°_f$; and (e) the establishment of complete equilibrium in the laboratory dissolution of minerals (Huang and Keller, 1972). The facts that our $\Delta G°_f$ calculated from dissolution data lie between the two end-membered values of albite and anorthite, and that there is a consistent decrease in $\Delta G°_f$ from Na-rich to Ca-rich plagioclase, suggest that the possible errors tend to compensate one another, and add confidence to the validity of our calculation.

TABLE 6. Polynomial Regression Analysis of Gibbs Free Energies of Formation ($\Delta G°_f$) for Plagioclase Feldspars

	Analysis of Variance		
	Degree of freedom	Sum of squares	Mean square
The best linear equation			
$\Delta G°_f = -893.24 - 0.726\ N_{An}$			
Regression	1	2632.27	2632.27
Residual	3	6.04	2.01
F = 1305.67 (1,3)			
$F_{1\%}$ (1,3) = 34.12			
$F_{5\%}$ (1,3) = 10.13			
The best quadratic equation			
$\Delta G°_f = -893.70 - 0.683\ N_{An} - 0.00048\ (N_{An})^2$			
Regression	2	2636.64	1318.32
Residual	2	1.67	0.83
F = 1570.85 (2,2)			
$F_{1\%}$ (2,2) = 99.00			
$F_{5\%}$ (2,2) = 19.00			
The best cubic equation			
$\Delta G°_f = -893.88 - 0.640\ N_{An} - 0.00179\ (N_{An})^2 + 0.00001\ (N_{An})^3$			
Regression	3	2636.79	878.93
Residual	1	1.53	1.53
F = 572.04 (3.1)			
$F_{1\%}$ (3,1) = 5403			
$F_{5\%}$ (3,1) = 216			

TABLE 7. Comparison of Gibbs Free Energies of Formation for Plagioclase Feldspars (kcal/mole)

Mineral*	Experimental $\Delta G°_f$	Others
Albite		
a ($Ab_{95}An_1Or_4$)	-897.1	-884.0 (Ab_{100})
b ($An_{99}An_1$)	-894.7	(Waldbaum, 1966)
Oligoclase		
a ($Ab_{75}An_{18}Or_7$)	-910.3	
b ($Ab_{80}An_{20}$)	-906.8	
Labradorite		
a ($ab_{50}An_{46}Or_4$)	-930.9	-932.4 ($Ab_{40}An_{59}Or_1$)**
b ($Ab_{52}An_{48}$)	-928.5	-931.1 ($Ab_{40}An_{60}$)**
Bytownite		
a ($Ab_{30}An_{67}Or_3$)	-948.5	
b ($Ab_{31}An_{69}$)	-942.7	
Anorthite		
a ($Ab_{12}An_{86}Or_2$)	-959.4	-955.6 (An_{100})
b ($Ab_{12}An_{88}$)	-957.7	(Barany, 1962)
High-K plagioclase		
a ($Ab_{44}Or_{56}$)	-896.4	
b ($Ab_{44}Or_{56}$)	-896.9	

* a: Specific mineral formula, b: Ideal structural formula
** Huang and Keller (1972)

Acknowledgments

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