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A resolution of discrepant thermodynamic properties for chamosite retrieved from experimental and empirical techniques

PETER J. SACCOCIA,* WILLIAM E. SEYFRIED, JR.
Department of Geology and Geophysics, University of Minnesota, Minneapolis, Minnesota 55455, U.S.A.

ABSTRACT

An important deficiency in the thermodynamic data for common rock-forming minerals involves chamosite, the Fe^{2+} end-member of chlorite solid solution. The ΔG°_f and ΔH°_f values for chamosite reported in the literature, as computed from both phase-equilibria data and empirical approaches, exhibit huge discrepancies of up to 210 kJ/mol. A small portion of the discrepancy (5–10%) is related to inconsistencies in the Al reference state chosen for the thermodynamic retrieval calculations. It is shown that the remainder can be assigned to an improper application of the van't Hoff relationship to compute standard-state thermodynamic properties (25 °C, 1 bar) for chamosite from equilibrium constants derived from high-temperature (575–625 °C) and high-pressure (2.07–6.00 kbar) phase-equilibria experiments. We have reinterpreted these previously published experimental results by taking explicit account of heat-capacity and entropy data for chamosite predicted from additivity models. Following this approach, we compute ΔG°_f and ΔH°_f for chamosite of -6495.13 ± 4.17 and -7101.97 ± 4.17 kJ/mol, respectively, values that are in excellent agreement with those computed from empirical techniques, after inconsistencies related to the Al reference state are taken into account. In this way, major discrepancies in previously reported thermodynamic data for chamosite are resolved.

INTRODUCTION

Chlorite is one of the most common minerals produced in low- to moderate-grade metamorphic environments. The compositional variability exhibited by natural chlorites (Foster, 1962) probably records important information pertaining to the f_{O_2}, temperature, pressure, aqueous solution composition, and protolith composition in a particular metamorphic or hydrothermal setting (e.g., Albee, 1962; Walshe, 1986; Shikazono and Kawahata, 1987). Therefore, accurate thermodynamic data for the components of chlorite are a prerequisite to model quantitatively how such intensive variables affect chlorite composition.

Thermodynamic properties for the Mg component of chlorite (clinochlore) have been constrained adequately by numerous high-temperature (>400 °C) and high-pressure (>1 kbar) phase-equilibria studies. Consistency among the various solid-solid and dehydration equilibria have been evaluated, and standard-state thermodynamic properties for clinochlore calculated, using curve fitting routines (Helgeson et al., 1978), linear mathematical programming (Berman, 1988), and least-squares techniques (Holland and Powell, 1990).

Reliable thermodynamic data for the Fe^{2+} component of chlorite (chamosite) are lacking, although a number of high-temperature and high-pressure phase-equilibria experiments involving Fe-rich chlorite have been performed (see Chernosky et al., 1988, for a comprehensive review). In many of these studies, problems with metastability and a lack of information pertaining to chlorite composition in experiment products hampered a thermodynamic analysis of the experimental results. An exception are the chlorite oxidation and sulfidation experiments of Bryndzia and Scott (1987). Thermodynamic properties for chamosite retrieved by Bryndzia and Scott (1987) are shown in Table 1, together with those obtained from empirical estimation techniques (Sverjensky, 1985; Walshe, 1986) and natural Fe-Mg partitioning data (Holland and Powell, 1990). As originally indicated by Chernosky et al. (1988), large discrepancies (up to 210 kJ/mol) exist between the ΔG°_f and ΔH°_f values obtained from the reversed phase-equilibria experiments of Bryndzia and Scott (1987) and those estimated from various empirical approaches. Clearly, this level of uncertainty precludes reliable use of the chamosite component of chlorite solid solution in thermodynamic models of metamorphic or hydrothermal processes over a wide range of temperature and pressure. Thus, the purpose of this paper is to review the possible sources of this important discrepancy and propose a resolution that brings into agreement thermodynamic data computed from phase equilibria with those obtained from empirical estimation techniques. In this paper, the nomenclature for trioctahedral chlorites proposed by Bayliss (1975) has been adopted. Accordingly, the stoichiometry $Fe_5Al_2Si_3O_{10}(OH)_8$ refers to chamosite

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* Present address: Woods Hole Oceanographic Institution, Woods Hole, Massachusetts 02543, U.S.A.

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TABLE 1. Summary of thermodynamic properties for chamosite at 298.15 K and 1 bar

Chamosite: $Fe_5Al_2Si_3O_{10}(OH)_8$			
ΔG_f° (kJ/mol)	ΔH_f° (kJ/mol)	S° (J/mol/K)	Reference
−6477.88* (−6490.88)†	−7080.83 (−7093.83)†	596.22	Walshe (1986)**
−6697.33 ± 27	−7222.84 ± 46	594.96 ± 54.4	Bryndzia and Scott (1987)‡
−6534.36*	−7148.44	559.00	Holland and Powell (1990)§
−6486.46 (−6499.46)†			Sverjensky (1985)‖

* Calculated here from the corresponding values of ΔH_f° and S°, together with S° data for the elements from Robie et al. (1979).

** The ΔH_f° calculated using the method of Tardy and Garrels (1974). S° value adopted by Walshe (1986) as taken from Helgeson et al. (1978).

† Values adjusted by −13.0 kJ/mol; see text for explanation.

‡ Retrieved from reversed high *T-P* phase-equilibria experiments.

§ Retrieved from natural Fe-Mg partitioning data.

‖ Calculated using a linear free energy correlation technique.

that is equivalent to the terms "daphnite" and "14-Å daphnite" appearing in some thermodynamic data bases.

SOURCES OF THE DISCREPANCY

A portion of the discrepancy shown in Table 1 can be attributed to the Al reference state selected for the approximation techniques. The ΔG_f° and ΔH_f° estimated for chamosite by Sverjensky (1985) and Walshe (1986) follow the Al reference state of Helgeson et al. (1978), which was shown by Hemingway et al. (1982) to be in error by approximately +6.5 kJ/mol Al. As a consequence, the estimated values of ΔG_f° and ΔH_f° for chamosite must be adjusted by −13.0 kJ/mol for proper comparison with other data sets (Table 1). Such an adjustment, however, can account for only 5–10% of the total discrepancy. Moreover, the uncertainties associated with these estimation techniques, beyond those related to thermodynamic reference states, are thought to be on the order of 4–8 kJ/mol (e.g., Sverjensky, 1985). These uncertainties are based on application of the estimation procedure to predict ΔG_f° of solid phases that were not used to calibrate the technique and that have ΔG_f° values already well established from phase equilibria. Thus, the source of the large discrepancies in ΔG_f° and ΔH_f° for chamosite cannot be readily accounted for by uncertainties associated with these predictive schemes.

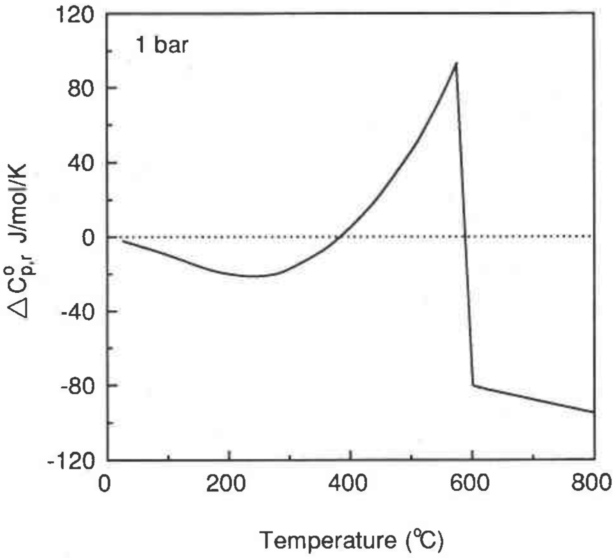

Fig. 1. The $\Delta C^\circ_{P,r}$ of Reaction 1 in text computed as a function of temperature. The $\Delta C^\circ_{P,r}$ is distinctly nonzero above 25 °C, consistent with a nonlinear dependence of log $K_{T,1}$ on temperature. For the solid phases in Reaction 1 other than chamosite, requisite heat-capacity data were from Berman (1988). Heat-capacity data for H_2O and O_2 gas were from Haar et al. (1984) and Kelley (1960), respectively. Since calorimetric data for pure iron chlorite are lacking, the heat capacity of chamosite was computed using the algorithm of Berman and Brown (1985).

An additional problem involves an improper application of the van't Hoff relationship by Bryndzia and Scott (1987) to compute thermodynamic properties for chamosite at the reference condition of 25 °C and 1 bar from high temperature (575–625 °C) and high-pressure (2.07–6.00 kbar) phase-equilibrium experiments. In their approach, equilibrium constants were retrieved from 575–625 °C at 1 bar for the following reaction:

$$\underset{\text{chamosite}}{Fe_5Al_2Si_3O_{10}(OH)_8} + \tfrac{5}{6}O_2 = \underset{\text{magnetite}}{\tfrac{5}{3}Fe_3O_4} + \underset{\text{Ky-An-Si}}{Al_2SiO_5} + \underset{\text{quartz}}{2SiO_2} + 4H_2O \qquad (1)$$

which describes oxidation of the chamosite component of chlorite solid solution. The van't Hoff relationship was then used to calculate ΔH_f° for chamosite; that is, the standard molal enthalpy of Reaction 1, ΔH_r°, was assumed to be independent of temperature, and the standard molal heat capacity of Reaction 1, $\Delta C^\circ_{P,r}$, was assumed to be zero. Similarly, a ΔG_f° for chamosite was retrieved from a linear extrapolation of the standard molal Gibbs free energy of Reaction 1, ΔG_r°, to 25 °C. The primary shortcoming of this retrieval technique is that equilibrium constants often appear to be linearly dependent on temperature if a small enough temperature interval is considered, which could lead to large errors if the reference temperature (25 °C) is far removed from the experimental conditions. For example, an analysis of the

TABLE 2. Summary of experimental results from Bryndzia and Scott (1987) used in this paper to reevaluate thermodynamic properties of chamosite

Expt.	Charge*	T (°C)	P (kbar)	log f_{O_2}	X_{cham}	log a_{cham}**	Products†
27	A	600	2.07	−16.44	0.155	−4.22	Chl-Qtz-An-Py-Po-Mt-Sp
	B	600	2.07	−16.44	0.136	−4.50	Chl-Tc-Usp-An-Py-Po-Mt-Sp
28	A	600	2.07	−16.44	0.120	−4.66	Chl-Tc-Usp-An-Py-Po-Mt-Sp
26	B	600	6.00	−16.41	0.222	−3.25	Chl-Qtz-Ky-Py-Po-Mt-Sp
30	A	600	6.00	−16.41	0.252	−3.04	Chl-Qtz-Ky-Py-Po-Mt-Sp
	B	600	6.00	−16.41	0.264	−2.93	Chl-Tc-Qtz-Ky-Usp-Py-Po-Mt-Sp
31	A	600	6.00	−16.41	0.223	−3.24	Chl-Qtz-Ky-Py-Po-Mt
	B	600	6.00	−16.41	0.258	−2.93	Chl-Tc-Qtz-Ky-Usp-Py-Po-Mt
34	B	600	6.00	−16.41	0.241	−3.09	Chl-Qtz-Ky-Gh-Py-Po-Mt
36	A	600	6.00	−17.05	0.399	−2.01	Chl-Qtz-Ky-Gh-Po-Mt
	B	600	6.00	−17.05	0.397	−2.02	Chl-Qtz-Ky-Gh-Po-Mt
41	A	575	4.50	−17.23	0.369	−2.24	Chl-Qtz-Si-Py-Po-Mt-Sp
	B	575	4.50	−17.23	0.334	−2.45	Chl-Qtz-Si-Py-Po-Mt-Sp
42	B	600	5.00	−16.48	0.219	−3.30	Chl-Qtz-Si-Py-Po-Mt-Sp
43	B	625	5.50	−15.80	0.197	−3.53	Chl-Qtz-Si-Py-Po-Mt-Sp

* Initial charge compositions: (A) Fe-Chl + Qtz + Al_2SiO_5 + Mt + Py + Sp + 0.1 *m* HI solution; (B) Mg-Chl + Qtz + Al_2SiO_5 + Mt + Tr + Sp + 0.1 *m* HI solution.

** Activity of $Fe_5Al_2Si_3O_{10}(OH)_8$ based on an ideal site mixing approach (see text for explanation).

† Mineral abbreviations: An, andalusite; Chl, chlorite; Gh, gahnite/hercynite(ss); Ky, kyanite; Mt, magnetite; Po, pyrrhotite; Py, pyrite; Qtz, quartz; Si, sillimanite; Sp, sphalerite; Tc, talc; Tr, troilite; Usp, ulvospinel/magnetite(ss).

$\Delta C^\circ_{P,r}$ of Reaction 1 indicates that the van't Hoff relationship cannot be properly applied, since $\Delta C^\circ_{P,r}$ is distinctly nonzero and is a complex function of temperature (Fig. 1). The large increase in $\Delta C^\circ_{P,r}$ at 575 °C is a consequence of the λ transitions exhibited by quartz and magnetite at this temperature, caused by structural and magnetic phase transitions, respectively (Berman, 1988). Furthermore, the effect of these λ transitions on the thermodynamic properties of Reaction 1 is magnified by reaction stoichiometry, since both quartz and magnetite appear on the same side of the reaction and have reaction coefficients greater than unity. In view of the fact that Bryndzia and Scott (1987) investigated a small temperature interval (575–625 °C), this heat-capacity analysis suggests that misuse of the van't Hoff relationship may explain the grossly discrepant ΔG°_f and ΔH°_f values for chamosite retrieved from experiment and empirical techniques.

REINTERPRETATION OF PHASE EQUILIBRIUM RESULTS

A more rigorous retrieval of ΔG°_f and ΔH°_f values for chamosite can be made by taking into account, explicitly, the heat capacity of chamosite predicted with the algorithm of Berman and Brown (1985). On the basis of a standard state of unit activity of the pure solid and H_2O at the temperature and pressure of interest and on unit fugacity of the hypothetical ideal gas at 1 bar and the temperature of interest, the equilibrium constant for Reaction 1 at the temperature and pressure of interest ($K_{T,P}$) can be written as:

$$\log K_{T,P} = 4 \log a_{H_2O} - \tfrac{5}{6} \log f_{O_2} - \log a_{cham}. \quad (2)$$

Since the aqueous phase in these experiments was dilute (distilled H_2O and 0.10 *m* HI solutions), the activity of H_2O can be closely approximated as unity (Helgeson et al., 1981). Values of $K_{T,P}$ can therefore be computed from knowledge of the f_{O_2} and the activity of chamosite in chlorite solid solution at the termination of each experiment. In this study, chamosite activities were evaluated by assuming ideal site mixing of five Fe atoms and one Al atom over six octahedral sites in the chamosite formula unit (e.g., Helgeson and Aagaard, 1985). A summary of experimental results required for the calculation of $K_{T,P}$ is given in Table 2.

Once $K_{T,P}$ has been determined, ΔG°_f and ΔH°_f values for chamosite can be retrieved from the solution of the familiar thermodynamic relationships:

$$\Delta G^\circ_r = -2.303RT \log K_{T,P} \quad (3)$$

$$\Delta G^\circ_r = \sum_i n_i \Delta G^\circ_{T,P} \quad (4)$$

$$\Delta G^\circ_f = \Delta G^\circ_{T,P,\mathrm{cham}} + S^\circ(T - T_r) - \int_{T_r}^{T} C^\circ_P \, dT + T \int_{T_r}^{T} d \ln T - V^\circ(P - P_r) \quad (5)$$

$$\Delta H^\circ_f = \Delta G^\circ_f + T_r \Delta S^\circ_f \quad (6)$$

where n_i is the reaction coefficient of the *i*th species, which is positive for products and negative for reactants, $\Delta G^\circ_{T,P}$ is the apparent standard Gibbs free energy of formation of *i* at the temperature and pressure of interest, following the conventions of Benson (1968) and Helgeson et al. (1978), and S°, V°, and C°_P are the standard molal entropy, volume, and heat capacity of chamosite at the reference temperature (T_r) and pressure (P_r) of 298.15 K and 1 bar, respectively. Thus, in addition to the C°_P of chamosite, the only information required is $\Delta G^\circ_{T,P}$ values for the other product and reactant species in Reaction 1 and V° and S° data for chamosite (Table 3). Supporting $\Delta G^\circ_{T,P}$ values were computed using thermodynamic data from Berman (1988) for quartz, magnetite, and the Al_2SiO_5 polymorphs, Haar et al. (1984) for H_2O, and Kelley (1960)

TABLE 3. Values of V°, S°, and C°_P coefficients* used in this study to compute ΔG°_f and ΔH°_f for chamosite from the high *T-P* phase-equilibria experiments of Bryndzia and Scott (1987)

V°	21.34 J/bar	k_1	-102.565×10^2
S°	583.20 J/mol/K	k_2	-122.769×10^5
k_0	1229.233	k_3	212.151×10^7

* For calculation of heat capacity in J/mol/K from $C^\circ_P = k_0 + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3}$. C°_P coefficients were computed using the algorithm of Berman and Brown (1985). See text for source of V° and S° data.

and Wagman et al. (1982) for O_2 gas. The V° of chamosite is well established from measurements of unit-cell parameters (e.g., McOnie et al., 1975). Owing to a lack of phase-equilibria constraints over a wide range of temperature, it was necessary to estimate S° for chamosite from the additivity model of Holland (1989). Following this approach, an S° of 542 J/mol/K is computed that represents the calorimetric and magnetic contribution but does not include provisions for site configurational entropy terms. Since the degree of order in chamosite is not presently well established, we have elected to add the ideal configurational entropy for chamosite (41.2 J/mol/K) to the calorimetric contribution; that is, we assume complete disorder. Although direct analogies cannot necessarily be drawn to the Mg component of chlorite, a comparison of the S° for clinochlore regressed from a large number of phase-equilibria experiments with the calorimetric value does indicate substantial disorder (Berman, 1988).

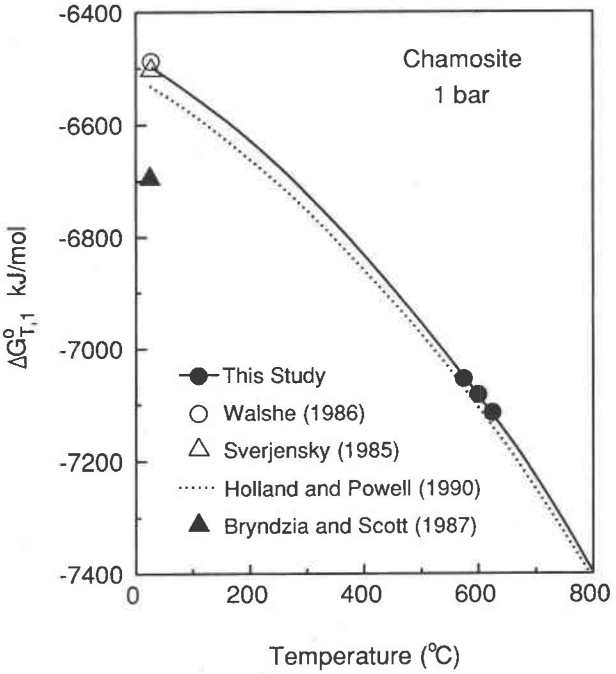

Fig. 2. Summary of $\Delta G^\circ_{T,1}$ values for chamosite (at 25 °C, $\Delta G^\circ_{T,1}$ is equivalent to ΔG°_f). The approach taken in this study was to first compute $\Delta G^\circ_{T,1}$ for chamosite at 575–625 °C (solid circles) from the experimental data of Bryndzia and Scott (1987). A ΔG°_f could then be computed by taking into account S° and C°_P data for chamosite determined from additivity models. The resulting free energy function is shown by the solid line. Note the excellent agreement between the results of this study and ΔG°_f values computed from various empirical techniques, after adjustments related to the Al reference state are taken into account.

The results of our thermodynamic analysis of the phase-equilibrium data of Bryndzia and Scott (1987) are outlined in Table 4. Reinterpreted in this way, the data yield ΔG°_f and ΔH°_f values for chamosite of -6495.13 ± 4.17 and -7101.97 ± 4.17 kJ/mol, respectively, values that are in excellent agreement with those computed from various empirical techniques, after corrections related to the Al reference state are considered (Fig. 2). Such agreement is encouraging and strongly suggests that the large discrepancies in ΔG°_f and ΔH°_f values for chamosite reported in the literature are related to heat-capacity effects. The results also serve to emphasize the utility of adopting heat-capacity and entropy data predicted from additivity models when direct constraints from calorimetry are absent. Some disagreement still exists, however, between the results of this study and $\Delta G^\circ_{T,1}$ values predicted using the chamosite (daphnite) data from Holland and Powell (1990), which are based on natural Fe-Mg exchange equi-

TABLE 4. Summary of thermodynamic properties for chamosite retrieved in this study from the high *T-P* phase-equilibria experiments of Bryndzia and Scott (1987)

T (°C)	*P* (kbar)	Log $K_{T,P}$	ΔG°_{r}* **	$\Delta G^\circ_{T,P}$* †	$\Delta G^\circ_{T,1}$* ‡	ΔG°_f* §	ΔH°_f* ‖
575	4.50	16.71 ± 0.15	−271.33 ± 2.43	−6959.54 ± 2.43	−7055.55 ± 2.43	−6501.35 ± 2.43	−7108.19 ± 2.43
600	2.07	18.16 ± 0.22	−303.59 ± 3.68	−7037.03 ± 3.68	−7081.18 ± 3.68	−6492.94 ± 3.68	−7099.78 ± 3.68
600	5.00	17.03	−284.68	−6975.86	−7082.54	−6494.28	−7101.12
600	6.00	16.62 ± 0.27	−277.86 ± 4.52	−6956.95 ± 4.52	−7084.97 ± 4.52	−6496.71 ± 4.52	−7103.55 ±4.52
625	5.50	16.69	−287.02	−6995.94	−7113.29	−6490.35	−7097.19
					Average:	−6495.13 ± 4.17	−7101.97 ± 4.17

* Values are in kJ/mol.

** Standard molal Gibbs free energy of Reaction 1 at *T* and *P*.

† Apparent standard molal Gibbs free energy of formation of chamosite at *T* and *P*.

‡ Apparent standard molal Gibbs free energy of formation of chamosite at *T* and 1 bar calculated by subtracting $V^\circ(P - 0.001)$ from $\Delta G^\circ_{T,P}$, where V° is the standard molal volume of chamosite at 298.15 K and 1 bar (21.34 kJ/kbar).

§ Standard molal Gibbs free energy of formation of chamosite from the elements at 298.15 K and 1 bar.

‖ Standard molal enthalpy of formation of chamosite from the elements at 298.15 K and 1 bar, consistent with a ΔS°_f value of −2035.35 J/mol/K, which was computed from the estimated S° of chamosite in Table 3 and S° data for the elements from Robie et al. (1979).

libria (Fig. 2). It is interesting to note that the two data sets agree reasonably well at high temperatures but diverge as the reference condition (25 °C) is approached, a result that can be largely attributed to differences in the $S°$ values adopted for chamosite. In effect, the smaller $S°$ for chamosite (559.0 J/mol/K) reported by Holland and Powell (1990) implies a more ordered crystal structure and leads to a less steep dependence of $\Delta G^{\circ}_{T,1}$ on temperature.

CONCLUDING REMARKS

The thermodynamic properties for chamosite derived in this study will undoubtedly require further refinement as additional phase-equilibria and calorimetry data become available. In particular, additional constraints on the magnitude of the configurational contribution to $S°$ for chamosite are needed, and the assumption of ideal mixing of atoms on sites in chlorite requires further testing. Nevertheless, the resolution of large discrepancies in ΔG°_{f} and ΔH°_{f} for chamosite proposed here will greatly increase the accuracy of thermodynamic models of metamorphic and hydrothermal settings where chlorite solid solution is a ubiquitous phase. In this regard, it should be emphasized that the retrieval calculations in this study relied upon supporting thermodynamic data for minerals from Berman (1988) and, therefore, the resulting ΔG°_{f} and ΔH°_{f} values for chamosite should only be used with this data base. If the retrieval calculations are performed with supporting thermodynamic data for minerals from Helgeson et al. (1978), the ΔG°_{f} and ΔH°_{f} values for chamosite are -6491.56 ± 6.95 and -7098.41 ± 6.95 kJ/mol, respectively.

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