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Abstract

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ON THE POLYTHERM OF SOLUBILITY OF THE SYSTEM
$(CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3)—H_2O$

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The specific features of the reciprocal system $(CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3)—H_2O$ required a special approach to its study. The method of isothermal dissolution of salt mixtures ([1]) that was used excluded the possibility of formation of metastable phases of the system (basic magnesium salts, trihydrate, aragonite, etc.), which complicate the investigation. Gradual, though very prolonged, isothermal dissolution of prepared mixtures of dolomite with salts of the system, with continuous stirring and with strictly defined experimental conditions maintained, made it possible to determine the general picture of equilibria and the conditions of stable existence of dolomite $(CaCO_3 \cdot MgCO_3)$ in the system at temperatures of 0, 25, 55, partially 70°, and at a partial pressure of carbon dioxide of about one atmosphere; for the 25° isotherm the CO_2 isobar ~ 0.0012 atm was additionally studied.

For a graphical representation of the results of the investigation, a quadrangular prism was used, on whose edges the temperature values were plotted, while on the base (a square) the compositions of the solutions were marked, expressed in Janecke percentages with the ratio $Ca^{2+} + Mg^{2+} = 100$ and $2HCO_3^- + SO_4^{2-} = 100$.

The isotherms 0, 25, 55, and 70° shown in Fig. 1 are sections through the prism, and lines *a*, *b* are projections of the polythermic curves corresponding to the joint crystallization of three phases. Both these curves, delimiting the field of existence of dolomite in the polytherm, gradually approach each other as the temperature is raised.

Study of the 25° isotherm at low partial pressure of CO_2 (about 0.0012 atm) showed that, with an overall sharp decrease in the solubility of all carbonates of the system (see Table 1), the field of dolomite among them is the smallest (Fig. 2,1),

Table 1

Solubility of the system $(CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3)—H_2O$ **at 25°**

No. of points	P_{CO2}, atm	Ca	Mg	$(HCO_3)_2$	SO_4	Ca	Mg	$(HCO_3)_2$	SO_4	Solid phases
		Composition of solutions, mM in 1000 g of solution	Composition of solutions, % according to Janecke							
1	1	8.10	1.18	9.28	–	87.28	12.72	100.0	–	dolomite (d) + calcite
2	0.0012	0.39	0.94	1.36	–	28.68	71.32	100.0	–	d + calcite
3	1	21.10	1.07	9.03	13.14	95.17	4.83	40.73	59.27	d + calcite + gypsum
4	0.0012	15.33	2.58	0.39	17.52	85.60	14.40	2.18	97.82	d + calcite + gypsum
5	1	2.50	11.26	13.76	–	18.17	81.83	100.0	–	d + magnesite
6	0.0012	0.32	1.20	1.52	–	21.05	78.95	100.0	–	d + magnesite

No. of points	P_{CO2}, atm	Ca	Mg	$(HCO_3)_2$	SO_4	Ca	Mg	$(HCO_3)_2$	SO_4	Solid phases
7	1	21.08	17.31	15.95	22.44	54.87	45.13	41.50	58.50	d + magnesite + gypsum
8	0.0012	15.47	3.53	0.47	18.53	81.42	18.58	2.48	97.52	d + magnesite + gypsum
9	1	20.47	–	7.52	12.95	100.0	–	36.74	63.26	calcite + gypsum
10	0.0012	15.97	–	0.38	15.59	100.0	–	2.38	97.62	calcite + gypsum

and many times smaller than at a CO_2 isobar of 1 atm (Fig. 2, 2); the polybaric curves and , with decreasing P_{CO_2}, approach one another, like curves *a* and in Fig. 1, and the general form of the two diagrams (the polytherm and the polybar of the system) is completely of the same type (Figs. 1 and 2). Thus, by varying the experimental conditions, we arrived at identical, mutually confirming results: the region of crystallization of dolomite in the system decreases as the temperature is raised or as P_{CO_2} is lowered; moreover, it reaches its maximum dimensions at temperatures between 30 and 45° (see Fig. 1), which, evidently, should be the most favorable for the synthesis of dolomite.

(Figure: Figures 1-3)

Fig. 1. Solubility polytherm of the system ($CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3$)–$H_2O$ at $P_{CO_2} \sim 1$ atm. *a* –dolomite + calcite + calcium sulfate, – dolomite + magnesite + calcium sulfate

Fig. 2. Solubility polybar of the system ($CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3$) –$H_2O$ at 25°: 1 –∼ 0.0012, 2 –∼ 1 atm. P_{CO_2}; –dolomite + calcite + gypsum, –dolomite + magnesite + gypsum

Fig. 3. Scheme of the evolution of the structure of the solubility diagram of the

system ($CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO_3$)–$H_2O$ with successive increase in temperature

The calcium sulfate region, which gradually contracts with temperature, changes only slightly after dehydration of gypsum (about 70°) (see Fig. 1), but it assumes its minimum dimensions at 25° and $P_{CO_2} \sim 0.0012$ atm, i.e., at low values of temperature and P_{CO_2} (Fig. 2, 1). The size of the gypsum field in the system at 25° depends to a large extent on the magnitude of the partial pressure of CO_2; depending on fluctuations of the latter and of the corresponding

changes in the solubility of the carbonates, gypsum either wedges into the region of the three carbonates or is wedged out, mutually interlayering with them under the polybaric (and polythermic) conditions considered (Figs. 1 and 2).

However, these parageneses of gypsum with the carbonates may be disrupted as the temperature rises. Judging from their course (see Fig. 1), curves *a* and *b* will intersect one another at a certain (higher) temperature at the nonvariant-equilibrium point of the system; the general structure and character of the solubility diagram will change accordingly. Fig. 3 gives an idea of the possible evolution of the structure of the diagram under the influence of temperature; the diagrams I and II derived by us graphically are in complete agreement with Kurnakov’ s correspondence principle and the phase rule, and also correlate well with the equations used for the geometric substantiation of the structure of liquidus diagrams of reciprocal systems (^{2}). The nonvariant point *d* (Fig. 3, *I*) corresponds to the simultaneous crystallization of four phases (the maximum number of phases of the system): dolomite, calcite, magnesite, and calcium sulfate. At the triple points *u*, *k* (Fig. 3, *II*) there coexist, respectively: dolomite, calcite, magnesite and calcite, magnesite, calcium sulfate, while the monovariant line *u*–*k* separates the adjacent fields of the two carbonates–calcite and magnesite. In other words, the evolution of the solubility diagram of the system under polythermic conditions must be accompanied by the disappearance of the parageneses of dolomite with calcium sulfate and by the appearance of new parageneses–calcite with magnesite; obviously, with an increase in P_{CO_2} we shall have, instead of the nodal points *u* and *k* (Fig. 3, *II*), crystallization lines of the same salts.

The results of the investigation of the polytherm of the system ($CaCO_3 + MgSO_4 \rightleftarrows CaSO_4 + MgCO$) $- H_2O$ are of theoretical interest and shed light on a number of questions in the geochemistry of sedimentary carbonate-sulfate rocks.

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CITED LITERATURE

[1] O. K. Yant' eva, *Izv. Sekt. fiz.-khim. anal.*, **20**, 252 (1950); **26**, 266 (1955).
[2] V. Ya. Anosov, *Izv. Sekt. fiz.-khim. anal.*, **17**, 73 (1949); **18**, 60 (1949).

Note: Figure translations are in progress. See original paper for figures.