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Estimating the free energy of formation of silicate minerals at high temperatures from the sum of polyhedral contributions

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ABSTRACT

The technique that we developed to estimate ΔG_f^0 of silicate minerals by summing the contribution of polyhedral components at 298 K (Chermak and Rimstidt, 1989) can be extended to predict the free energy of formation of silicate minerals at higher temperatures. This approach is particularly useful for clays and zeolites, which are geologically abundant and geochemically reactive but have few data for their ΔG_f^0 at temperatures above 25 °C. Multiple linear regression (MLR) was used to find the contribution of ${}^{[4]}Al_2O_3$-${}^{[6]}Al_2O_3$-${}^{[6]}Al(OH)_3$-${}^{[4]}SiO_2$-${}^{[6]}MgO$-${}^{[6]}Mg(OH)_2$-${}^{[6]}CaO$-${}^{[8-z]}CaO$-${}^{[6-8]}Na_2O$-${}^{[8-12]}K_2O$-${}^{[6]}FeO$-${}^{[6]}Fe(OH)_2$-${}^{[6]}Fe_2O_3$ components to the total ΔG_f^0 and ΔH_f^0 at 298 K for a selected group of silicate minerals (Chermak and Rimstidt, 1989). The g_i coefficients from this model can be extrapolated to higher temperatures using the equation

$$g_{i,T} = h_{i,298} - T\left(\frac{h_{i,298} - g_{i,298}}{298}\right),$$

where g_i and h_i are the respective molar free energy and enthalpy contribution of one mole of each oxide or hydroxide component at 298 K. The g_i of H_2O was found to vary depending upon the cation with which the H_2O was associated. Therefore, g_{H_2O} was determined by two linear regressions: one for Na^+ and the other for Ca^{2+}. Experimentally measured ΔG_f^0 vs. predicted ΔG_f^0 for 21 minerals used in the model have associated differences of 0.19%, 0.20%, and 0.22% at 400, 500, and 600 K, respectively. Experimentally measured ΔG_f^0 vs. predicted ΔG_f^0 for four, three, and two minerals not used in the model have associated differences of 0.36%, 0.34%, and 0.13% at 400, 500, and 600 K, respectively.

INTRODUCTION

Several techniques exist for estimating the free energy of formation of silicate minerals at 298 K (see the discussion in Chermak and Rimstidt, 1989), but there are few techniques for estimating ΔG_f^0 of silicate minerals at higher temperatures (Helgeson et al., 1979; Helgeson et al., 1981). This paper describes a way to determine the contribution of oxide and hydroxide components to the ΔG_f^0 of silicate minerals at higher temperatures; these contributions can then be used to estimate the ΔG_f^0 of other minerals for which there are currently no data. Such estimates can be used to model silicate mineral equilibria in geologic processes such as diagenesis, hydrothermal alteration, and low-grade metamorphism.

The technique presented here is based on the observation that silicate minerals act as a combination of polyhedral units (Hazen, 1985, 1988). Chermak and Rimstidt (1989) showed that the ΔG_f^0 and the ΔH_f^0 of selected silicate minerals could be estimated by summing the contributions of their individual oxide and hydroxide polyhedral building blocks. In this paper we show how the molar free energy and enthalpy contributions of individual polyhedral components at 298 K ($g_{i,298}$ and $h_{i,298}$) determined for ${}^{[4]}Al_2O_3$-${}^{[6]}Al_2O_3$-${}^{[6]}Al(OH)_3$-${}^{[4]}SiO_2$-${}^{[6]}MgO$-${}^{[6]}Mg(OH)_2$-${}^{[6]}CaO$-${}^{[8-z]}CaO$-${}^{[6-8]}Na_2O$-${}^{[8-12]}K_2O$-${}^{[6]}FeO$-${}^{[6]}Fe(OH)_2$-${}^{[6]}Fe_2O_3$[1] polyhedra can be used to estimate the ΔG_f^0 of silicate minerals containing these components at higher temperatures.

METHODS

A multiple linear regression (MLR) technique was used to estimate the contribution (g_i and h_i) of ${}^{[4]}Al_2O_3$-${}^{[6]}Al_2O_3$-${}^{[6]}Al(OH)_3$-${}^{[4]}SiO_2$-${}^{[6]}MgO$-${}^{[6]}Mg(OH)_2$-${}^{[6]}CaO$-${}^{[8-z]}CaO$-${}^{[6-8]}Na_2O$-${}^{[8-12]}K_2O$-${}^{[6]}FeO$-${}^{[6]}Fe(OH)_2$-${}^{[6]}Fe_2O_3$ components to the total ΔG_f^0 and ΔH_f^0 of a selected group of silicate minerals (Chermak and Rimstidt, 1989). The g_i and h_i values from this regression model are used to estimate the ΔG_f^0 and ΔH_f^0 of other silicate minerals from a weighted sum of the contribution of each oxide and hydroxide component: $\Delta G_f^0 = \Sigma\, n_i g_i$, and $\Delta H_f^0 = \Sigma\, n_i h_i$, where n_i is the number of moles of the oxide or hydroxide per formula unit and g_i and h_i are the respective molar free en-

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[1] The notation ${}^{[8-z]}CaO$ refers to Ca with an unknown coordination number, as in zeolites.

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ergy and molar enthalpy contributions of each oxide or hydroxide component.

At 298 K, experimentally measured ΔG_f^0 and ΔH_f^0 vs. predicted ΔG_f^0 and ΔH_f^0 for the minerals used in the model have associated average residuals of 0.26% and 0.24%, respectively. For minerals not used in the model for which there are experimentally determined calorimetric data, the average difference between measured and predicted values of ΔG_f^0 for 18 minerals is 0.25%. That difference for ΔH_f^0 for 20 minerals is 0.22%.

The basis for this estimation model is the development of a function to extrapolate the g_i values to higher temperatures. Assuming that the change in $\Delta C_{P,r}$ (the heat capacity of reaction) from 298 K to high temperature is equal to zero allows us to create a temperature function, $g_{i,T}$, for each polyhedral component using the relation G = H − TS. The $g_{i,298}$ and $h_{i,298}$ values for oxide and hydroxide polyhedra used in this relation are from Chermak and Rimstidt (1989), and the relationship of these variables at 298 K is

$$g_{i,298} = h_{i,298} - 298 s_{i,298} \tag{1}$$

where $g_{i,298}$, $h_{i,298}$, and $s_{i,298}$ are the respective molar free energy, enthalpy, and entropy of formation from the elements of one mole of the polyhedral component at 298 K and one bar. Equation 1 can be rearranged to

$$s_{i,298} = \left(\frac{h_{i,298} - g_{i,298}}{298}\right). \tag{2}$$

Integrating the relationship $(\partial \Delta G/\partial T)_P = -\Delta S$ (see for example, Equation 4-13 in Nordstrom and Munoz, 1985) gives

$$g_{i,T} - g_{i,298} = -s_{i,298}\,(T - 298). \tag{3}$$

Note that this assumes that $\partial \Delta C_{P,r}/\partial T = 0$ and P is constant. Substituting Equation 2 into Equation 3 gives

$$g_{i,T} - g_{i,298} = -T\left(\frac{h_{i,298} - g_{i,298}}{298}\right) + 298\left(\frac{h_{i,298} - g_{i,298}}{298}\right), \tag{4}$$

which can be simplified to find $g_{i,T}$

$$g_{i,T} = h_{i,298} - T\left(\frac{h_{i,298} - g_{i,298}}{298}\right). \tag{5}$$

This is a linear function with an intercept of $g_i = h_i$ at 0 K and a slope of $[(h_{i,298} - g_{i,298})/298]$.

In addition, it was realized during the course of this study that the g_{H_2O} values published in Chermak and Rimstidt (1989) could be improved by accounting for the cation with which the H_2O is associated. Whereas $g_{H_2O,298}$ in Chermak and Rimstidt (1989) is for H_2O associated with either Na^+ or Ca^{2+}, more accurate estimates of ΔG_f^0 of hydrous phases were found when H_2O associated with Na^+ and Ca^{2+} were regressed separately. MLR was used to calculate the values for $g_{H_2O,298}$ in association with Na^+ and Ca^{2+}. The same 29 minerals used in Chermak and Rimstidt (1989) were broken into their polyhedral components, and MLR was used to determine that $g_{H_2O,298} = -230.82$ kJ mol^{-1} for H_2O associated with Na^+ and that $g_{H_2O,298} = -240.57$ kJ mol^{-1} for H_2O associated with Ca^{2+}. The g_i values of the other components did not change significantly in these new MLR.

TABLE 1. Values of $g_{i,T}$ (kJ mol^{-1}) for individual polyhedral components

Polyhedral component	Temperature function $g_{i,T} = h_{i,298} - T\left(\frac{h_{i,298} - g_{i,298}}{298}\right)$
$^{[4]}Al_2O_3$	$g_i(T) = -1716.2 + 0.2848T$
$^{[6]}Al_2O_3$	$g_i(T) = -1690.2 + 0.3209T$
$^{[6]}Al(OH)_3$	$g_i(T) = -1319.6 + 0.4626T$
$^{[4]}SiO_2$	$g_i(T) = -911.0 + 0.1913T$
$^{[6]}MgO$	$g_i(T) = -660.1 + 0.1047T$
$^{[6]}Mg(OH)_2$	$g_i(T) = -941.6 + 0.3011T$
$^{[6]}CaO$	$g_i(T) = -696.7 + 0.0923T$
$^{[8-z]}CaO$	$g_i(T) = -736.0 + 0.0871T$
$^{[6-8]}Na_2O$	$g_i(T) = -683.0 + 0.0352T$
$^{[8-12]}K_2O$	$g_i(T) = -735.2 + 0.0413T$
$^{[6]}FeO$	$g_i(T) = -290.6 + 0.0184T$
$^{[6]}Fe(OH)_2$	$g_i(T) = -596.1 + 0.1812T$
$^{[6]}Fe_2O_3$	$g_i(T) = -939.2 + 0.5471T$
$H_2O(Na)$	$g_i(T) = -283.2 + 0.1760T$
$H_2O(Ca)$	$g_i(T) = -293.0 + 0.1760T$

Note: Temperature in Kelvin.

RESULTS

Table 1 shows the $g_i(T)$ functions for the polyhedral components considered in this model. Tables 2a and 2b show experimentally measured ΔG_f^0 vs. those predicted using the coefficients generated by the functions in Table 1. The average difference between the predicted and the measured values is 0.19% for ΔG_f^0 at 400 K, 0.20% for ΔG_f^0 at 500 K, and 0.22% for ΔG_f^0 at 600 K. Note that only data at 298 K were used to develop the estimation model for these phases. The accuracy of the model was tested by predicting the thermodynamic properties of some minerals not used to develop the model. Table 2b compares the model's results with calorimetrically determined thermodynamic data for four (400-K), three (500-K), and two (600-K) minerals and gives associated differences. Average residuals for these minerals are 0.36% for ΔG_f^0 at 400 K, 0.34% for ΔG_f^0 at 500 K, and 0.13% for ΔG_f^0 at 600 K.

Table 3 describes the algorithm to estimate the ΔG_f^0 of a silicate material using the model described above. It shows, as an example, the estimation of ΔG_f^0 for an illite $[K_{0.75}(Al_{1.75}Mg_{0.25})Si_{3.5}Al_{0.5}O_{10}(OH)_2]$ at 500 K. The estimated ΔG_f^0 of this illite is −5335.1 kJ mol^{-1} at 400 K, −5209.4 kJ mol^{-1} at 500 K, and −5084.0 kJ mol^{-1} at 600 K.

The g_i coefficients predicted for higher temperatures by this model are well correlated with the $\Delta G_{f,T}^0$ of the free oxide or hydroxide components, just as they are at 298 K (Chermak and Rimstidt, 1989). For example, compar-

TABLE 2A. Comparison of measured ΔG^0_f vs. predicted ΔG^0_f (kJ mol^{-1}) at 400, 500, and 600 K for minerals used in the model

Mineral	ΔG^0_f (400) meas./pred.	% difference	ΔG^0_f (500) meas./pred.	% difference	ΔG^0_f (600) meas./pred.	% difference
1. Kaolinite	−3689.9/−3702.3	0.34	−3582.2/−3591.7	0.26	−3474.8/−3481.0	0.18
2. Muscovite	−5471.3/−5461.5	0.18	−5344.0/−5335.6	0.16	−5217.3/−5209.7	0.14
3. Margarite	−5722.9/−5728.5	0.10	−5593.4/−5600.4	0.12	−5464.4/−5472.2	0.14
4. Talc	−5406.0/−5395.5	0.19	−5278.4/−5267.9	0.20	−5151.4/−5140.2	0.21
5. Pyrophyllite	−5140.0/−5135.5	0.09	−5014.2/−5006.8	0.15	−4888.9/−4878.0	0.22
6. Microcline	−3664.6/−3663.9	0.02	−3587.7/−3590.2	0.07	−3511.0/−3516.6	0.16
7. Low albite	−3634.9/−3639.0	0.11	−3558.9/−3565.6	0.19	−3483.1/−3492.2	0.26
8. Anorthite	−3924.8/−3930.9	0.16	−3849.0/−3855.0	0.16	−3773.5/−3779.0	0.14
9. Fayalite	−1345.4/−1350.5	0.37	−1312.3/−1315.1	0.21	−1279.6/−1279.7	0.00
10. Leucite	−2820.3/−2829.4	0.32	−2766.1/−2774.9	0.32	−2712.5/−2720.3	0.30
11. Tremolite	−5689.2/−5686.1	0.05	−5567.1/−5564.9	0.04	−5445.7/−5443.7	0.04
12. Jadeite	−2789.3/−2784.3	0.18	−2728.3/−2728.3	0.00	−2667.5/−2672.2	0.18
13. Diopside	−2977.0/−2988.3	0.38	−2918.7/−2930.9	0.42	−2860.6/−2873.5	0.45
14. Merwinite	−4261.8/−4266.2	0.11	−4186.0/−4189.9	0.10	−4110.6/−4113.5	0.07
15. Grossular	−6150.9/−6168.9	0.29	−6029.7/−6053.3	0.39	−5908.9/−5937.8	0.48
16. Zoisite	−6359.7/−6366.5	0.11	−6226.7/−6233.5	0.11	−6094.1/−6100.5	0.11
17. Grunerite	−4375.7/−4373.7	0.04	−4266.0/−4263.7	0.05	−4156.4/−4153.7	0.06
18. Riebeckite	−4582.4/−4552.3	0.66	−4466.9/−4429.5	0.84	−4351.5/−4306.7	1.00
19. Chrysotile	−3921.8/−3929.5	0.20	−3811.8/−3820.6	0.23	−3702.3/−3711.7	0.25
20. Prehnite	−5687.3/−5688.9	0.03	−5560.6/−5563.8	0.06	−5434.6/−5438.6	0.07
21. Analcime	−3001.8/−3005.3	0.12	−2927.4/−2933.3	0.20	−2853.3/−2861.3	0.28
		Average = 0.19		Average = 0.20		Average = 0.22

Note: 2, 4, 6, 7, 9–14, and 19 Robie et al. (1978); 1, 3, 5, 8, 15, 16, and 20 Hemingway et al. (1982); 17 and 18 Makarov et al. (1984); 21 Johnson et al. (1982).

ison was made between the $g_{i,T}$ from these models and the ΔG^0_f (Table 4) at 400, 500, and 600 K for the simple oxide or hydroxide components. Figure 1 is a plot of $g_{i,600}$ vs. $\Delta G^0_{f,600}$, in which the corresponding equation of $g_{i,600} = -2.842 + 1.026\ \Delta G^0_{f,600}$ has an $R^2 = 0.999$ (R is the coefficient of correlation). Equations for the regression lines at 400 and 500 K are $g_{i,400} = -39.76 + 0.982\ \Delta G^0_{f,400}$ ($R^2 = 0.996$) and $g_{i,500} = -10.53 + 1.023\ \Delta G^0_{f,500}$ ($R^2 = 0.998$). Note that the free energy of formation of these components is always more negative when they are in the lattice of a silicate mineral than when they exist as a pure phase. This means that in most cases mixtures of pure oxides and hydroxides are unstable relative to complex silicates. This is consistent with our geological experience, which shows that complex silicate minerals (feldspars, amphiboles, micas, etc.) are more common and abundant than simple oxides and hydroxides (corundum, brucite, periclase, wüstite, etc.). These correlation equations can be used to approximate a $g_{i,T}$ for polyhedra not determined by this model (Chermak and Rimstidt, 1989). However, the errors associated with these estimates are unknown and may be large.

The slope of the line $[h_{i,298} - g_{i,298}]/298$ for each polyhedron (the temperature coefficient in Table 1) is an indication of its change in stability as a function of temperature. The steeper the slope, the more unstable the component becomes in the silicate lattice relative to the elements with increasing temperature. The $Al(OH)_3$ and Fe_2O_3 polyhedra have the steepest associated slopes and the $^{[6,8\text{-}z]}$CaO, $^{[6\text{-}8]}Na_2O$, $^{[8\text{-}12]}K_2O$, and $^{[6]}$FeO polyhedra have relatively shallow slopes.

Extrapolation of thermodynamic data from 298 K to higher temperatures using the assumption of constant $\Delta C_{P,r}$ becomes less reliable with increasing temperature. Differences between measured and predicted ΔG^0_f become larger (≈0.5%) at temperatures above 650 K. Possible reasons for this are that many of the minerals in the data base go through phase transitions between 700 and 900 K, and that at higher temperatures the assumption that $\Delta C_{P,r} = 0$ is less accurate (Nordstrom and Munoz, 1985). This model can still be used with caution above temperatures of 650 K, but errors in estimates become larger.

CONCLUSIONS

The technique presented here is a simple and effective way to estimate the ΔG^0_f of silicate minerals from 298 to 650 K. The only data needed for this estimation technique are the chemical composition and the coordination

TABLE 2B. Comparison of measured ΔG^0_f vs. predicted ΔG^0_f (kJ mol^{-1}) at 400, 500, and 600 K for minerals not used in the model

Mineral	ΔG^0_f (400) meas./pred.	% difference	ΔG^0_f (500) meas./pred.	% difference	ΔG^0_f (600) meas./pred.	% difference
1. Kyanite	−2392.5/−2396.3	0.16	−2341.9/−2345.1	0.14	−2291.4/−2293.9	0.11
2. Ca-Olivine	−2159.8/−2153.9	0.27	−2120.7/−2116.4	0.20	−2081.8/−2078.8	0.14
3. Natrolite	−5178.5/−5200.2	0.42	−5041.9/−5075.6	0.67		
4. Scolecite	−5443.7/−5474.7	0.57				
		Average = 0.36		Average = 0.34		Average = 0.13

Note: 1 and 2 Hemingway et al. (1982); 3 and 4 Johnson et al. (1983).

TABLE 3. Method of estimation of ΔG_f^0 at temperature for a mineral in kJ mol^{-1}

1. Determine chemical composition.
2. Determine coordination based on known structures.
    - A. For calcium zeolite minerals with an unknown coordination number, the polyhedron is simply represented with a "z."
    - B. For 1:1 phyllosilicate minerals, distribute the octahedral cations as 0.6666 hydroxide and 0.3333 oxide. For 2:1 phyllosilicate minerals, the octahedral cations are distributed as 0.3333 hydroxide and 0.6666 oxide.
    - C. For chlorites, distribute cations into the interlayer in the order $Al^{3+} > Fe^{2+} \geq Mg^{2+} > Fe^{3+}$ until the $(OH)_{\text{interlayer total}} = 8$. The remaining cations are then distributed into the octahedral sheet following the method in 2B.
3. Determine the number of polyhedra, n, of each component in the formula unit.
4. Determine the $g_{i,T}$ value for each polyhedron using the equations in Table 1.
5. Multiply n by the $g_{i,T}$ values. The interlayer thermodynamic contribution for chlorites is then calculated by multiplying ΔG_f^0 of free oxide or hydroxide at temperature (Table 4) by the corresponding values of n determined in 2C.
6. Calculate ΔG_f^0 at temperature for the mineral of interest by summing the polyhedral contributions

Example: Estimation of the ΔG_f^0 of an illite at 500 K

1. Chemical formula = $K_{0.75}(Al_{1.75}Mg_{0.25})Si_{3.5}Al_{0.50}O_{10}(OH)_2$.
2. In this structure the polyhedra are: $^{[4]}Al_2O_3$, $^{[6]}Al_2O_3$, $^{[6]}Al(OH)_3$, $^{[4]}SiO_2$, $^{[6]}MgO$, $^{[6]}Mg(OH)_2$, and $^{[8\text{-}12]}K_2O$.
3. The number of each polyhedra is 0.2500 $^{[4]}Al_2O_3$, 0.5833 $^{[6]}Al_2O_3$, 0.5833 $^{[6]}Al(OH)_3$, 3.500 $^{[4]}SiO_2$, 0.1666 $^{[6]}MgO$, 0.08333 $^{[6]}Mg(OH)_2$), and 0.3750 $^{[8\text{–}12]}K_2O$.
4. $\Delta G_f^0 = [0.2500\ (g_{^{[4]}Al_2O_3,500}) + 0.5833\ (g_{^{[6]}Al_2O_3,500}) + (g_{^{[6]}Al(OH)_3,500}) + 3.500\ (g_{^{[4]}SiO_2,500}) + 0.1666\ (g_{^{[6]}MgO,500}) + 0.0833\ (g_{^{[6]}Mg(OH)_2,500}) + 0.3750\ (g_{^{[8\text{-}12]}K_2O,500})]$
   $\Delta G_f^0 = [(0.2500)(-1573.8) + (0.5833)(-1529.8) + (0.5833)(-1088.3) + (3.500)(-815.3) + (0.1666)(-607.7) + (0.0833)(-791.1) + (0.3750)(-714.6)]$
5. $\Delta G_f^0 = -5209.4$ kJ·mol^{-1}.

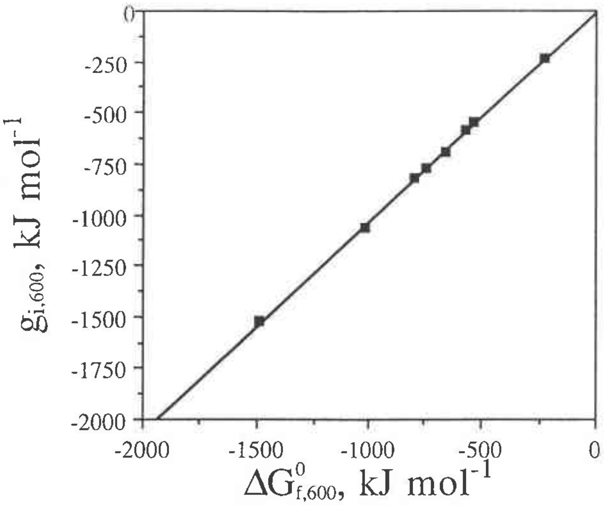

Fig. 1. Graph of the values of $g_{i,600}$ vs. $\Delta G^0_{f,600}$ from Table 4.

of the polyhedra in the mineral of interest. The approximate error associated with temperature estimates below ≈650 K ΔG_f^0 is 0.25%. Estimates above temperatures of ≈650 K will likely have associated uncertainties >0.5%.

Although this technique seems to give reliable results for most cases, it should be used with some caution. There is no question that experimentally determined thermodynamic data are more accurate than these estimates and should be used when available. Furthermore, users should always consider whether the predictions of this approach make sense in terms of their geological and geochemical experience. Also note the other caveats discussed in Chermak and Rimstidt (1989, p. 1029–1030).

This technique to estimate the free energy of formation of silicate minerals is simple and reasonably accurate. It produces estimates of the Gibbs free energy of formation of minerals for temperatures from 298 to 650 K that can be used when thermodynamic data are nonexistent. Using thermodynamic data generated from this model, high temperature activity and activity diagrams can be constructed (Chermak, 1989). Adding minerals containing other components, such as Li_2O, BeO, SrO, or $Fe(OH)_3$, to the regression data set would allow expansion of the model to a much wider range of compositions.

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TABLE 4. Measured ΔG_f^0 for each oxide or hydroxide compared to $g_{i,T}$ (kJ mol^{-1})

Polyhedron	400 K		500 K		600 K	
	ΔG_f^0	$g_{i,400}$	ΔG_f^0	$g_{i,500}$	ΔG_f^0	$g_{i,600}$
$^{[6]}Al_2O_3$	−1550.2	−1602.3	−1518.6	−1573.8	−1487.2	−1545.3
$^{[6]}Al(OH)_3$	−1107.7	−1134.6	−1061.1	−1088.3	−1014.9	−1042.0
$^{[4]}SiO_2$	−837.7	−834.5	−819.4	−815.3	−801.2	−796.2
$^{[6]}MgO$	−558.2	−618.2	−547.3	−607.7	−536.6	−597.3
$^{[6]}Mg(OH)_2$	−802.3	−821.2	−771.9	−791.1	−741.7	−761.0
$^{[6]}CaO$	−592.7	−659.7	−582.3	−650.5	−571.9	−641.3
$^{[6]}FeO$	−244.2	−258.0	−237.6	−249.9	−231.1	−241.7
$^{[6]}Fe_2O_3$	−714.9	−720.3	−688.1	−665.6	−661.9	−610.9

Note: Thermodynamic data from Robie et al. (1978), except $^{[6]}Al(OH)_3$, which is from Hemingway et al. (1982).

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