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Short Communication

Solid-Solute Phase Equilibria in Aqueous Solutions X. Solubility Constant and Stability of Norsethite[a]

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Summary. The solubility constant of norsethite, $BaMg(CO_3)_2$, was determined for the first time. Also, a new method was developed which permits the precipitation of pure norsethite from homogeneous solution. The solubility measurements were performed at 25°C in $0.20\,mol \cdot dm^{-3}$ sodium perchlorate media of constant ionic strength. It was shown that norsethite dissolves congruently in this solution. The *pH* variation method was used to obtain a stoichiometric solubility constant which was extrapolated to zero ionic strength by use of the *Davies* equation.

The resulting thermodynamic solubility constant was incorporated in a comprehensive computer model which permits solubility calculations in complex systems. Thus, the conditions for norsethite formation in the environment and in the laboratory can be predicted. Furthermore, the stability of norsethite with respect to witherite ($BaCO_3$) and the various magnesium carbonate phases was calculated.

Keywords. Solubility; Thermodynamic data; Stability; Norsethite; Witherite; Carbonates.

Phasengleichgewichte in wäßrigen Lösungen, 10. Mitt. Löslichkeitskonstante und Stabilität von Norsethit (Kurze Mitt.)

Zusammenfassung. Die Löslichkeitskonstante von Norsethite, $BaMg(CO_3)_2$, wurde erstmals bestimmt. Es wurde auch eine neue Methode entwickelt, die die Ausfällung von reinem Norsethit aus homogener Lösung gestattet. Die Löslichkeitsmessungen wurden bei 25°C in $0.20\,mol \cdot dm^{-3}$ $NaClO_4$-Lösungen konstanter Ionenstärke durchgeführt. Es konnte gezeigt werden, daß sich Norsethit unter diesen Bedingungen kongruent löst. Mit Hilfe der *pH*-Variationsmethode wurde eine stöchiometrische Löslichkeitskonstante erhalten, die mit der *Davies*-Gleichung auf unendliche Verdünnung extrapoliert wurde.

Die erhaltenen Daten wurden in ein Computermodell zur Berechnung von Löslichkeiten in komplexen Systemen aufgenommen, mit dem die Bedingungen für die Bildung von Norsethit in der Natur und im Laboratorium vorhergesagt werden können. Außerdem wurde die Stabilität von Norsethit in bezug auf Witherit ($BaCO_3$) und verschiedene Magnesiumcarbonatphasen berechnet.

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[a] For Part IX, see Ref. [1]

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Introduction

Norsethite, $BaMg(CO_3)_2$, was first discovered in the Westvaco trona mine in Wyoming [2]. Although it is an uncommon mineral, norsethite has received a considerable amount of attention because it is structurally related to dolomite, $CaMg(CO_3)_2$, but can be formed at low temperature [3]. Therefore, the study of the stability relations of norsethite may help to understand the origin of dolomite and other ordered rhombohedral double carbonate minerals [4].

The first synthetic norsethite was prepared by the solid state reaction of $BaCO_3$ and $MgCO_3$ at 500°C [5]. Later, the method to synthesise norsethite progressed to the reaction of solid $BaCO_3$ with dilute $MgCl_2$ and $NaHCO_3$ solutions at room temperature [6]. Nesquehonite ($MgCO_3 \cdot 3H_2O$) can also be used as the source of Mg^{2+} [7]. The synthesis of norsethite was then improved to the direct precipitation from Ba^{2+}, Mg^{2+}, and CO_3^{2-} solutions [4]. It has also been reported that norsethite can be formed by grinding a mixture of Na_2CO_3, barium chloride, and magnesium chloride [8]. Recently, the vibrational spectra of norsethite have been measured, and the thermodynamic solubility product has been predicted [9].

In the present study, the solubility constant of norsethite was determined experimentally for the first time. Also, a new method was developed which permits the precipitation of pure norsethite from homogeneous solution. The stability of norsethite with respect to witherite ($BaCO_3$) and various magnesium carbonates was derived using the thermodynamic solubility constant obtained in this work.

Results and Discussion

Solubility constant of norsethite

X-ray diffractograms and SEM photos of our norsethite samples taken before and after the solubility measurements confirmed that no other phase was formed during the experiments. The solubility constant of norsethite according to the reaction

$$1/2\,\mathrm{BaMg(CO_3)_{2(s)}} + 2\,\mathrm{H}^+_{(I)} \rightleftharpoons 1/2\,\mathrm{Ba}^{2+}_{(I)} + 1/2\,\mathrm{Mg}^{2+}_{(I)} + \mathrm{CO_{2(g)}} + \mathrm{H_2O}_{(I)} \qquad (1)$$

was determined as $\log{}^*K_{ps0} = 10.06 \pm 0.04$ at 298.15 K and $I_c = 0.20\,\mathrm{mol \cdot dm^{-3}}$ $NaClO_4$. The ratio of $[Ba^{2+}]$ to $[Mg^{2+}]$ in the solution was found to be 0.99±0.03; this proves that norsethite dissolves congruently. The results obtained in our laboratory are shown in Fig. 1.

Three phase equilibrium norsethite-witherite-solution

In order to understand the three phase equilibrium norsethite-witherite-solution properly, an accurately determined solubility constant of witherite is necessary. The solubility of witherite can be represented as

$$\mathrm{BaCO_{3(s)}} + 2\,\mathrm{H}^+_{(I)} \rightleftharpoons \mathrm{Ba}^{2+}_{(I)} + \mathrm{CO_{2(g)}} + \mathrm{H_2O}_{(I)}, \qquad (2)$$

and the corresponding solubility constant was determined as $\log{}^*K_{ps0} = 9.96 \pm 0.02$ at 298.15 K and $I_c = 0.20\,\mathrm{mol \cdot dm^{-3}}$ $NaClO_4$.

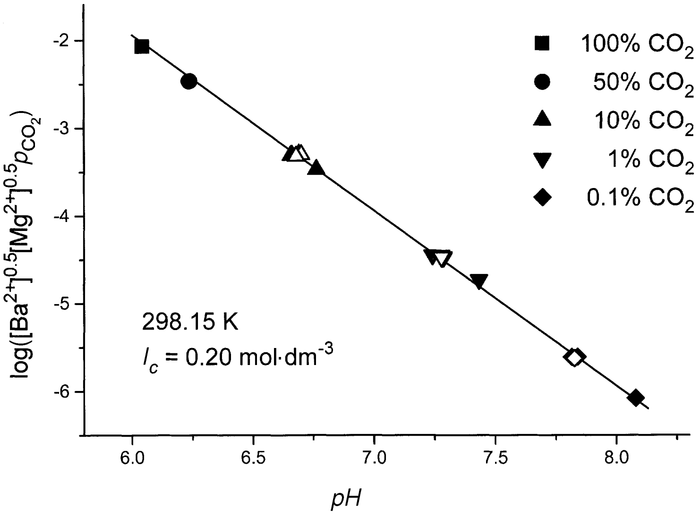

Fig. 1. Solubility of norsethite at 298.15 K and $I_c = 0.20\,\text{mol}\cdot\text{dm}^{-3}$ $NaClO_4$; open symbols correspond to the three-phase equilibrium norsethite-witherite-solution; the straight line has the theoretical slope of -2

The experimental values for the solubility of norsethite in the presence of witherite are shown as open symbols in Fig. 1. The results of this study were found to be $\log{}^*K_{ps0} = 10.08 \pm 0.04$ for norsethite, $\log{}^*K_{ps0} = 9.97 \pm 0.05$ for witherite, and $[Ba^{2+}]/[Mg^{2+}] = 0.62 \pm 0.05$. The solubility constants of norsethite and witherite determined here are much the same as those obtained in pure norsethite or witherite solutions. However, the ratio of $[Ba^{2+}]$ to $[Mg^{2+}]$ indicates the precipitation of witherite by the obvious action of the added $BaCO_3$ as seed crystals.

Subtracting Eq. (1) from Eq. (2) results in Eq. (3) which represents the three phase equilibrium norsethite-witherite-solution:

$$2\,BaCO_{3(s)} + Mg^{2+}_{(l)} \rightleftharpoons BaMg(CO_3)_{2(s)} + Ba^{2+}_{(l)} \tag{3}$$

$\log K$ of this reaction is -0.20; thus, the resulting ratio $[Ba^{2+}]/[Mg^{2+}]$ is 0.63 which agrees very well with the value determined experimentally (see above).

It should be noted that the solubility product $\log K_{s0}$ of witherite obtained in this work by converting $\log{}^*K_{ps0}$ to $\log K_{s0}$ after extrapolation to zero ionic strength employing the *Davies* equation [10] is by 0.10 higher than the value determined by *Busenberg* and *Plummer* ($\log K_{s0} = -8.56$ [11]). However, these authors reported that the $BaCO_3$ synthesized by them was significantly coarser than most of the commercial reagent grade materials; therefore, their solubility product is expected to be slightly lower than ours. The excellent agreement between the calculated and experimentally determined $[Ba^{2+}]/[Mg^{2+}]$ ratio strongly supports the reliability and internal consistency of the solubility constants obtained in this work. Moreover, our $\log K_{s0}$ value (-8.36) for norsethite and that predicted by *Böttcher et al.* [9] agree within the usual experimental error.

Stability of norsethite at 298.15 K

The solubility constants of norsethite and witherite determined in this work were incorporated into our carbonate database to calculate the stability of norsethite at 298.15 K. Solubility constants of the other phases have been reported by *Königsberger et al.* [12]. The results of the calculation are:

1. witherite + magnesite $\rightleftharpoons$ norsethite

$$\Delta G^{\ominus} = 3.77\,\mathrm{kJ \cdot mol^{-1}}$$

2. witherite + nesquehonite $\rightleftharpoons$ norsethite + 3 H_2O

$$\Delta G^{\ominus} = -16.6\,\mathrm{kJ \cdot mol^{-1}}$$

3. witherite $+\frac{1}{5}$ (hydromagnesite + CO_2) $\rightleftharpoons$ norsethite + H_2O

$$\Delta G^{\ominus} = -13.8\,\mathrm{kJ \cdot mol^{-1}}$$

Thus, saturated solutions of congruently soluble norsethite are supersaturated with respect to magnesite and witherite. However, magnesite does not precipitate under ambient conditions and, only the addition of seed crystals of witherite results in the precipitation of $BaCO_3$. The corresponding three-phase equilibrium is attained easily.

Synthesis of norsethite

The main advantage of the method developed in our laboratory is that rather large quantities of pure norsethite can be obtained in a relatively short period of time. The yield is about 2.5 g norsethite for every litre of one month old solution containing Ba^{2+}, Mg^{2+}, and HCO_3^-. It should be noted that proper composition of the solutions is very important in order to produce pure norsethite. If one ingredient

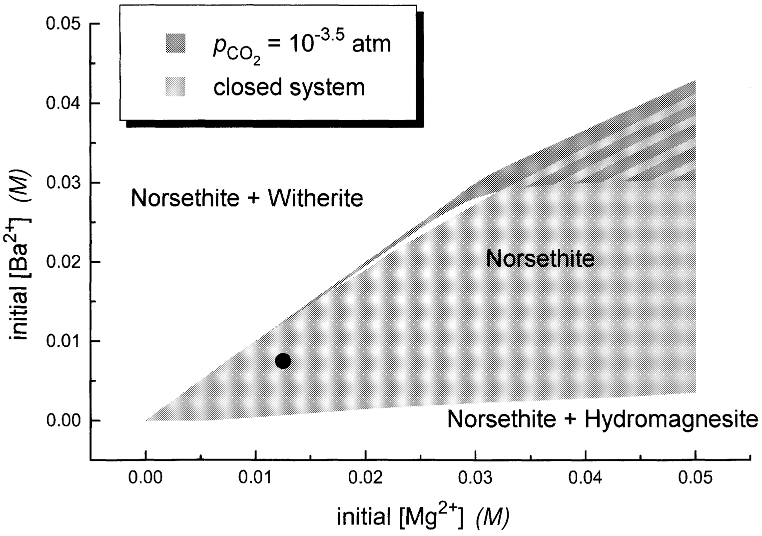

Fig. 2. Prediction for the precipitation of norsethite from 0.125 *M* $NaHCO_3$ solution; the dot corresponds to our experimental conditions for the synthesis of norsethite

is out of its portion, the product will be either witherite or hydrated magnesium carbonate or a mixture of one of these with norsethite [4, 6, 7].

The prediction of the precipitation of pure norsethite from 0.125 M $NaHCO_3$ solution was performed using ChemSage [13] and is shown in Fig. 2. It can clearly be seen that it is much easier to prepare norsethite in a closed system since the field for the formation of pure norsethite is much larger than in a system which is open to the atmosphere. This is in accordance with our experiments that a mixture of norsethite and hydromagnesite was obtained in the containers which were not very tight during the synthesis process. The computer simulation also shows that the carbonate solutions [4] are less favourable in comparison to the closed hydrogencarbonate system (a much narrower Ba^{2+} and Mg^{2+} concentration range was calculated).

The formation of norsethite in trona mines at ambient temperature and atmospheric CO_2 partial pressure can also be explained using the thermodynamic data derived in this work.

Experimental

Analytical grade reagents, bidistilled water, and prehumidified high purity (99.996%) CO_2 gas or defined CO_2/N_2 mixtures were employed throughout. Witherite was a commercial product of Fluka ($\geq$99%) and used without further purification. Solubility measurements were performed by the *pH* variation method at a constant ionic strength of $0.20\,\mathrm{mol\cdot dm^{-3}}$ in glass jacketed semi-micro cells [14] thermostatted at 25±0.03°C. The galvanic cell can be represented as

$$\mathrm{Ag|AgCl|0.01\,mol\cdot dm^{-3}\,NaCl/0.19\,mol\cdot dm^{-3}\,NaClO_4}$$
$$\mathrm{|0.20\,mol\cdot dm^{-3}\,NaClO_4|\,test\ solution\,(}I_\mathrm{c}\mathrm{ = 0.20\,mol\cdot dm^{-3}\,NaClO_4)|\,GE}$$

where GE is a glass electrode (Hamilton slimtrode P/N: 238’150). The Ag|AgCl reference electrodes of thermal-electrolytic type were home made and equipped with *Wilhelm*-type salt bridges [15]. Details of the potentiometric measurements and the electrode calibration are given in Ref. [1].

In this work, the precipitation of norsethite was achieved by adding an equal volume of a 0.25 M $NaHCO_3$ solution to a solution containing 0.015 M $BaCl_2$ and 0.025 M $MgCl_2$. The container was tightly closed, the mixture was left at room temperature for one day, and then placed in a water bath. The solution was kept at 80°C and gently shaken for about four weeks. The purity of the norsethite was checked by chemical and X-ray diffraction analyses. The concentrations of Ba^{2+} and Mg^{2+} were determined by AAS (Hitachi 8001).

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