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The Gibbs energy of formation of huntite, $CaMg_3(CO_3)_4$, at 298 K and 1 bar from electrochemical cell measurements

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ABSTRACT

New data are presented for the ΔG_f° for huntite, $CaMg_3(CO_3)_4$. Measurements were made using new third-kind electrochemical cells that do not require a complicated model for solute speciation or corrections for liquid-liquid junction potentials. The average value of $\Delta G_f^\circ[CaMg_3(CO_3)_4(s)]$ (−4195.6 ± 6.4 kJ/mol) measured in these electrochemical cells agrees, within experimental error, with values determined calorimetrically (e.g., −4203.4 ± 1.6 kJ/mol: Hemingway and Robie, 1973) and electrochemically (−4188.6 ± 1.0 kJ/mol: Gamsjäger, 1989). Our results demonstrate the utility of this new electrochemical method in the study of metal carbonate equilibria of geochemical importance.

INTRODUCTION

An immense amount of Mg-bearing carbonate minerals precipitate worldwide in the oceans ($\approx 16 \cdot 10^{12}$ mol/yr: Morse and Mackenzie, 1990). The average flux of $MgCO_3$ to oceanic sediments (as both dolomite and as $MgCO_3$ in calcite) is $\approx 4.4 \cdot 10^{12}$ mol/yr of $MgCO_3$, which, when integrated over geologic time, has produced a reservoir of $\approx 1 \cdot 10^{21}$ mol of $MgCO_3$ in carbonate rocks and sediments (see Morse and Mackenzie, 1990). These minerals are a large and potentially reactive sink for C. In spite of the abundance of these minerals, their stability at low temperatures and the pathways for their diagenesis remain poorly understood, largely because of experimental difficulties in determining ΔG_f° values.

Some methods of estimating ΔG_f° values (calorimetry, solubility experiments) are complicated because dissolution of the minerals releases a gas phase or because secondary minerals precipitate as the mineral dissolves. Precipitation of secondary minerals during a solubility experiment complicates the interpretation of the changes in solute concentrations with time. Furthermore, conversion of solute concentrations to thermodynamic activities commonly requires a model for solute complexation in a complicated mixture. Such experiments can be precise, yet the resulting ΔG_f° values may contain large uncertainties that arise from the speciation model chosen to account for such complexation.

Calorimetry on carbonate minerals is likewise difficult. Estimation of ΔH_f° values from low-temperature dissolution calorimetry is complicated by slow CO_2 (and heat) loss from the solution after the mineral dissolves (e.g., Adami and Conway, 1966). Although there have been significant recent advances in this field (Capobianco, 1986; Navrotsky and Capobianco, 1987; Chai and Navrotsky, 1993), there remains a need for low-temperature methods of determining ΔG_f° values for carbonate minerals.

We are testing a new class of metal-carbonate electrodes of the third kind (Rock et al., 1994; Casey et al., in preparation) that offers several significant advantages. First, calculation of the ΔG_f° values does not require a model for speciation of solutes in complex aqueous mixtures. Second, there is no correction for a liquid-liquid electrolyte junction potential. Third, the reversibility of the cell reaction can be established reliably through the existence of a Nernstian response of the electrode and from the absence of hysteresis in the relation between cell current and cell voltage. Fourth, only minuscule fractions of the mineral react with the aqueous solution to achieve metastable equilibrium in the cell, which is a distinct advantage in cases where the solid is precious or where large changes in solute concentrations can cause precipitation of secondary minerals.

Huntite was chosen for study with this electrode because it forms only a limited range of solid solutions and because a significant range of ΔG_f° values have been reported. Garrels et al. (1960) estimated the Gibbs energy of formation from the elements at 25 °C and 1 bar of a huntite sample from Tea Tree Gully, South Australia, in a set of solubility experiments where the transient pH was extrapolated to infinite time to yield a $\Delta G_f^\circ[CaMg_3(CO_3)_4(s)]$ = −4216.2 kJ/mol (no error limits reported). Hemingway and Robie (1973) determined $\Delta G_f^\circ[CaMg_3(CO_3)_4(s)]$ = −4203.4 ± 1.6 kJ/mol by combining solu-

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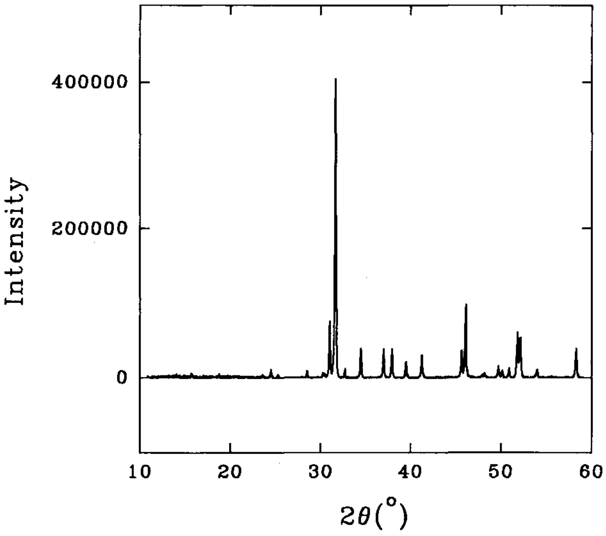

Fig. 1 Powder X-ray diffraction pattern of huntite from Tea Tree Gulley, South Australia.

tion calorimetric data with third-law entropies reported by Hemingway and Robie (1972). Helgeson et al. (1978) evaluated the thermodynamic stability of huntite by combining the third-law entropies estimated by Hemingway and Robie (1972) with calorimetric enthalpies of dissolution reported by Hemingway and Robie (1973). Helgeson et al. (1978) recommended a similar value for $\Delta G_f^0[\mathrm{CaMg3(CO_3)_4(s)}]$, −4203.707 kJ/mol (no error limits reported). Königsberger and Gamsjäger (1987) employed electrochemical cell measurements to estimate $\Delta G_f^0[\mathrm{CaMg_3(CO_3)_4(s)}] = -4180.0 \pm 9.6$ kJ/mol, which agrees well with the value inferred from field geochemical evidence by Schott and Dandurand (1975) of −4174.17 ± 8.0 kJ/mol. Gamsjäger (1989) later revised the previous estimate to −4188.6 ± 1.0 kJ/mol. The reported range in Gibbs energies of formation corresponds to a variation of about 7.4 orders of magnitude in the equilibrium solubility product of huntite at 25 °C.

EXPERIMENTAL METHODS

Huntite sample

The sample of huntite, from Tea Tree Gulley, South Australia, was provided by the Smithsonian Institution (NMNH no. 113007). X-ray diffraction analysis showed the material to be pure (Fig. 1), and chemical analyses of samples from this location are reported in Table 1. This mineral was disaggregated in a mortar, and the undamaged crystals were hand-picked for experimental study. The crystals were then lightly ground to a grain size of approximately 25–75 μm, and the resulting powder was added to the cell without additional cleaning. This Tea Tree Gulley huntite was also employed in previous calorimetric measurements of the thermodynamic state functions (Hemingway and Robie, 1972, 1973).

TABLE 1. Chemical analysis of huntite sample from Tea Tree Gulley, South Australia (from Skinner, 1958)

	1	2
MgO	34.4	33.2
CaO	16.0	15.6
CO_2	50.4	48.9
Cl_2	tr.	n.d.
Insol.	nil	n.d.
Total	100.8	97.7

Note: 1 = the analysis was performed at the Geology Department, University of Adelaide; 2 = the analysis was performed by J.T. Hutton, Soils Division, C.S.I.R.O; n.d. = not determined; tr = trace amounts.

Electrochemical cell

The electrochemical cell is a third-kind electrode, where a metal (i.e., Cd^0) in contact with a slightly soluble salt of the metal (i.e., $CdCO_3$) provides a measure of the activity of a dissolved salt with a common anion and cations that are not directly electroactive, e.g., $Ca_{0.25}Mg_{0.75}CO_3$ (Rock et al., 1994). The cell diagram is

$$\mathrm{Cd(Hg)(two\text{-}phase)}\,|\,\mathrm{CdCO_3(s),\ Ca_{0.25}Mg_{0.75}CO_3(s)}\,|$$
$$\mathrm{CaCl_2}(\mathrm{aq}, m_1),\ \mathrm{MgCl_2}(\mathrm{aq}, m_2)\,|\,\mathrm{Hg_2Cl_2(s)}\,|\,\mathrm{Hg(l)}. \quad (1)$$

The postulated equations for the electrode reactions are

$$\mathrm{Cd(Hg)} + \mathrm{Ca_{0.25}Mg_{0.75}CO_3(s)}$$
$$= \mathrm{CdCO_3(s)} + 0.25\mathrm{Ca^{2+}}(\mathrm{aq}, m_1)$$
$$+ 0.75\mathrm{Mg^{2+}}(\mathrm{aq}, m_2) + 2e^- \quad (2)$$

$$\mathrm{HgCl_2(s)} + 2e^-$$
$$= 2\mathrm{Hg(l)} + 2\mathrm{Cl^-}(\mathrm{aq}, 2m_1 + 2m_2). \quad (3)$$

The sum of Equations 2 and 3 yields the postulated equation for the net cell reaction:

$$\mathrm{Cd(Hg)} + \mathrm{Ca_{0.25}Mg_{0.75}CO_3(s)} + \mathrm{Hg_2Cl_2(s)}$$
$$= 2\mathrm{Hg(l)} + \mathrm{CdCO_3(s)} + 0.25\mathrm{Ca^{2+}}(\mathrm{aq}, m_1)$$
$$+ 0.75\mathrm{Mg^{2+}}(\mathrm{aq}, m_2) + 2\mathrm{Cl^-}(\mathrm{aq}, 2m_1 + 2m_2). \quad (4)$$

Application of the Nernst equation to Equation 4 and introduction of mean ionic activity coefficients yields

$$E^0 = E + \frac{\mathrm{R}T}{2\mathrm{F}}\ln[m_1^{0.25}m_2^{0.75}(2m_1 + 2m_2)^2$$
$$\times\ \gamma^{3(0.25)}_{\pm(\mathrm{CaCl_2},m_1)}\gamma^{3(0.75)}_{\pm(\mathrm{MgCl_2},m_2)}]. \quad (5)$$

Measurement of E at known molalities (m_1 and m_2), together with values of the mean ionic activity coefficients, gives E^0 for the cell reaction described by Equation 3, from which $\Delta G_f^0[\mathrm{Ca_{0.25}Mg_{0.75}CO_3(s)}]$ can be calculated and converted to $\Delta G_f^0[\mathrm{CaMg_3(CO_3)_4(s)}]$. Cell solutions (Table 2) were chosen so that a very small fraction of the mineral dissolves (typically $<10^{-6}$ mol) to reach equilibrium.

The electrochemical cells were constructed using standard methods (Ives and Janz, 1961), including preparation of the calomel and two-phase Cd amalgam in the

TABLE 2. Results of measurements on cells of the type given by Eq. 1 at 25 °C and 1 bar

Cell	$CaCl_2$ (m_1)	$MgCl_2$ (m_2)	$\gamma_{\pm1}$*	$\gamma_{\pm2}$*	E (V)**	δG^0_{rxn} (kJ/mol)	ΔG_f^0† (kJ/mol)
1‡	0.2080	0.6525	0.4965	0.5268	0.7723	−144.780	−1047.46
2‡	0.1064	0.3365	0.4563	0.4713	0.7977	−144.262	−1048.28
3	0.03792	0.9392	0.5240	0.5610	0.7747	−146.245	−1046.29
4	0.03594	0.9220	0.5202	0.5561	0.7711	−145.322	−1047.22
5	0.008564	0.9139	0.5141	0.5482	0.7730	−144.494	−1048.04
6	0.1147	0.3507	0.4566	0.4723	0.7885	−142.869	−1049.67
7	0.01026	0.05377	0.5583	0.5617	0.8484	−140.660	−1051.88
8	0.01934	0.1003	0.5097	0.5151	0.8311	−141.607	−1050.93
9	0.04517	0.2319	0.4646	0.4747	0.8036	−142.329	−1050.21

Note: results are reported with an extra significant digit in this table, but not in the main body of the paper, in order to minimize the round-off error in calculations.

* Activity coefficients were calculated from the program PHRQPITZ (Plummer et al., 1988).

** Precision of the measured cell voltages are all within ±0.20 mV.

† Values of the $\Delta G_f^0[Ca_{0.25}Mg_{0.75}CO_3(s)]$ correspond to formation from the elements at 298.15 K and 1 bar.

‡ Data were collected at 32.4 °C and corrected to 25.0 °C using our measured cell voltage temperature coefficient.

absence of oxygen and silicon-fluid treatment of the inner cell surfaces. Pt electrode leads were inserted through small holes in the bases of the electrode compartment, encased in Teflon tubing (Fig. 2), and sealed to the cell with epoxy. The portion of the Pt leads within the cell and the lower sections of the cell compartments were isolated from contact with the epoxy sealer by melting small pieces of paraffin in place with a heat gun. The cells were charged with solids and solution under an Ar atmosphere. Cell solution was transferred by pipette to the top of the mirror-bright Cd amalgam and calomel electrodes; the carbonate solids were then added to the Cd amalgam electrode chamber. After all solid and liquid constituents were added to the cell, the cell was again purged with Ar and sealed from the atmosphere with tight-fitting plastic caps, which were covered securely with Parafilm.

Electromotive force measurements were made with a Tektronix 2510G digital voltameter and checked frequently with a Leeds and Northrup K-3 potentiometer standardized with a Weston standard cell (Eppley Laboratories), which was compared with four other such standard cells. The calibrations of the potentiometer and the standard cell are thus traceable to the National Institute of Standards and Technology.

Solution analyses

The cell solutions were made up from reagent-grade chloride salts ($CaCl_2 \cdot 2H_2O$ and $MgCl_2 \cdot 6H_2O$). Ca and Mg concentrations of the cell electrolytes were confirmed by analysis using a Thermal Jarrell-Ash Inductively Coupled Plasma Atomic-Emission Spectrometer (ICP-AES). The sensitivity of this method is approximately 0.05 ppm of metal in solution. Chloride concentrations were determined coulometrically on a Labconco digital chloridometer. The precision and accuracy of these methods are better than 1–3%, as determined by repeated analysis of samples and standards.

Thermodynamic data

Calculation of $\Delta G_f^0[Ca_{0.25}Mg_{0.75}CO_3(s)]$ from the Gibbs energy change for the cell reaction (Eq. 4) requires knowl-

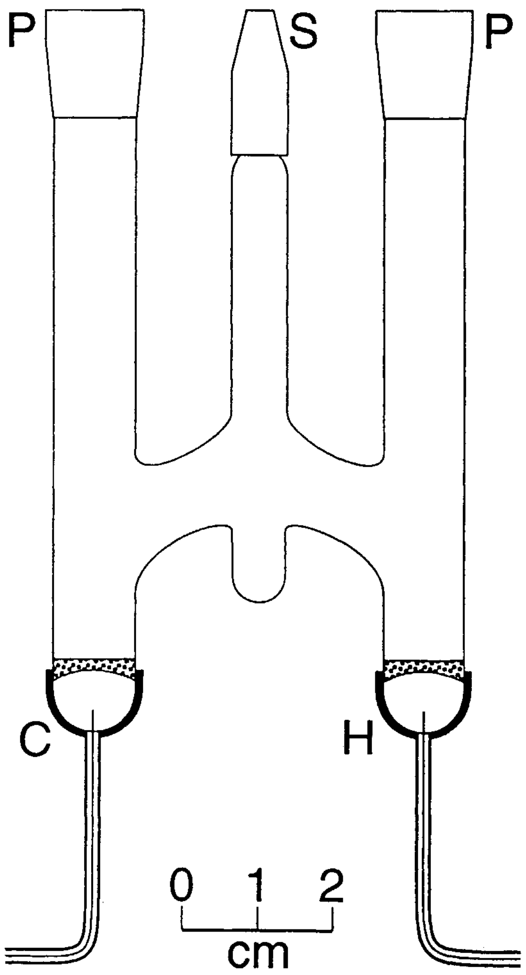

Fig. 2. Cell diagram. C is the outer cell compartment, which contains the $Cd(Hg)/CdCO_3(s)$, $CaMg_3(CO_3)_4(s)$. H is the inner cell compartment, which contains the $Hg_2Cl_2(s)/Hg(l)$ electrode. The cell is covered with plastic caps. S is a cap for covering the septum, which connects the cell to reservoirs. P denotes a plastic cap for the cell compartment. Stippled areas indicate carbonate- or calomel-containing phases.

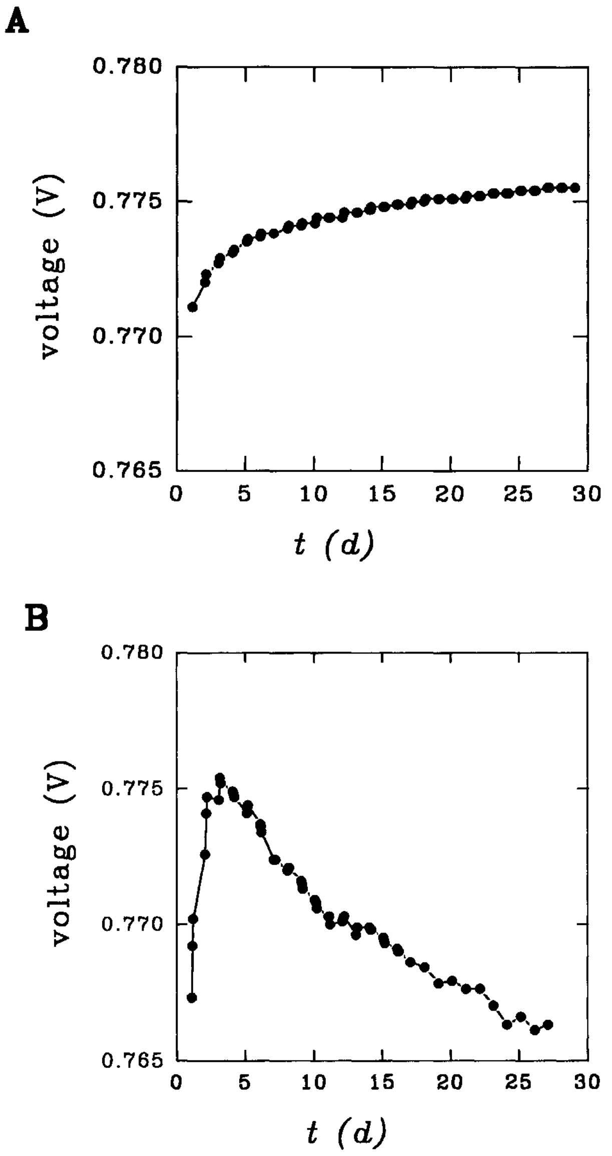

Fig. 3. (**A**) The change with time of the voltage of cell 3 (Table 2). (**B**) The change with time of the voltage of cell 1 (Table 2).

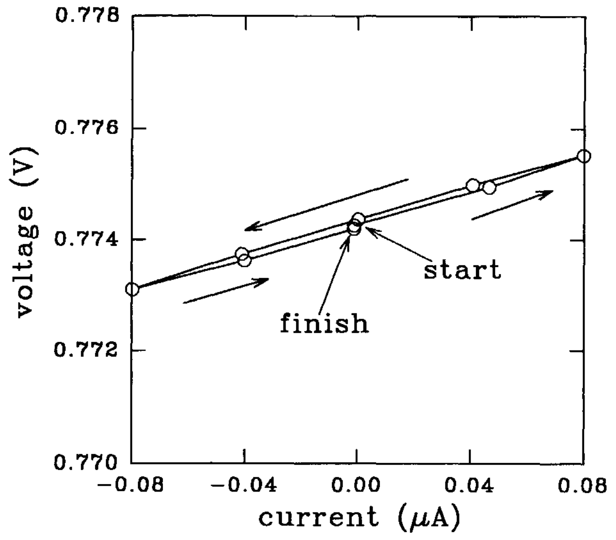

Fig. 4. Variation in the measured potentials for cell 5 (Table 2) with induced currents.

edge of the activity coefficients of $CaCl_2$(aq) and $MgCl_2$(aq) and the Gibbs energies of formation of Cd(Hg)(s) and $CdCO_3$(s). The activity coefficients are available from the study of Robinson and Bower (1966). They also can be calculated using the Pitzer ion-ion interaction approach incorporated into the computer program PHRQPITZ (Plummer et al., 1988). For our cell electrolytes, the $\gamma_{\pm}$ (mix) values calculated from the two sources differ by <1%, which is not surprising, since the PHRQPITZ program incorporates the Robinson and Bower (1966) data.

Calculation of the $\Delta G_f^0[Ca_{0.25}Mg_{0.75}CO_3(s)]$ values also requires ΔG_f^0 values of other constituents in the equations for the cell reaction (Eq. 4). These values were taken from Wagman et al. (1982): $\Delta G_f^0[Mg^{+2}(aq)] = -454.8$, $\Delta G_f^0[Ca^{+2}(aq)] = -553.58$, $\Delta G_f^0[Cl^-(aq)] = -131.228$, $\Delta G_f^0[Hg_2Cl_2(s)] = -210.745$, and $\Delta G_f^0[CdHg)] = -9.740$ kJ/mol. The value of $\Delta G_f^0[Cd(CO_3)(s)] = -671.07 \pm 1.1$ kJ/mol was used in evaluating Equation 4 and is from a separate study (Rock et al., 1994), which compares well with the value of −669.4 kJ/mol reported by Wagman et al. (1982).

RESULTS

Cell voltages are stable (Fig. 3A) after an initial equilibration period that varies from a few hours to days. A representative example is shown in Figure 3A for the solution composition of 0.03792*m* $CaCl_2$ and 0.9392*m* $MgCl_2$ with huntite solid. The equilibrium period results in part from relaxation of the Hg-Cd amalgam, which is injected into the cell at 75 ± 10 °C and undergoes phase separation upon cooling to 25 °C. The solution compositions and voltages for all cells are summarized in Table 2.

The Nernstian response of the electrode is indicated when cells containing different cell solutions yield similar ΔG_{rxn}^0 values ($2FE^0$; Table 2), as required by Equation 5. The total range in E^0 values with changes in solution composition is <2%. The Nernstian response of the electrode is strong evidence for metastable equilibrium between the solid and the cell solution.

The absence of hysteresis in the voltage vs. current relation is also strong evidence the cell solution achieved metastable equilibrium with the electrolyte. The cell voltage responds reversibly to small perturbations of current, which should give an absence of hysteresis when cells are in equilibrium (Fig. 4). In these reversibility experiments, the voltage values were measured as currents and were both increased and decreased. As seen in Figure 4, the cell voltages do not depend on the prior history of the

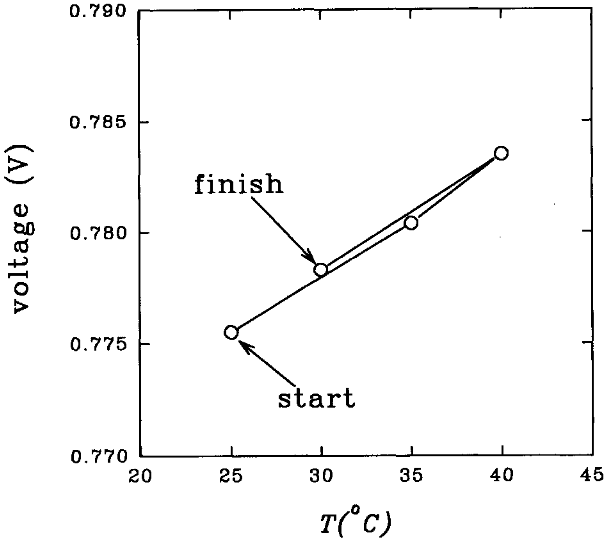

Fig. 5. Variation in the measured potentials for cell 8 (Table 2) with changing temperature.

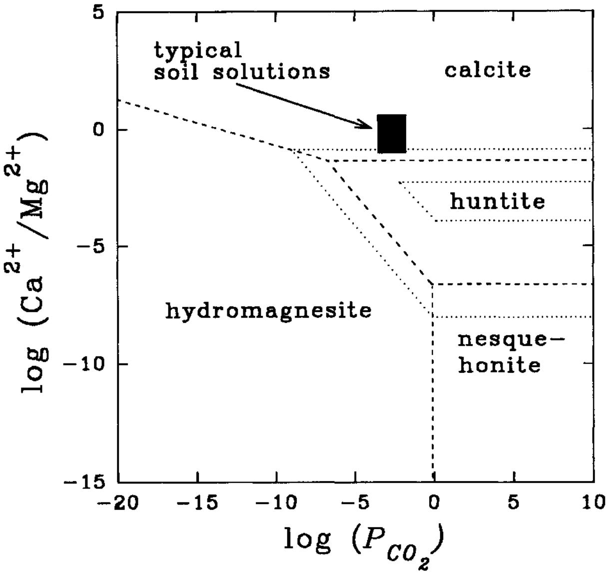

Fig. 6. Stability diagram with our value for $\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4]$ = −4195.6 kJ/mol (dashed line), Königsberger and Gamsjäger's (1987) value of −4180 kJ/mol (inner dotted line), and Robie et al. (1978) value of −4203.4 kJ/mol (outer dotted line).

cell. This figure is representative of the huntite cells 3–9. The range of hysteresis found from start to finish was 0.01–0.2 mV. For cells 1 and 2, the corresponding range was about 8 mV, indicating significant irreversibility, consistent with the changes in the cell voltages for these two cells over time.

The data for huntite cells 1 and 2 (Table 2) were collected at 32.4 °C. The data from these cells were corrected from 32.4 to 25.0 °C by using the average of the temperature-dependence data from cells 3, 7, 8, and 9; a representative graph of the temperature-dependence data is seen in Figure 5. The temperature coefficient (dE/dT) was determined from the slope of E vs. T to be 0.4205 ± 0.058 mV/K. The temperature coefficient was used to correct the voltages measured at 32.4–25 °C. For the difference in temperature of 7.4 °C, we subtracted 0.0031 V from the measured voltages of cells 1 and 2 at 32.4 °C.

The changes in the voltage for cell 3 (Fig. 3A) over time is typical for cells 3–9 (Table 2), which all became stable within ±2.0 mV. For these cells, the value of E was determined by taking the average voltage over the period 5–29 d. However for cells 1 and 2 (Table 2), the cell voltages fell steadily over the same period (Fig. 3B). In these two cases, the value of E was obtained by least-squares extrapolation of the data to $t = 0$ in the period 5–27 d.

We found no evidence of calcite precipitation in the experiments, although such precipitation would be detectable at concentrations of 2–3 wt% or greater. This sensitivity was determined by X-ray analysis of artificial mixtures of huntite and reagent-grade calcite. The presence of calcite could not be detected in these mixtures at concentrations <2–3 wt% using our standard protocol for analysis. We could not extract sufficient amounts of huntite to analyze from all cells; solids were extracted from the cells 5–7 after these experiments, X-rayed, and found to be pure.

When combined with Equation 4, the cell voltages from ΔG°_{rxn} (Eq. 4) = $-2FE^{\circ}_{rxn}$ yield a value of $\Delta G^{\circ}_{f}[Ca_{0.25}Mg_{0.75}CO_3(s)] = -1048.89 \pm 1.59$ kJ/mol, which in turn gives a value of $\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4(s)] = -4195.6 \pm 6.4$ kJ/mol. Our estimate for the uncertainty is the average error of the results reported in Table 2.

Discussion

The value of −4195.6 ± 6.4 kJ/mol obtained in this study for $\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4(s)]$ is, within experimental error, in agreement with Gamsjäger's (1989) value of −4188.63 ± 1.0 kJ/mol and the −4203.4 ± 1.6 and −4203.7 kJ/mol values of Hemingway and Robie (1973) and Helgeson et al. (1978), respectively (Table 3). The effect of the range in measured and calculated values for $\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4(s)]$ on the predicted stability of this mineral is illustrated in Figure 6, where the phase boundaries for various magnesian carbonates are shown. As one

Table 3. Comparison of reported $\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4(s)]$ values

$\Delta G^{\circ}_{f}[CaMg_3(CO_3)_4(s)]$ (kJ/mol)	Uncertainty (±kJ/mol)	Source
−4195.6	±6.4	This study
−4188.63	±1.0	Gamsjäger (1989)
−4180	±9.6	Königsberger and Gamsjäger (1987)
−4203.4	±1.6	Hemingway and Robie (1973)
−4216.2	not reported	Garrels et al. (1960)
−4203.707	not reported	Helgeson et al. (1978)
−4174.17	±8.0	Schott and Dandurand (1975)

can see, the ±11.7-kJ/mol range in values translates to a range of over 10^2 in values of $\mathrm{Ca^{2+}/Mg^{2+}}$.

The uncertainty in the $\Delta G^{\circ}_{f}[\mathrm{CaMg_3(CO_3)_4(s)}]$ value is geochemically important because it causes the mineral stability field to span the chemistry of important natural settings. In the organic-rich horizon of soils, for example, the partial pressure of carbon dioxide is commonly well beyond the atmospheric value of $10^{-3.5}$ atm because of the activity of heterotrophic bacteria and root respiration. The activity ratio of $\mathrm{Ca^{2+}/Mg^{2+}}$ in most natural waters varies from $10^{-1.0}$ to $10^{+0.5}$, with the lower range of values corresponding to evaporated brines. These regions are shown in Figure 6 to lie close to the stability region for transformation of calcite to huntite, depending upon which value for $\Delta G^{\circ}_{f}[\mathrm{CaMg_3(CO_3)_4(s)}]$ is chosen. That huntite is such a rare mineral indicates that the conditions for formation are not common. Refluxing of Mg-rich brines through calcium carbonate minerals produces microscopic domains of dolomite (e.g., Morse and Mackenzie, 1990); huntite domains are not reported. Because the stability region of huntite lies so close the regions for calcite and magnesite (or hydromagnesite), accurate values of $\Delta G^{\circ}_{f}[\mathrm{CaMg_3(CO_3)_4(s)}]$ are needed to model pathways of evolution of these Mg-rich solutions, such as evaporated seawater.

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