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THE SOLUBILITY AND FREE ENERGY OF FORMATION OF NATURAL KUTNAHORITE

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ABSTRACT

The thermodynamic solubility-product of kutnahorite, $CaMn(CO_3)_2$, was measured following its dissolution in CO_2-saturated deionized water and dilute NaCl solutions at 5°, 25° and 40°C. The logarithm of the equilibrium ion activity products derived from solution parameters and model estimates of the ion activity coefficients are: -21.88 ± 0.06, -21.81 ± 0.07 and -21.60 ± 0.04 at 5°, 25° and 40°C, respectively. The free energy of formation of kutnahorite at 25°C and one atmosphere total pressure calculated from these results is -1961.8 kJ mol^{-1}. Discrepancy with previous measurements is interpreted to result from the formation of a disordered phase covering the surface of the mineral. This phase, "pseudokutnahorite", determines the solubility product at low temperatures. It is nearly two orders of magnitude more soluble than kutnahorite (pK° = 20.0 ± 0.1 at 25°C) but has a similar chemical composition.

Keywords: kutnahorite, pseudokutnahorite, solubility, free energy of formation.

SOMMAIRE

Le produit de solubilité thermodynamique de la kutnahorite, $CaMn(CO_3)_2$, a été déterminé suite à sa dissolution dans l'eau déionisée et des solutions diluées de NaCl saturées en CO_2 à 5°, 25° et 40°C. Les logarithmes des produits des activités ioniques à l'équilibre obtenus à partir de la composition des solutions et des coefficients d'activité estimés sont: -21.88 ± 0.06, -21.81 ± 0.07 et -21.60 ± 0.04 à 5°, 25° et 40°C, respectivement. L'énergie libre de formation de la kutnahorite à 25°C et un atmosphère de pression totale, calculée à partir de ces résultats, est égale à -1961.8 kJ mol^{-1}. L'écart par rapport aux résultats antérieurs peut s'expliquer par la formation d'une phase à structure désordonnée à la surface du solide. Cette phase, la "pseudokutnahorite", détermine le produit de solubilité à basses températures. Sa solubilité est nettement plus élevée (pK° = 20.0 ± 0.1 à 25°C) que la kutnahorite, mais sa composition chimique est similaire.

Mots-clés: kutnahorite, pseudokutnahorite, solubilité, énergie libre de formation.

INTRODUCTION

Kutnahorite, $CaMn(CO_3)_2$, is an isotype of dolomite and, in fact, has been referred to as "manganese dolomite" (Frondel & Bauer 1955). It is a relatively rare mineral. Kutnahorite and manganese-bearing calcite are usually found associated with epithermal or hydrothermal ore deposits (*e.g.*, Frondel & Bauer 1955, Bodine 1963, Tsusue 1967) and regionally metamorphosed terranes (*e.g.*, Wenk & Maurizio 1978). Authigenic kutnahorite or mixed Mn–Ca–Mg carbonate phases also appear to form in marine sediments (Lynn & Bonatti 1965, Calvert & Price 1970, Pedersen & Price 1982, Boyle 1983). Their formation may explain the observed supersaturation of deep-sea carbonate-rich pore waters in sediments with respect to calcite in the reduced manganese zone (Emerson *et al.* 1980, Sayles 1981, 1985, Boyle 1983, de Lange 1986) and could have a significant influence on the accumulation of calcite and the diagenesis of these deep-sea sediments (Piper & Williamson 1977). The accurate determination of the thermodynamic solubility of kutnahorite at low temperatures is therefore essential to the interpretation of the behavior of this mineral in natural waters.

In spite of numerous investigations on the thermodynamics of mixing in the system $CaCO_3$–$MnCO_3$ (Goldsmith & Graf 1957, de Capitani & Peters 1981, Fubini & Stone 1983, Capobianco & Navrotsky 1987) at high temperatures and the possible significance of kutnahorite formation in marine sediments, the solubility of kutnahorite at low temperatures has been the subject of only one previous study. Garrels *et al.* (1960) determined the stability of a number of carbonate minerals, including kutnahorite, following their dissolution in water saturated with carbon dioxide at 25°C and one atmosphere total pressure. The thermodynamic solubility of kutnahorite calculated from the Gibbs free energy of formation (-1950 kJ mol^{-1}, 25°C and one atmosphere total pressure) reported in their study and the free energies of formation of Ca^{2+}, Mn^{2+} and CO_3^{2-} (Robie *et al.* 1978) corresponds to a pK° = -log K° = 19.84. In this study, the solubility product of kutnahorite was measured in deionized water and dilute NaCl solutions ($\leq$ 0.2 M) at 5°, 25° and 40°C.

SAMPLE PREPARATION AND SOLUBILITY MEASUREMENTS

Samples of natural kutnahorite from Kutna-Hora, Czechoslovakia and Sterling Hill mine, New Jersey were obtained for this study. These samples were chosen because their chemical composition and powder-diffraction spectra were found to be consistent with that of end-member kutnahorite. However, the reflections that distinguish the ordered kutnahorite from a disordered equivalent cannot be detected with confidence by X-ray powder diffraction (Goldsmith & Graf 1957, Goldsmith 1983, Iwafuchi *et al.* 1983). Nevertheless, the chemical and single-crystal X-ray-diffraction analyses of samples found at these sites have confirmed the presence of kutnahorite (Frondel & Bauer 1955, Peacor *et al.* 1987). Furthermore, the mineralogy of one of the Sterling Hill samples (KH-2) was confirmed by X-ray analysis (by P. J. Dunn of the Smithsonian Institution; J.L. Baum, pers. comm.).

The samples were ground to a coarse powder (< 600 μm). The Kutna-Hora sample was found to contain large amounts of pyrite, which was removed from the carbonate with heavy liquids. Individual samples were separated into two fractions (*i.e.*, <64 μm and >64 μm) by wet sieving and dried at 110°C for several days. Each fraction was passed through a Frantz magnetic separator three times in order to remove traces of pyrite and calcite. Visible contaminants were removed with tweezers under a binocular microscope (40 ×). Finally, a portion of the samples was analyzed by atomic absorption spectrophotometry following dissolution in 20 mL of concentrated HCl (Ultrex) and dilution to 1 L in a 2000 ppm KCl solution. Aqueous standards were prepared accordingly. A physical description of the samples, results of the analyses and the calculated stoichiometry of the bulk solids are presented in Table 1.

Most of the solubility measurements presented in this study are based on the behavior of the two Sterling Hill samples. The Kutna-Hora sample was found to depart significantly from the end-member stoichiometry, and dissolution–oxidation of the associated pyrite contaminant led to misinterpretable measurements of alkalinity and pH.

TABLE 1. PHYSICAL AND CHEMICAL DESCRIPTION OF KUTNAHORITE SAMPLES USED IN THIS STUDY

Sample	Description	Location	Source
KH-1	Cleavage fragment, pink	Sterling Mine, Sussex Co., New Jersey	Excalibur Mineral Company Dover, N. J.
KH-2	Cleavage fragment, pink	Sterling Mine, Sussex Co., New Jersey	Mr. John L. Baum Hamburg, N. J.
KH-3	Small crystals, opaque, white with pyrite	Holy Trinity Church, Kutna'Hora, Czechoslovakia	Excalibur Mineral Company Dover, N.J.

Sample	Weight percent					Stoichiometry[1]
	Ca	Mn	Mg	Fe	Na	
KH-1	16.86	25.19	0.392	0.28	0.009	$Ca_{.47}Mn_{.51}Mg_{.018}Fe_{.006}CO_3$
KH-2	14.94	27.65	0.476	0.27	0.015	$Ca_{.41}Mn_{.56}Mg_{.022}Fe_{.005}CO_3$
KH-2[2]	14.78	27.32	0.479	0.30	0.005	$Ca_{.41}Mn_{.56}Mg_{.022}Fe_{.006}CO_3$
KH-3	18.97	10.05	2.24	1.84	N.D.	$Ca_{.51}Mn_{.35}Mg_{.100}Fe_{.035}CO_3$
EXP-25	14.64	27.88	0.441	0.28	N.D.	$Ca_{.41}Mn_{.57}Mg_{.020}Fe_{.006}CO_3$

[1] Assuming all cations are in a carbonate matrix.
[2] With the exception of this sample (cleavage fragment) and EXP-25 (fine-grained precipitate, see text), all other samples were analyzed after being crushed to powders. N.D.: not determined.

The solubility of kutnahorite was determined in both open and closed systems in CO_2-saturated deionized water or NaCl solutions at 5°, 25° and 40°C. Deionized water was prepared by pumping distilled water through a Millipore Milli–Q system. The resistivity of the deionized water was always greater than 15 Mohm cm^{-1}. Dilute NaCl solutions were prepared with reagent-grade chemical dissolved in deionized water. Instrumental-grade (>99.99%) carbon dioxide was used to saturate the initial solutions and maintain the $P(CO_2)$ constant during the open-system experiments.

In the open system, 0.8 to 4.0 g of kutnahorite was suspended in 350 mL of a filtered (0.45 μm Millipore) solution presaturated in CO_2. The temperature of the solution was maintained at ±0.1°C by circulating water through the jacketed reaction vessel from a constant-temperature bath. The 500-mL reactor was fitted with a PVC lid with holes for insertion of a gas-dispersion tube, combination glass electrode, stirrer, and for addition and withdrawal of solution. Stirring of the solution was provided by a two-bladed glass propeller powered by an adjustable electric motor mounted above the reaction vessel. This system prevented grinding of the kutnahorite particles against the bottom of the reaction vessel by a magnetic stirrer.

During a typical run, 10 to 15 aliquots of the equilibrating solution were withdrawn, filtered through a 0.45 μm Millipore filter and analyzed to follow the stoichiometry of the dissolving solid as a function of time. The volume of the equilibrating solution was maintained constant during the first twelve hours by replenishment with the filtered CO_2-saturated starting solution. In general, dissolutions were carried out for 24 to 96 hours. The concentrations of dissolved Ca, Mn and Mg in each aliquot were determined by atomic absorption spectrophotometry (Perkin–Elmer model 5100) in an air–acetylene flame following appropriate dilution with a 10% HCl solution. Blanks and aqueous standards were prepared to match the composition of the unknown solutions (*i.e.*, deionized water or NaCl solution in 10% HCl). The precision of these analyses is estimated to be better than ±3%. Carbonate alkalinity (*i.e.*, $A_C = [HCO_3^-] + 2[CO_3^{2-}]$) and chloride ion concentration in the aliquots were determined by potentiometric titrations, using standardized dilute HCl solutions and $AgNO_3$ solutions, respectively. Detection of the end point was computed by the second derivative method using a Radiometer TTT81 digital titrator. The precision of these

TABLE 2. MEASUREMENTS OF OPEN-SYSTEM SOLUBILITY OF KUTNAHORITE IN DEIONIZED WATER AND DILUTE NaCl SOLUTIONS AT 5°, 25° AND 40°C

EXP#	T (°C)	Sample	W_{solid} (g)	[NaCl] (M)	time (hour)	$[Ca^{2+}]$	$[Mn^{2+}]$	$[Mg^{2+}]$	A_c (meq/l)	pH	Stoichiometry	pK_K°
						(mole/l x 10^5)						
16	5.0	KH-2	1.800	0.0	∞/47.75[1]	73.0	91.5	5.41	3.53	5.30	$Mn_{.534}Ca_{.433}Mg_{.031}CO_3$	21.95
17	5.0	KH-2	2.003	0.0	∞/46	74.5	99.0	4.42	3.91	5.30	$Mn_{.556}Ca_{.419}Mg_{.025}CO_3$	21.83
18	5.0	KH-2	1.800	0.0	∞/74.25	72.0	95.0	4.64	3.75	5.30	$Mn_{.552}Ca_{.421}Mg_{.027}CO_3$	21.89
19	5.0	KH-2	2.000	0.0	∞/92.5	78.0	100	5.00	3.81	5.30	$Mn_{.547}Ca_{.426}Mg_{.027}CO_3$	21.83
1	25.0	KH-1	0.996	0.0	∞/7.5	61.5	70.0	2.83	2.97	5.30	$Mn_{.539}Ca_{.439}Mg_{.021}CO_3$	21.82
3	25.0	KH-1	1.971	0.0	28	58.7	69.2	3.00	2.883	5.299	$Mn_{.528}Ca_{.448}Mg_{.023}CO_3$	21.86
4	25.0	KH-1	1.500	0.0	∞/31	59.0	69.0	3.00	2.90	5.32	$Mn_{.527}Ca_{.450}Mg_{.022}CO_3$	21.82
5	25.0	KH-1	1.197	0.0	∞/28.5	67.0	73.0	2.64	2.87	5.32	$Mn_{.507}Ca_{.473}Mg_{.020}CO_3$	21.76
6	25.0	KH-1[1]	0.800	0.0	25	72.1	74.8	3.35	2.891	5.340	$Mn_{.504}Ca_{.474}Mg_{.023}CO_3$	21.67
7	25.0	KH-1[1]	1.000	0.0	21	71.1	73.2	3.25	2.963	5.320	$Mn_{.494}Ca_{.484}Mg_{.022}CO_3$	21.71
8	25.0	KH-2	1.500	0.0	53	72.3	75.4	3.63	2.591	5.268	$Mn_{.502}Ca_{.474}Mg_{.024}CO_3$	21.90
9	25.0	KH-2	2.011	0.0502	∞/22	87.5	101	5.03	4.04	5.35	$Mn_{.522}Ca_{.452}Mg_{.026}CO_3$	21.74
10	25.0	KH-2	2.000	0.0503	∞/22	85.0	95.5	4.50	3.69	5.34	$Mn_{.516}Ca_{.459}Mg_{.024}CO_3$	21.88
11	25.0	KH-2	2.004	0.0508	45	79.3	100.5	4.89	3.828	5.33	$Mn_{.542}Ca_{.431}Mg_{.026}CO_3$	21.88
12	25.0	KH-2	1.800	0.0508	51	86.1	103.9	4.25	3.720	5.340	$Mn_{.532}Ca_{.441}Mg_{.026}CO_3$	21.83
13	25.0	KH-2	2.500	0.201	48	106	134	5.70	4.848	5.342	$Mn_{.540}Ca_{.431}Mg_{.029}CO_3$	21.88
14	25.0	KH-2	2.000	0.201	∞/29	118	135	5.00	4.87	5.38	$Mn_{.523}Ca_{.457}Mg_{.019}CO_3$	21.74
15	25.0	KH-1	1.800	0.203	∞/35	108	125	5.34	4.88	5.38	$Mn_{.524}Ca_{.453}Mg_{.022}CO_3$	21.82
20	40.0	KH-2	1.900	0.0	∞/53	53.5	68.5	3.22	2.53	5.40	$Mn_{.546}Ca_{.428}Mg_{.026}CO_3$	21.61
21	40.0	KH-1&KH-2	2.000	0.0	54	51.5	69.2	3.14	2.715	5.404	$Mn_{.559}Ca_{.416}Mg_{.024}CO_3$	21.55
22	40.0	KH-2	1.200	0.0	77.25	52.9	68.4	2.95	2.512	5.395	$Mn_{.551}Ca_{.425}Mg_{.024}CO_3$	21.61
23	40.0	KH-2	1.500	0.0	77.25	53.9	65.9	2.72	2.405	5.411	$Mn_{.540}Ca_{.438}Mg_{.022}CO_3$	21.64

[1] ∞/time means that equilibrium solution parameters were extrapolated to infinite time using inverse time plots.

titrations was better than 0.4%. Measurements of pH were made using a combination glass electrode (Radiometer GK2401C) in unstirred solutions with the bubbler raised over the solution, immediately before sampling the solution. The electrode was calibrated before and after each measurement with a set of three NBS buffers (4.008, 6.865 and 7.413 at 25°C: Bates 1973). The precision of the pH measurements was estimated to be better than ±0.005 pH units.

The procedure used for the closed-system measurements has been described previously (Mucci 1983). Kutnahorite (0.5 g) was added to 60 mL polycarbonate bottles filled with filtered CO_2-saturated deionized water and placed in a constant-temperature water bath. After various periods of equilibration, 6 to 69 days, the bottles were stabilized and kutnahorite allowed to settle before the pH of the solution was measured. The combination electrode was inserted in the neck of the bottle as soon as it was opened. The electrode was fitted with a piece of Tygon tubing and Parafilm to form an air-tight seal to prevent CO_2 exchange with the atmosphere. Immediately after the pH measurement, the solution was drawn from the bottle using a 60 cm^3 syringe, filtered through a 0.45 μm Millipore filter, and analyzed as described above.

RESULTS

Experimental results of the open- and closed-system measurements are presented in Tables 2 and 3, respectively. In some open-system experiments, equilibrium was not reached, and the data (*i.e.*, pH, $[Ca^{2+}]$, $[Mn^{2+}]$) were extrapolated linearly to infinite time using inverse time plots ($t^{-1/2} = 0$, Fig. 1). Results obtained from extrapolation compare favorably with those for which the solution reached equilibrium (see Table 2). Reaction times required to reach equilibrium decreased with increasing amounts of reacted solid but most significantly with increasing temperature.

The stoichiometry of the dissolving solid was calculated from the slope of the $[Ca^{2+}]$, $[Mg^{2+}]$ and alkalinity *versus* $[Mn^{2+}]$ in the solution during the period of dissolution (Fig. 2). In all cases, the composition of the dissolving solid corresponds closely to its bulk composition (Tables 1, 2).

The thermodynamic solubility-product of kutnahorite is defined as the equilibrium constant for the dissolution reaction of the mineral into its ionic components:

$$CaMn(CO_3)_2 \rightleftharpoons Ca^{2+} + Mn^{2+} + 2\,CO_3^{2-} \qquad (1)$$

therefore,

$$K_{sp}^{\circ} = a_{Ca^{2+}}\, a_{Mn^{2+}}\, (a_{CO3^{2-}})^2 \qquad (2)$$

$$= \{[Ca^{2+}][Mn^{2+}][CO_3^{2-}]^2\}\,\{\gamma_t(Ca^{2+})\gamma_t(Mn^{2+})\gamma_t(CO_3^{2-})^2\} \qquad (3)$$

$$= \{[Ca^{2+}]_f[Mn^{2+}]_f[CO_3^{2-}]_f{}^2\}\,\{\gamma_f(Ca^{2+})\gamma_f(Mn^{2+})\gamma_f(CO_3^{2-})^2\} \qquad (4)$$

and,

$$pK^{\circ} = -\log K^{\circ} \qquad (5)$$

where K_{sp}° is the equilibrium thermodynamic solubility-product and a_i, [i], and γ_t(i) are, respectively, the thermodynamic activity, total concentration and activity coefficient of species i. The subscript "f" refers to the free (*i.e.*, uncomplexed) rather than total ion concentrations and activity coefficients. According to these definitions, the activity of the one-phase solid is equal to unity.

The free-ion concentration of the ionic species involved in the reaction were calculated using a slightly modified version of WATEQF (Plummer *et al.* 1976, Ball *et al.* 1980). Free-ion activity coefficients were estimated from an extended Debye–Hückel equation (Plummer & Busenberg 1982). Association constants for the various species considered in the calculations are presented in Table 4. Whereas other ion pairs (*e.g.*, $MnCO_3^{\circ}$) are undoubtedly present in the experimental solutions, they need not be considered explicitly. A pK° of 19.94 is obtained if the solubility is recalculated from the equilibrium pH of Garrels *et al.* (1960), 5.58 ($P(CO_2) = 1$ and $[Ca^{2+}] = [Mn^{2+}]$), and these ion-interaction parameters.

The thermodynamic solubility-products determined from the open-system experiments are presented in Table 2. The data obtained at 25°C in solutions of various NaCl concentrations are plotted as a function of the square root of the ionic

TABLE 3. CLOSED-SYSTEM SOLUBILITY OF KUTNAHORITE IN DEIONIZED WATER AT 25°C

Solid	Equilib. period (days)	$[Ca^{2+}]$	$[Mn^{2+}]$	$[Mg^{2+}]$	A_c (meq/L)	pH	pK°
		(mole/L x 10^5)					
KH-1,2	6	67.4	79.7	3.63	3.191	5.458	21.36
KH-2	8	72.9	79.2	---	3.165	5.527	21.24
KH-1,2	13	66.9	80.6	3.68	3.208	5.649	20.97
KH-2	18	92.6	84.8	3.48	3.246	5.805	20.56
KH-1,2	20	70.9	81.0	3.68	3.256	5.836	20.56
KH-1,2	33	69.4	78.8	3.55	3.170	6.154	20.02
KH-1,2	69	65.4	48.7	--	2.516	6.825	19.99

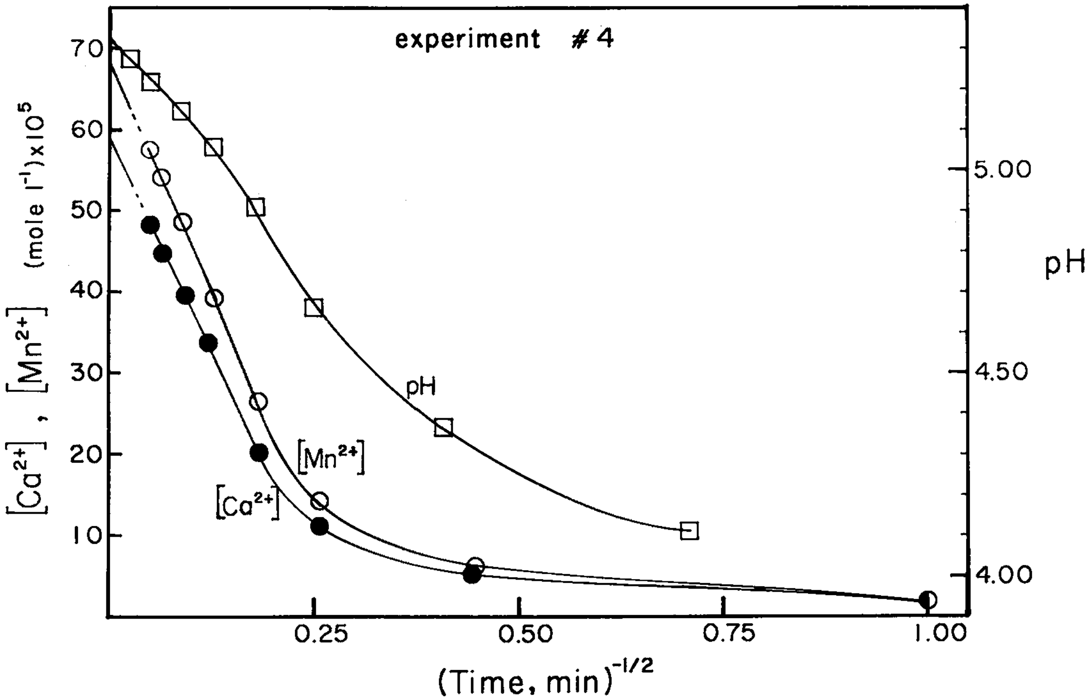

FIG. 1. Inverse time plot and extrapolation of pH, $[Ca^{2+}]$ and $[Mn^{2+}]$ following the dissolution of kutnahorite in deionized water at 25°C in an open system (Expt. #4).

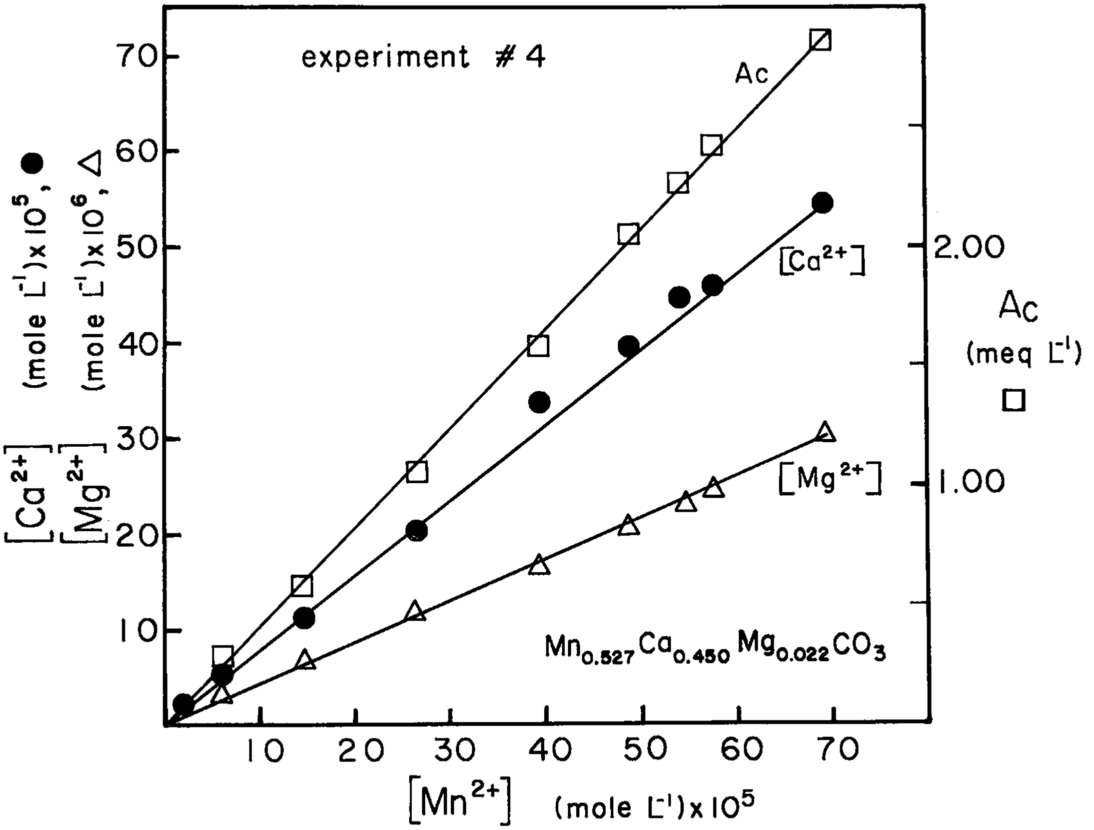

FIG. 2. Stoichiometry of dissolving kutnahorite in CO_2-saturated deionized water at 25°C in an open system (Expt. #4). A_C is the carbonate alkalinity.

strength in Figure 3. The consistency of the calculated pK° with increasing ionic strength appears to indicate that the association model used in this study is adequate in describing ionic interactions over the range of concentrations investigated. Results of individual dissolution-experiments at a given temperature were averaged and values of -21.88 ± 0.06, -21.81 ± 0.07 and -21.60 ± 0.04 were obtained for the logarithm of the equilibrium constants at 5°, 25° and 40°C, respectively.

Nearly a month was required for the solid to reach equilibrium in the closed-system experiments. After this period, the calculated pK° (average of two measurements for t ≥ 33 days, see Table 3) was 20.00 ± 0.02 at 25°C.

DISCUSSION

Previous measurements

The solubility of kutnahorite determined in this study at 25°C in the open system is almost two orders of magnitude lower than the value determined by Garrels *et al.* (1960). In their experiments, Garrels *et al.* (1960) added several grams of finely ground carbonate to 500 mL of distilled water maintained at a constant CO_2 partial pressure of one atmosphere. The solution was stirred with a teflon-coated magnetic bar, and the equilibrium pH was obtained from extrapolation after 12 to 18 hours of reaction. Garrels *et al.* (1960) only monitored variations of pH with time and would not have observed that the dissolution of kutnahorite becomes incongruent after an initial period of congruent dissolution. In an attempt to reproduce their results, ~4 grams of kutnahorite were allowed to equilibrate with distilled water at 25°C for a period of more than 8 days. After reaching an ion activity product approaching equilibrium (log IAP = -21.81 at approximately 24 hours), the $[Ca^{2+}]/[Mn^{2+}]$ ratio decreased slightly before increasing above the stoichiometry of the dissolving solid, whereas the variation of pH with time increased markedly. The extrapolated pH following the onset of the incongruent episode was 5.58, a value identical to that reported by Garrels *et al.* (1960). As indicated above, this equilibrium pH corresponds to a pK° of 19.94, similar to the results of the closed-system solubility measurements.

It should be noted that the more rapid attainment of an apparent equilibrium pH in the experiments of Garrels *et al.* (1960) can be attributed to the larger amount of solid used, the size of the solid grains and, possibly, the grinding of these grains by the magnetic stirrer during dissolution. These facts could also explain their failure to observe the initial congruent dissolution of kutnahorite during their experiments.

The onset of the episode of incongruent dissolution could be interpreted to indicate the formation of a disordered mixed carbonate phase on the surface of the mineral grains. The "disordered kutnahorite" (Peacor *et al.* 1987) or "pseudokutnahorite" (Capobianco & Navrotsky 1987), which is more likely to form than kutnahorite at low temperatures (Goldsmith & Graf 1957, Fubini & Stone 1983, Capobianco & Navrotsky 1987), would be responsible for the observed increased solubility.

After 7 days of equilibration, a very fine-grained precipitate formed overnight as a result of a power failure and lack of stirring. A temporary decrease in $P(CO_2)$ resulted in an increase of the saturation state of the solution and eventual precipitation. The precipitate remained in suspension without stirring. It was separated from the kutnahorite that settled at the bottom of the reactor, filtered on a 0.45 µm Millipore filter, washed with Milli-Q water and dried at room temperature. The solid was analyzed by X-ray diffraction and by atomic absorption spectrophotometry after dissolution in HCl as described above. The stoichiometry of the precipitate, $Mn_{0.57}Ca_{0.41}Mg_{0.020}Fe_{0.006}CO_3$, is similar to that of the starting material (EXP-25, Table 1). Preliminary refinement of the structure using the Rietveld method (Rietveld 1967, 1969, Raudsepp *et al.* 1990) and peak-width data show significant differences in microstructure between the laboratory precipitate and the kutnahorite starting material (F.C. Hawthorne and M. Raudsepp, pers. comm.). The laboratory precipitate is disordered but well crystallized as opposed to the natural kutnahorite, which gives much broader diffraction peaks, as are often observed in natural dolomite. Further structural work is under way to better define occupancy in the two cationic sites.

TABLE 4. SUMMARY OF RELEVANT THERMODYNAMIC DATA

Reaction	-log k			Source
	5°C	25°C	40°C	
$CaHCO_3^+ = Ca^{2+} + HCO_3^-$	0.90	1.11	1.18	1
$MgHCO_3^+ = Mg^{2+} + HCO_3^-$	1.02	1.07	1.11	2
$MnHCO_3^+ = Mn^{2+} + HCO_3^-$	1.26	1.28	1.33	3
$NaHCO_3^\circ = Na^+ + HCO_3^-$		-0.25		4
$CaCO_3^\circ = Ca^{2+} + CO_3^{2-}$	3.13	3.22	3.38	1
$MgCO_3^\circ = Mg^{2+} + CO_3^{2-}$	2.85	2.98	3.08	3
$NaCO_3^- = Na^+ + CO_3^{2-}$		1.27		5
$MnCl^+ = Mn^{2+} + Cl^-$		0.607		3
$MnCl_2^\circ = Mn^{2+} + 2Cl^-$		0.041		3
$MnCl_3^- = Mn^{2+} + 3Cl^-$		-0.305		3
$CO_2(g) = CO_2(aq)$	1.192	1.468	1.625	1
$CO_2(aq) + H_2O = H^+ + HCO_3^-$	6.516	6.352	6.297	1
$HCO_3^- = H^+ + CO_3^{2-}$	10.554	10.329	10.222	1

Sources: 1 Plummer & Busenberg (1982), 2 Lesht & Bauman (1978), 3 Ball et al. (1980), 4 Garrels et al. (1961), 5 Garrels & Thompson (1962).

Thermodynamic properties

The Gibbs free energy of the reaction (Eqn. 1) can be calculated according to the following relation:

$$\Delta G_r^\circ = -RT \ln K_{sp}^\circ \qquad (6)$$

where R is the gas constant (≡ 8.314 J K^{-1} mol^{-1}) and T is in K. The values calculated from the solubility constants at 5°, 25° and 40°C are 116.5 ± 0.3, 124.5 ± 0.4 and 129.5 ± 0.2 kJ mol^{-1}, respectively. The standard free energy of formation of kutnahorite is obtained from the free energy of the reaction (Eqn. 1) and the free energies of formation ΔG_f° of the species involved in the reaction:

$$\Delta G^\circ_{f\,CaMn(CO3)2} = \Delta G^\circ_{f\,Ca^{2+}} + \Delta G^\circ_{f\,Mn^{2+}} + 2\Delta G^\circ_{f\,CO_3^{2-}} - \Delta G_r^\circ \qquad (7)$$

Substituting the value of ΔG_r° obtained from Eqn. (6) at 25°C and the ΔG_f° of the ions (Robie *et al.* 1978) into Eqn. (7), $\Delta G^\circ_{f\,kutnahorite}$ = (-553.54) + (-228.0) + 2(-527.9) - 124.5 = -1961.8 kJ mol^{-1} at 25°C and 1 atm. total pressure.

In contrast to calcite, experimental results indicate that the solubility of kutnahorite decreases slightly with decreasing temperature. The influence of temperature on the equilibrium constant is given by the Van't Hoff equation:

$$\frac{\delta \ln K}{\delta T} = \frac{\Delta H^\circ}{RT^2} \qquad (8)$$

where ΔH° is the standard enthalpy change for a given reaction. If ΔH° is constant over the range of temperatures investigated, Eqn. (7) can be integrated to yield:

$$\ln \frac{K(T_2)}{K(T_1)} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad (9)$$

A value of ΔH_r° on the order of 12.6 kJ mol^{-1} is obtained. Whereas ΔH_r° may not be constant over

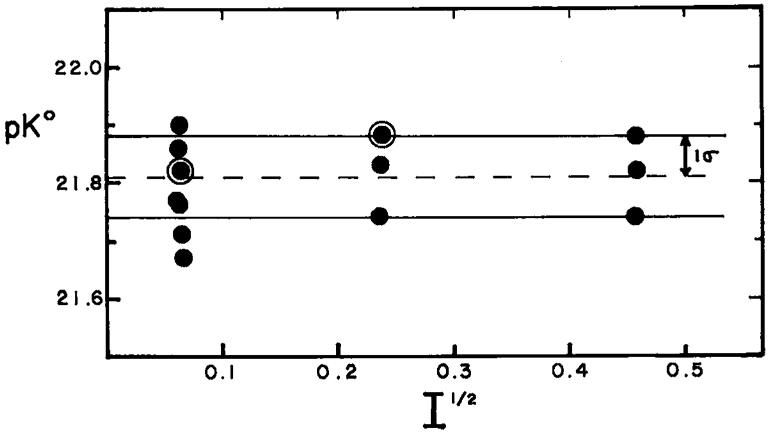

FIG.3. The equilibrium ion activity product of kutnahorite in water and dilute NaCl solutions at 25°C as a function of the square root of the ionic strength.

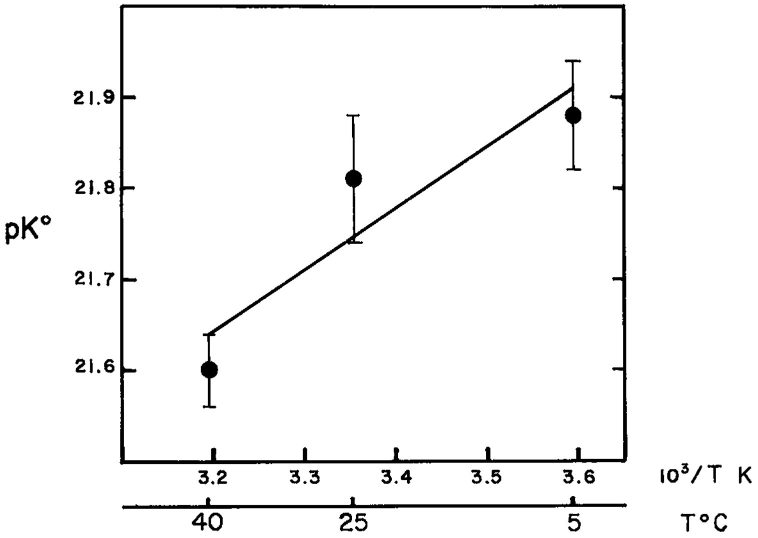

FIG. 4. The solubility of kutnahorite in water as a function of the inverse of temperature over the range investigated.

the temperature range investigated in this study (see Fig. 4), the number of determinations and the associated standard errors do not allow for a more accurate estimate.

CONCLUSION

The solubility of kutnahorite was measured in deionized water and dilute NaCl solutions at 5°, 25° and 40°C. The long-term solubility behavior of the mineral indicates that it is unlikely that an ordered phase would form at these low temperatures. This is supported by the observation that the precipitation of a disordered phase following the onset of an incongruent dissolution of kutnahorite controls the ion activity product of $CaMn(CO_3)_2$ in solution. This phase, "pseudokutnahorite", of similar chemical composition to kutnahorite, is nearly two orders of magnitude more soluble than the ordered mineral.

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