BULLETIN OF THE MINERAL RESEARCH AND EXPLORATION INSTITUTE OF TURKEY

Foreign Edition April 1978 Number : 90

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Bu nüshada yazı işlerini fiilen idare edenler - Editors :
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SOLUBILITY OF COLEMANITE MINERAL IN CO_2 — CONTAINING WATER AND GEOLOGICAL FORMATION OF THIS MINERAL

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ABSTRACT. — In this research, the solubility of colemanite samples in CO2-containing water —whether in original or calcined form, at a series of temperature conditions—were studied. For solubility studies the time, temperature and pH values were taken as parameters. Parallel to this, the tests on solubilities of the Mineral in distilled water were also carried out in order to compare them with the solubilities in CO2-containing water.

The general equation for the solubilities of the hydrated boron Minerals in CO2-containing water is shown as: $xCaO.yB_2O3.zH_2O+xCO2+nH2O \quad xCaCO3+2yH_3BO3+[(z-3y)+n]H_2O$ It was established that the temperature and pH directly affected the solubilities. It was found that for the calcined Mineral, z 0, the solubility of B_2O3 in the crystal structure was higher with respect to original mineral. Besides these, the solubilities of $CaCO_3$ mineral (calcite) in different concentrations of boric acid solution were investigated, in order to see to what degree the above reaction could be two-directional. At the end of the studies, the theory about the hydrothermal formation of the hydrated boron minerals, was confirmed once more. Parallel to this, causes of the presence of pseudomorph calcites, — especially those appearing in the colemanite mines — could also be explained.

In addition, some results which would enlighten the chemical reaction for the productions of boric acid and borax from boron minerals, were also put forward.

I. INTRODUCTION AND HISTORY

Although representing only a small percent of the earth's crust, a wide range of boron minerals is known. Up-to-date, more than 50 boron minerals were discovered. However, only a few occur in commercially important reserves such as, for example, colemanite.

Except the worldwide known minerals — such as ulexite, colemanite, pandermite and tineal—practically all of the boron minerals discovered to date, occur mostly as local concentrations within these deposits and complex minerals.

Boron minerals, and in particular colemanite, occur in very few areas, Western Turkey being one of them. Colemanite occurrences of Turkey may be classified into four main groups, as follow:

1. Kestelek locality, Mustafakemalpaşa, County, Bursa Province;
2. Bigadiç, Balıkesir Province;
3. Emet, Kütahya Province;
4. Kırka, Seyitgazi, Eskişehir Province.

Various studies on the chemical properties', geology and the origin of the Turkish colemanite ores, occurring in the areas described above, have been carried out (1-6, 14, 19-22, 25).

Furthermore, detailed studies on the solubilities of colemanite and some other important boron minerals in various acids, as well as physico-chemical studies concerning the mechanics and the solubility reactions of these minerals were determined (9-l3, 15, 24, 26, 31-36). Along with the solubility of colemanite in acids, Its solubility in ordinary water was also studied (l, 16, 28). Some studies on the solubility of boron minerals in basic medium were also carried out (5, 6, 18, 27).

On the other hand, studies on the solubility of colemanite in CO_2-containing water are limited in number. In one of such studies, the production of H_3BO_3 by replacing the B_2O_3 contained in colemanite with CO_2 has been tried (4). Some other tests were carried out applying another method where instead of colemanite, ulexite was used and its solubility in the CO_2-containing water was studied in detail (7). In another research, tests were made on the conversion of colemanite into borax, by reacting colemanite with CO_2 in sea water (16). And it was stated that in this type of research the yield, at 5°C of temperature was around 75%.

There is another interesting research on the solubilities of various boron minerals— and in this instance of colemanite—in EDTA solutions (8).

The analyses of the colemanite samples taken from the Kestelek colemanite ore beds, 27 km east of Mustafakemalpaşa, have shown that these samples are entirely composed of $CaCO_3$. Judging from the external appearance of these samples, they consist of coarse monoclinal crystals. However, the crystal system of the known calcite ($CaCO_3$) minerals is hexagonal or rhombohedral (e.g. calcite and aragonite). Thus, it may be concluded that the samples taken from this locality are calcite minerals of pseudomorph structure. It is equally possible to conclude that the composition of the colemanite crystals, i.e. $2CaO.3B_2O_3.5H_2O$, has been converted into $CaCO_3$ as a result of their contact with the CO_2-containing waters occurring in nature throughout the geological ages, with their monoclinal external appearance preserved. To strengthen such a view, however, detailed understanding of the solubility of colemanite in CO_2-containing waters is essential: and this may be expressed by the following formula:

$$2CaO.3B_2O_3.5H_2O+2CO_2+nH_2O \qquad 2CaCO_3+6H_3BO_3+(n-4)H_2O$$

The principal object of these studies was to understand the degree of reversibility of this reaction and to explain the formation of the pseudomorph calcite crystals, as well as to clarify the geological formation of these minerals. Thus, tests were carried out on the solubility of colemanite samples, in their original as well as calcined forms at a series of temperatures, in water containing CO_2 at various time and temperature conditions.

Colemanite samples used in the present study were obtained from the collection of the Department of Industrial Chemistry of the İstanbul University, while the calcite (marble) used in the comparative studies was supplied by the Geology Department, Faculty of Science, University of Ankara.

The samples of colemanite and calcite (marble) used in this study, although very pure, were re-analyzed prior to investigations and their compositions were determined to be 27.29 % CaO, 50.80 % B_2O_3, 21.79 % H_2O for colemanite, and 55.92 % CaO, 43.94 % CO_2 for marble. The B_2O_3/CaO ratio of colemanite having the above composition, is 1.86 by weight.

II. CALCINATION STUDIES

METHODS AND APPARATUS USED

Static method was applied in calcination tests. For this purpose the samples were heated at predetermined temperatures until they reached a fixed weight. A normal muffle furnace was used for these tests.

The main purpose of the present study was to obtain necessary calcined material to be used m the tests and determine the relationship between the thermal decomposition and solubihty of the calcined material, since the thermolysis of the colemanite mineral has been previously studied in great detail by many workers (I, 30).

Samples were calcined at 50, 100, 150, 200, 250, 300, 350, 400,450, 500, 550, 600 650 and 700 C temperatures, which were considered sufficient. Loss of water (that is decrease in weight) of colemanite under increased temperatures is shown graphically in Figure I.

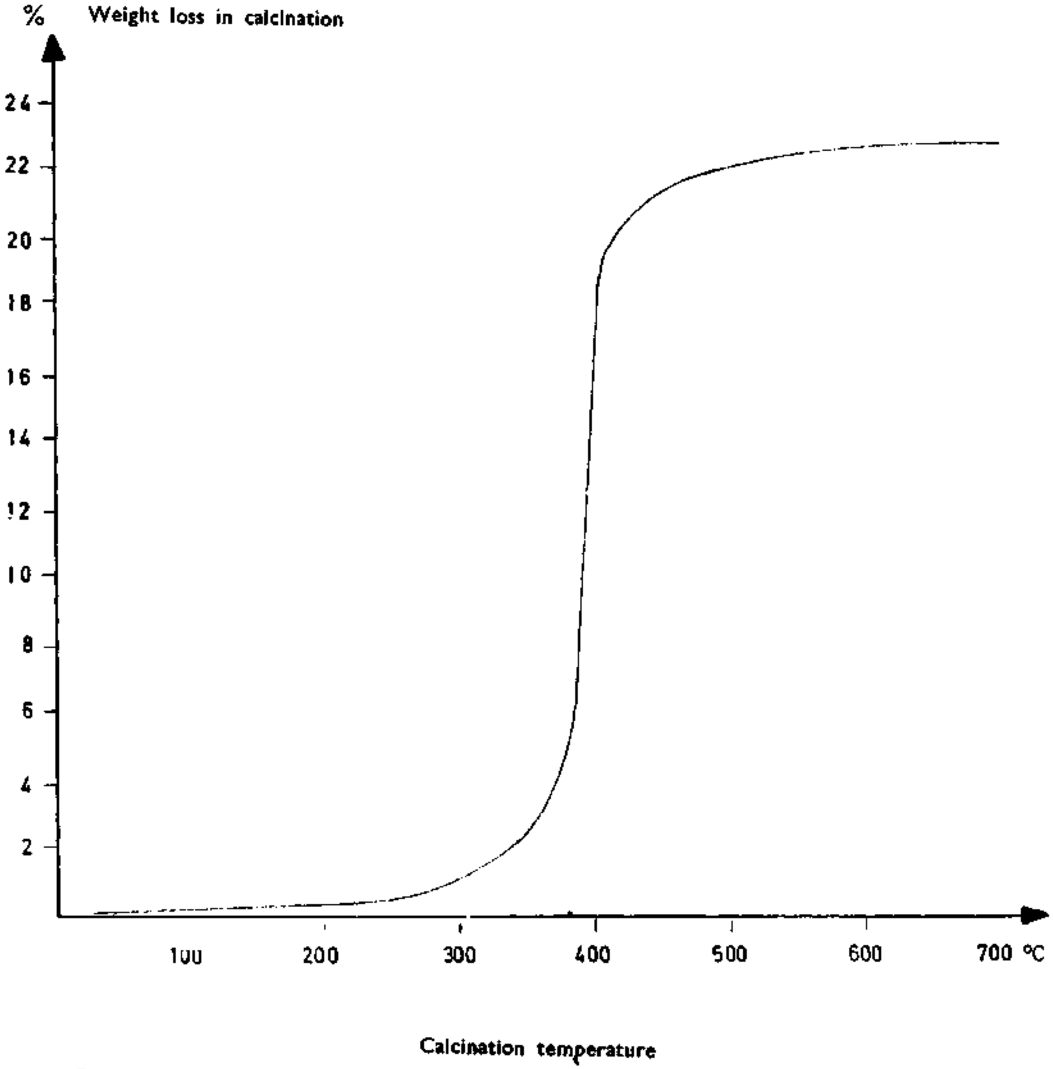

Fig. I - Calcination, curve of colemanite.

The product resulting from the calcination process has a different composition, which is due to the loss of water. Table I shows the composition of samples calcined at a series of temperatures and can be used in the comparison of the solubilities of various calcination products in CO_2-containing waters.

Table I - Composition of calcinated colemanite products (in %)

Temperature (°C)	CaO (%)	B_2O_3 (%)	H_2O (%)
Original	27.28	50.81	21.91
50	27.28	50.81	21.91
100	27.29	50.84	21.86
150	27.30	50.85	21.84
200	27.32	50.90	21.74
250	27.40	51.03	21.48
300	27.61	51.42	20.73
350	27.95	52.06	19.51
400	33.39	62.19	3.61
450	34.79	64.81	0.31
500	34.84	64.89	0.21
550	34.93	65.07	—
600	34.93	65.07	—
650	34.93	65.07	—
700	34.93	65.07	—

III. STUDIES ON SOLUBILITY

METHODS AND APPARATUS

1. Solubility in distilled water: Colemanite samples in their original and calcined forms were ground to a 100-mesh fineness, and solubility of 1.0000 gr of the samples in 100 ml of distilled water with afixed pH value (pH=5.5) was determined. Solubility tests at unvariable rate of stirring and room temperature, during a definite duration of time, were conducted; the residual unsoluble matter was strained and weighed, and the percentage of the dissolved portion of the 1.0000-gr sample was determined. Values thus obtained can also be expressed in terms of «mgr sample/100 ml water».

2. Solubility in CO_2-containing water: The conditions for this test were identical except that a CO_2-saturated medium was used. Tests were carried out at room temperature and at 50°C, for I, 2 and 3-hour periods.

3. Similar tests were further repeated with 100 ml of NaOH solutions, with pH = 12, with and without CO_2, at room temperature and at 50°C.

4. To establish the reversibility of solubility, 1.0000 gr of calcite sample was dissolved in 100 ml of H_3BO_3 solutions (I %, 2 %, 3 %, 4 % and saturated). For these tests the time and temperature were taken as variable parameters.

5. The pH values of the solutions resulting from tests I, 2, and 4 were determined.

6. Amounts of CaOand B_2O_3 resulting from solvation tests carried out in CO_2-containing water were determined. Similarly, the CaO amount in the solutions resulting from tests carried out and described in paragraph 4 were also determined.

a. For the tests of CaO: The sample solution was made alkaline by the addition of NH_3, and the determination was carried out complexometrically using the disodium EDTA solution method.

b. For the test of B_2O_3: Titration was carried out by using mannitol in standard solution of NaOH.

Solubility tests in water containing CO_2, as well as in basic solutions, were carried out in an apparatus, as shown in Figure 2.

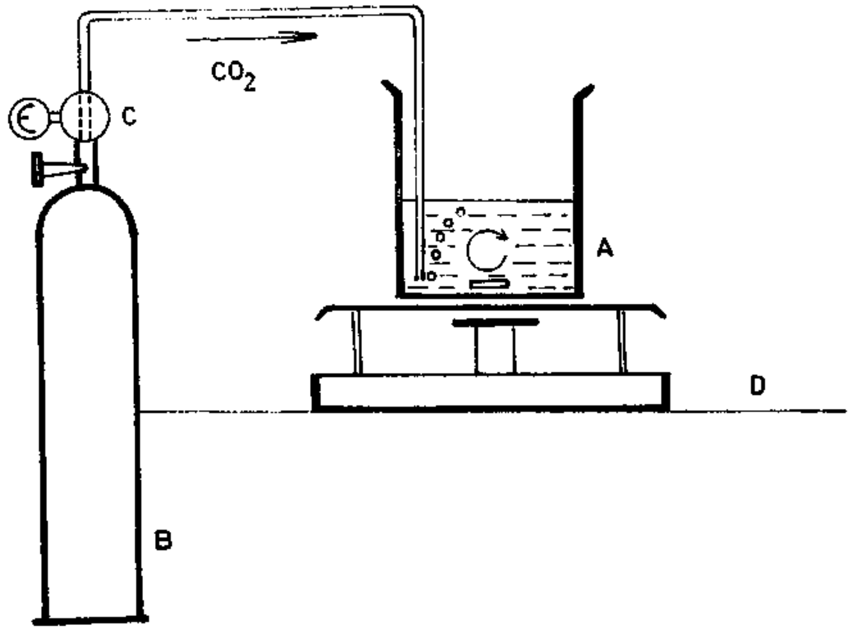

Fig. 2 - Apparatus used in tests.
A - Reaction vessel; B - CO_2 tube; C - Gas regulator; D - Magnetic agitator.

CONCLUSIONS

1. Solubility in distilled water

Tests were carried out at room temperature for a period of one hour only. The percentage of the solubility of 1.0000 gr of calcined colemanite sample in 100 ml of distilled water (pH=5.5) and the pH values of the resulting solutions under increased calcination temperatures are shown in Table 2.

2. Solubility in CO_2-containing water

A. Tests *performed at room temperature.* — Results obtained from the solubility tests of the original and calcined colemanite samples performed at room temperature in CO_2-containing water are given in Table 3. The values given in this Table relate to the tests conducted for a period of one hour only.

Table 2 - Solubility of colemanite in distilled water

Temperature (°C)	*pH*	*Amount of the sample solved (%)*
Original	9.08	5.50
50	9.14	6.78
100	9.14	6.80
150	9.14	6.88
200	9.14	7.14
250	9.08	7.38
300	9.08	8.80
350	9.08	15.68
400	9.08	26.54
450	9.14	38.00
500	9.14	39.00
550	9.14	39.00
600	9.14	39.00
650	9.14	39.00

Table 3 - Solubility of colemanite in 1-hour period at room temperature

Temp. of calc. (°C)	*pH at the end of the test*	*Amount of the dissolved sample (%)**	*Amount of CaO in the sample (mg)*	*Amount of CaO in the solution (mg)*	*Solution of CaO in the sample (mg)*	*Amount of B_2O_3 in the sample (mg)*	*Amount of B_2O_3 in the solution (mg)*	*Solution of B_2O_3 in the sample (%)*	*B_2O_3/CaO ratio in the solution***
Original	6.5	22.50	272.78	84.12	30.84	508.12	121.87	23.98	1.45
50	6.4	23.50	272.78	79.63	29.19	508.13	97.49	19.00	1.22
100	6.3	23.06	272.90	44.86	16.44	508.35	94.01	18.49	2.09
150	6.3	27.78	272.96	49.35	18.08	508.47	107.94	21.23	2.19
200	6.3	27.42	273.24	72.90	26.68	508.98	100.98	19.84	1.38
250	6.3	29.23	273.95	75.15	27.43	510.31	135.80	26.61	1.81
300	6.4	38.31	276.06	56.08	20.31	514.18	208.92	40.63	3.72
350	6.1	51.82	279.48	45.98	16.45	520.61	355.16	68.22	7.72
400	6.3	52.02	333.88	61.69	18.47	621.93	564.08	90.70	9.14
450	6.2	49.79	347.93	38.69	11.12	648.11	602.38	92.94	15.57
500	6.1	48.32	348.37	34.99	10.04	648.94	612.83	94.43	17.51
550	6.2	47.47	349.31	34.99	10.02	650.68	612.83	94.18	17.51
600	6.2	47.89	349.31	35.89	10.27	650.68	612.83	94.18	17.07
650	6.2	48.74	349.31	67.29	19.26	650.68	584.97	89.90	8.69

pH of the distilled water used in the test is 5.5.

*** Figures represent the soluble part of 1-gr sample in percent, under the test conditions.**

**** B_2O_3/CaO ratio in the sample is 1.86.**

The study of Table 3 will show that the rate of solubility of the colemanite samples tested, is proportionate with the calcination temperature and that the solubility of B_2O_3 contained in the mineral is much higher, as shown in columns 6 and 9. The values given in column 10, on the other hand, further confirm this fact. Actually the B_2O_3/CaO ratio, which is only 1.86 in the original sample, is in the range of 15.50-17.50 in calcined samples, at temperatures higher than 450°C. Data thus obtained clearly indicate that the B_2O_3 contained in the sample is dissolved as the calcination process advances, whereas CaO remains in solid phase, forming $CaCO_3$ after reacting with CO_2.

Similar tests were repeated with testing times increased to two and three hours. Results obtained, however, were more or less identical: the volume of the tested material was unchanged and a certain degree of saturation and equilibrium was attained as shown by the following equation:

$$2CaO.3B_2O_3.xH_2O + 2CO_2 + nH_2O \rightleftarrows 2CaCO_3 + 6H_3BO_3 + (n+x-9)H_2O$$

Comparison of the values given in Tables 3 and 2, however, shall clearly show that, although the rate of solubility is considerably higher in the case of tests conducted in CO_2-containing water, the difference is not in direct proportion to the calcination temperature.

Figure 3, on the other hand, shows that the solubility of the samples tested in CO_2-containing water is closely related to the calcination (decomposition) of colemanite. Calcination curves given in Figure 3 further indicate that the solubility values of the colemanite samples are maximum at the temperature interval where colemanite is entirely decomposed.

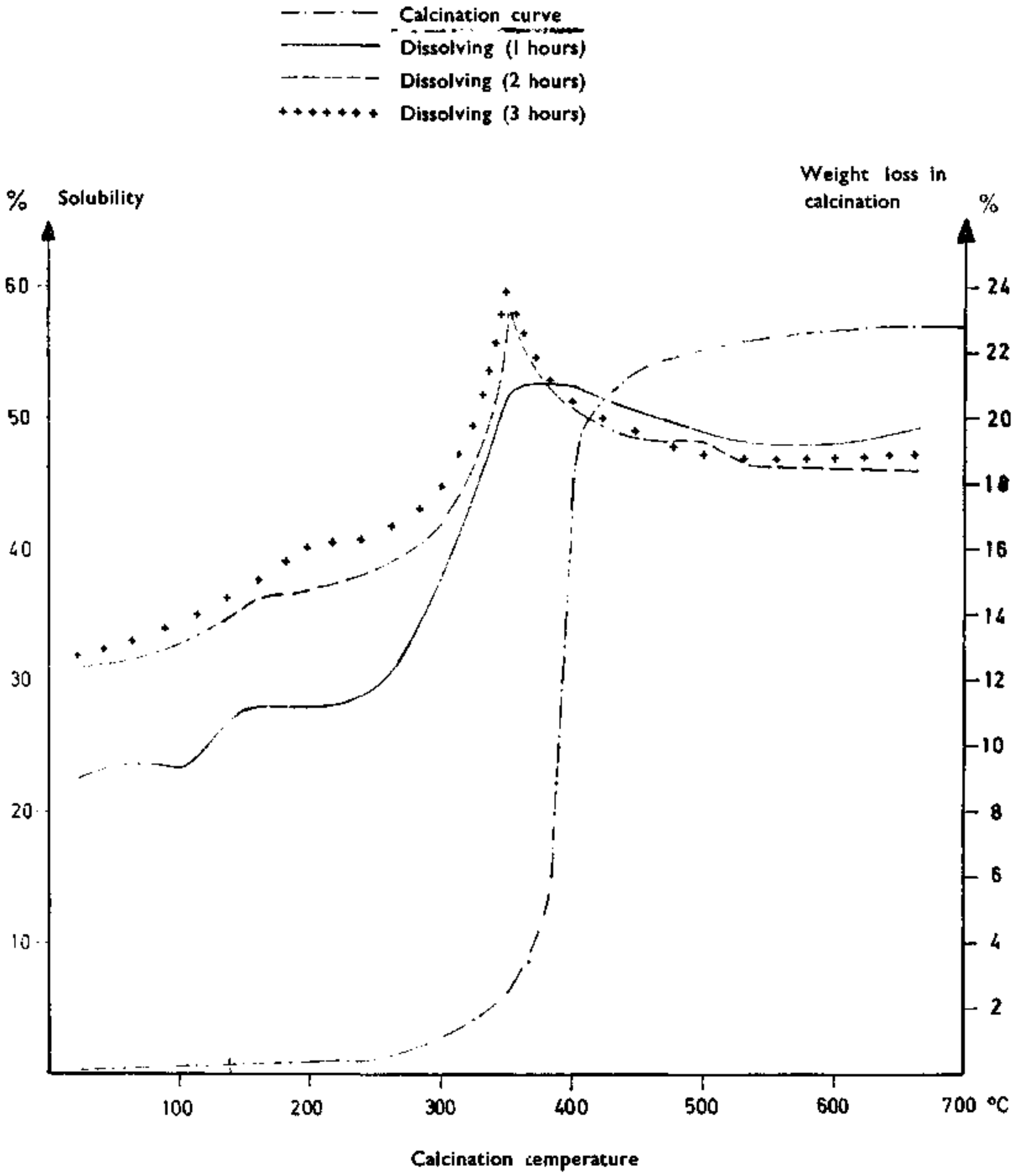

Fig. 3 - Solubility of colemanite at room temperature and calcination curve.

8. Tests *performed at* 50°C *temperature.* — Results obtained from the solubility tests of the original and calcinated colemanite samples in CO_2-containing water, at 50°C temperature, are shown in Table 4. The values given express the solubility tests carried out for one hour.

Table 4 - Solubility of colemanite in 1-hour period at 50°C

Temp. of calc. (°C)	*pH at the end of the* test	*Amount of the dissolved sample* (%)*	*Amount of CaO in the sample (mg)*	*Amount of CaO in the solution (mg)*	*Solution of CaO in the sample (%)*	*Amount of B_2O_3 in the sample (mg)*	*Amount of B_2O_3 in the solution (mg)*	*Solution of B_2O_3 in the sample (%)*	*B_2O_3/CaO ratio in the solution***
Original	5.8	30.00	272.78	47.11	17.27	508.12	299.50	58.94	6.36
50	5.5	40.69	272.78	33.65	12.33	508.13	306.42	60.30	9.11
100	5.8	41.27	272.90	33.65	12.33	508.35	320.34	63.01	9.52
150	5.8	42.62	272.96	33.65	12.32	508.47	334.27	65.74	9.93
200	5.5	43.74	273.24	33.65	12.31	508.98	344.37	67.76	10.25
250	5.7	46.97	273.95	33.65	12.28	510.31	354.47	69.46	10.53
300	5.7	49.23	276.06	33.65	12.19	514.18	410.88	79.91	12.21
350	5.6	53.93	279.48	33.65	12.04	520.61	494.44	94.97	14.69
400	5.5	46.59	333.88	33.65	10.08	621.93	598.90	96.30	17.80
450	5.5	44.82	347.93	33.65	9.67	648.11	612.83	94.56	18.21
500	5.4	42.48	348.37	33.65	9.66	648.94	619.80	95.51	18.42
550	5.4	42.90	349.31	33.65	9.63	650.68	619.80	95.25	18.42
600	5.4	42.21	349.31	22.43	6.42	650.68	626.76	96.32	27.94
650	5.4	41.29	349.31	22.43	6.42	650.68	626.76	96.32	27.94

pH of the distilled water used in the test is 5.5.

* Figures represent the soluble part of 1-gr sample in percent, under the test conditions.

** B_2O_3/CaO ratio in the sample is 1.86.

Comparison of the values given in Tables 3 and 4 shows that the solubility of the calcined colemanite samples in CO_2-containing water increases with the increase in temperature of the solvent. However, this is not the case when the temperatures of the calcined samples exceed 450°C.

It is further evident from the comparison of these tables that the solution process at 50°C develops rather in favor of B_2O_3 (see last column in both Tables).

The graph given in Figure 4 shows the solubility of the calcined colemanite samples in CO_2-containing water as directly proportional to temperature of the solvent.

When similar tests were carried out increasing the time of procedure to 2 or 3 hours, results obtained were not much different.

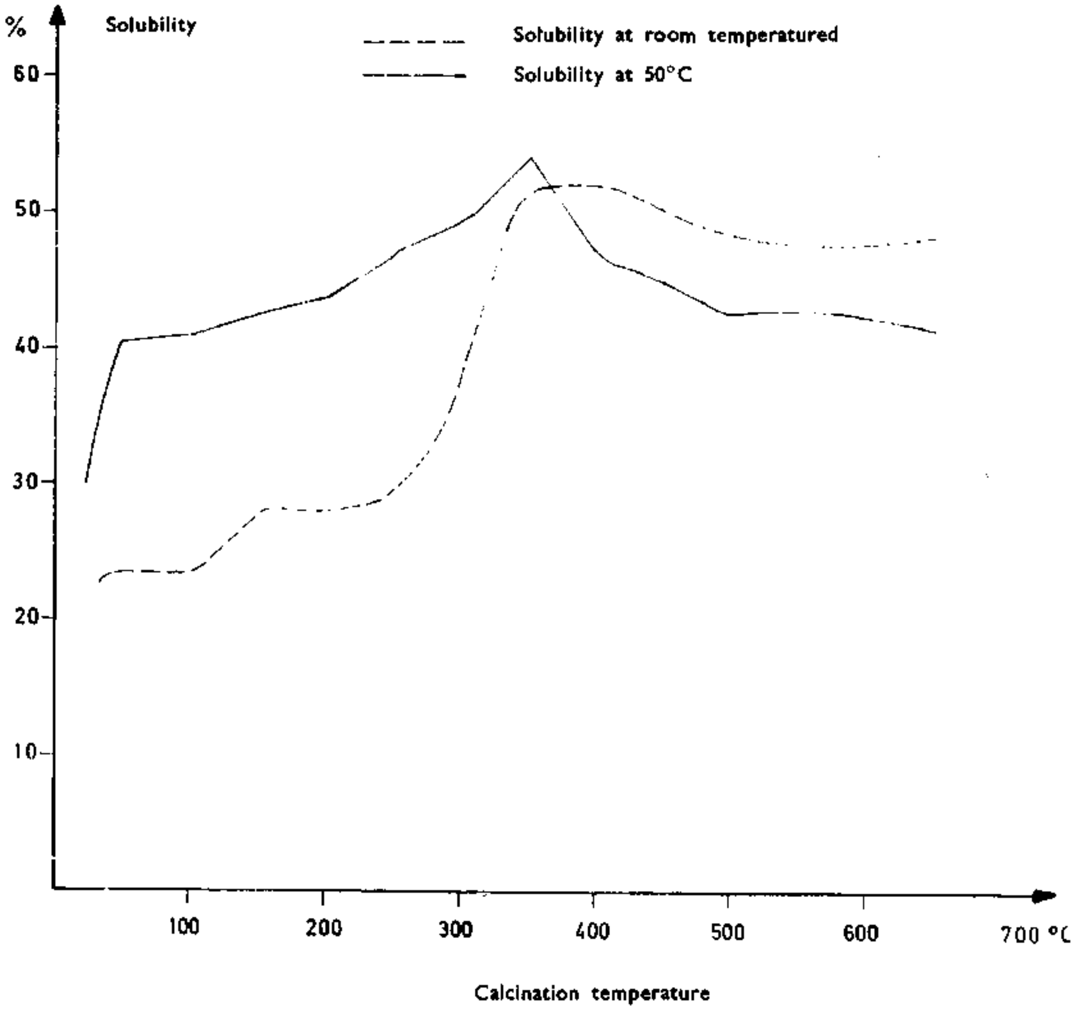

Fig. 4 - Solubility of calcinated colemanite in CO_2-containing water at various temperatures.

However, it should be noted that the solubility of B_2O_3 in CO_2-containing water at 50°C is much higher, as can be also observed in Figure 5.

Figure 5 shows the solubility of the B_2O_3 and CaO components of the mineral under increased calcination temperatures. Time of procedure: 3 hours.

It should, however, be noted that although the rate of solubility of CaO, compared to that of B_2O_3, seems to be considerably lower, the Ca++ ions found in the solution are, in fact, converted into $CaCO_3$ by reacting with CO_2 present in the solution. Taking also into consideration the pH values of the solutions, the CaO of the mineral which appears as dissolved is, actually, a bicarbonate formed as the result of the following reaction:

$$CaCO_3 + CO_2 + H_2O \rightleftharpoons Ca(HCO_3)_2$$

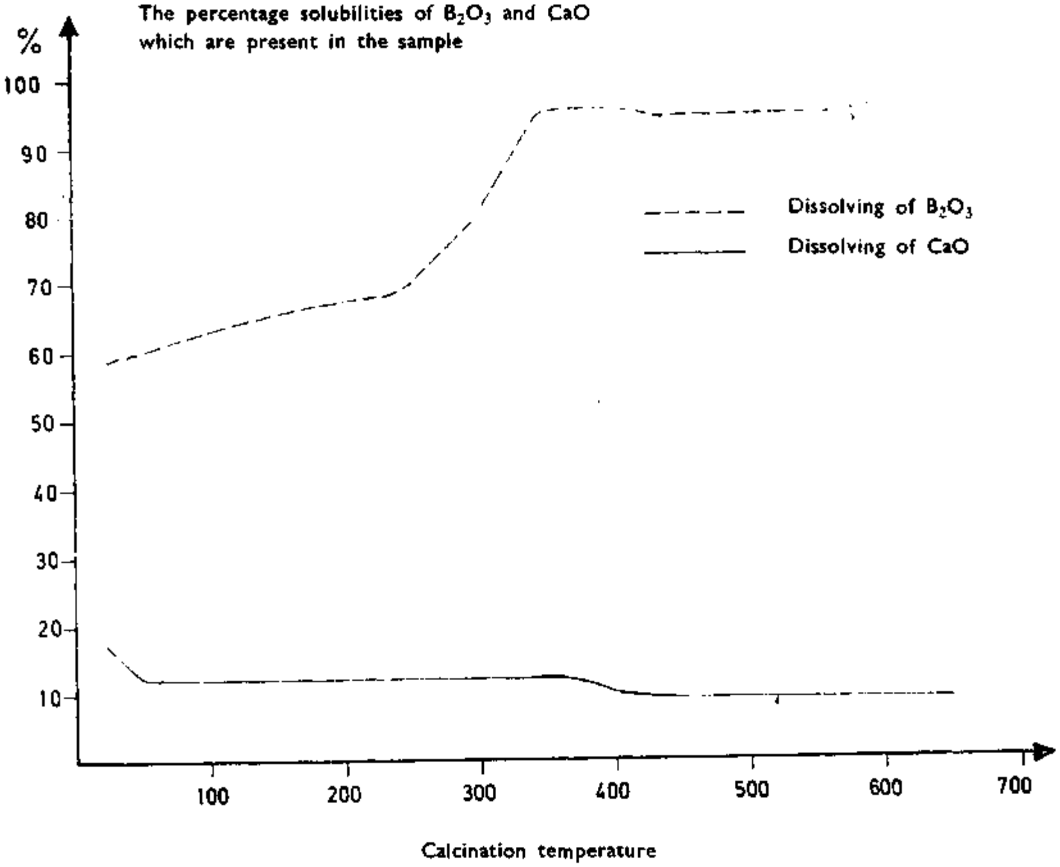

Fig. 5 - Percentage solubilities of the B_2O_3 and CaO components of the calcined colemanite sample dissolved in CO_2-containing water at 50°C.

3. Solution of crystals

Parallelly to the above-described studies, solution tests were also conducted on the colemanite crystals weighing I gr each, and using the same apparatus and methods. Table 5 summarizes the results of the tests carried out at room temperature and at 50°C during I, 2 and 3 hours.

The study of the values given in the tables clearly shows that the solubility of colemanite crystals is directly proportional to temperature and time. Moreover, it can be said that this solubility process develops clearly in favor of B_2O_3, because the B_2O_3/CaO ratio of 1.86 observed in the original crystals is considerably higher in the resulting solutions.

4. Tests of continuous solubility

Solubility tests so far carried out for maximum 3 hours time indicated that, when conditions are right, crystals could be dissolved completely. For this purpose, tests were made in order to attain complete solution of the colemanite crystals at room temperature by using an apparatus shown in Figure 6.

Table 5a - Solubility of colemanite crystals at room temperature in CO_2-containing water

Time (hour)	*pH at the end of tests*	*Amount of the soluble sample (%)**	*Amount of CaO in the sample (mg)*	*Amount of CaO in the solution (mg)*	*Solution of CaO in the sample (%)*	*Amount of B_2O_3 in the sample (mg)*	*Amount of B_2O_3 in the solution (mg)*	*Solution of B_2O_3 in the sample (%)*	*B_2O_3/CaO ratio in the solution***
1	4.9	0.71	272.78	5.61	2.06	508.12	13.93	2.74	2.48
2	5.6	3.34	272.78	11.22	4.11	508.12	27.86	5.48	2.48
3	5.5	4.84	272.78	11.22	4.11	508.12	31.34	6.17	2.79

Table 5b - Solubility of colemanite crystals at 50°C in CO_2-containing water

Time (hour)	*pH at the end of tests*	*Amount of the soluble sample (%)**	*Amount of CaO in the sample (mg)*	*Amount of CaO in the solution (mg)*	*Solution of CaO in the sample (%)*	*Amount of B_2O_3 in the sample (mg)*	*Amount of B_2O_3 in the solution (mg)*	*Solution of B_2O_3 in the sample (%)*	*B_2O_3/CaO ratio in the solution***
1	5.4	1.36	272.78	5.61	2.06	508.12	10.35	2.04	1.84
2	5.5	4.94	272.78	15.70	5.75	508.12	34.82	6.35	2.22
3	5.7	5.52	272.78	17.94	6.58	508.12	41.78	8.22	2.33

PH of the distilled water=5.5.

* Figures represent the soluble part of 1 gr of the sample in percent, under the test conditions.

** B_2O_3/CaO ratio in the sample is 1.86.

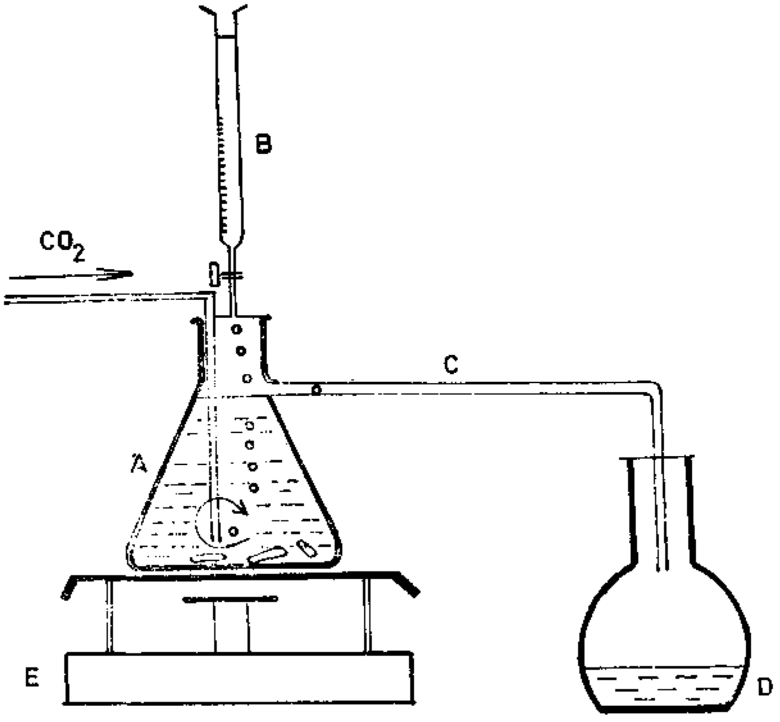

Fig. 6 - Apparatus used in continuous solubility tests.
A - Reaction vessel; B - Distilled water container; C - Overflow pipe;
D - Collector; E - Magnetic agitator.

A crystal sample of approx. 5-gr weight is placed in a vessel (A), where distilled water flows from reservoir (B) with a flow rate of 50 ml/hour. A carbon dioxide flow, supplied by a CO_2-tube, is sent to vessel (A), at a stable rate. The overflow from vessel (A)—which is regularly agitated—passes through pipe (C) and is gathered in vessel (D), where previously some NaOH was placed. When vessel (D), which is I liter in volume, is filled, it is replaced by an empty one, and the amount of B_2O3 in the vessel is measured.

This test was successfully conducted until the total B_2O_3 content of 5-gr crystal in vessel (A) was transported to vessel (D). This solubility test was carried out at room temperature. After the process of solution was completed, i.e. the total B_2O_3 content of the crystal sample in vessel (A) was transported to vessel (D), it was analytically proved that a $CaCO_3$ mass, equivalent to the CaO content of the crystal, remained in vessel (A).

Thus, the following results were obtained:

	gr
Weight of the colemanite crystal	**4.996**
CaO content of the crystal: 4.996×0.2727	**1.363**
Equivalent of $CaCO_3$: 1.363×100/56	**2.434**
Weight of $CaCO_3$ in vessel (A)	**2.450**

Similar tests were also carried out using ulexite mineral and it was observed again that the crystal was completely dissolved, and replaced by $CaCO_3$ (7).

Table 6 summarizes the results obtained from continuous solubility tests.

Table 6 - Continuous solubility tests of the crystals

Kind of crystal	*Weight of crystal (gr)*	*Content of crystal (mg)*		*Amount of B_2O_3 solved (mg)*			*Total amount of B_2O_3 (solved) (mg)*
		CaO	*B_2O_3*	*First week*	*Second week*	*Third week*	
Colemanite	**4.996**	**1372**	**2682**	**505**	**985**	**1030**	**2520**
Ulexite	**5.009**	**692**	**2149**	**2143**	**—**	**—**	**2143**

Thus, it was established that both in the case of colemanite and ulexite minerals, the B_2O_3 — which is an acidic anhydrite — may be replaced by CO_2 — which is another acidic anhydrite— when sufficient amount of CO_2 is present in the CO_2 — containing water. In conclusion, it may be definitely stated that with time the boron mineral can be converted into $CaCO_3$.

5. Solubilities in basic medium

At the same time similar solubility tests were carried out, in a pH=12 medium, in water with and without CO_2, for a duration of 2 hours. These tests were conducted at room temperature and at 50°C. Solubility results obtained under these conditions and depending on various calcination temperatures are shown in Table 7. The values given in this Table express percentage of the matter of one gram of sample dissolved in 100 ml of solvent.

Table 7 - Solubility of colemanite samples in basic media

Calcination temperature (°C)	*Percentage of the dissolved portion of one gram of sample in 100 ml of the solvent*			
	At room temp. without CO_2	*At room temp. in CO_2-containing medium*	*At 50°C without CO_2*	*At 50°C in CO_2-containing medium*
Original Sample	8.93	36.93	15.28	44.40
50	9.02	36.50	15.32	42.10
100	9.67	35.90	16.32	41.13
150	9.09	32.65	13.29	41.07
200	12.74	34.60	16.40	40.46
250	11.94	35.26	13.44	47.55
300	14.87	35.89	15.78	48.33
350	17.83	54.64	21.17	53.99
400	37.06	49.85	45.56	46.00
450	47.49	44.50	56.34	40.33
500	46.55	42.79	50.57	40.96
550	43.70	43.20	50.30	40.00
600	42.80	42.59	49.60	40.27
650	41.10	38.60	50.20	40.23

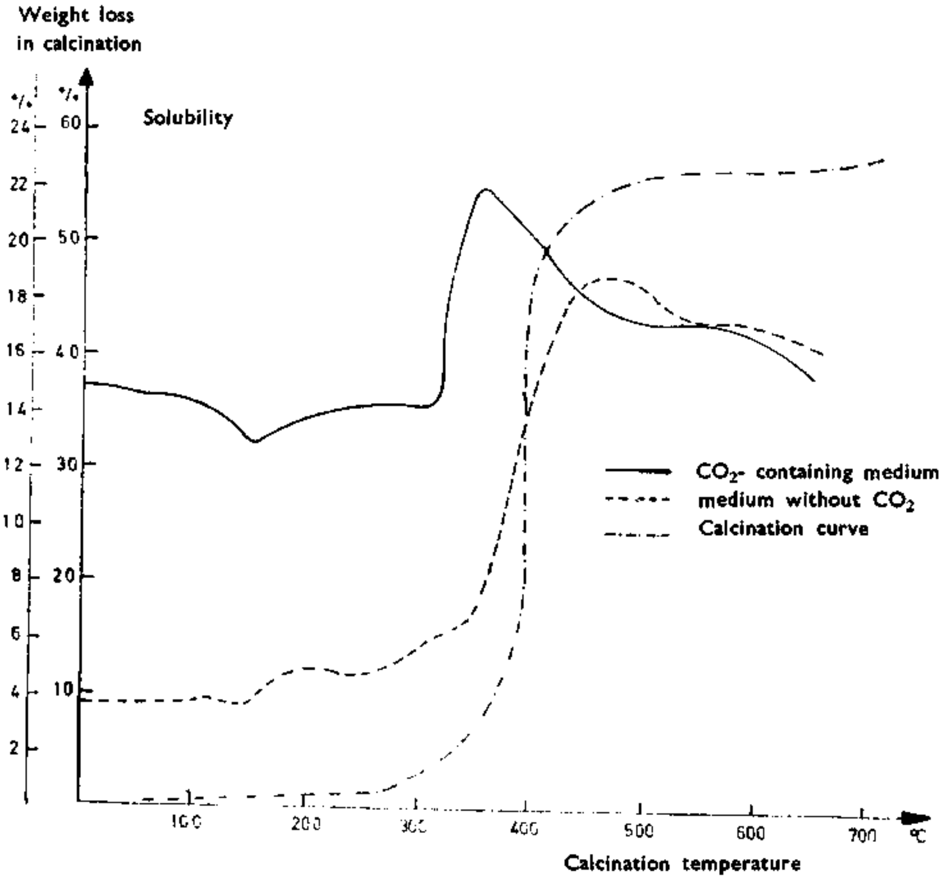

Fig. 7 - Solubility of colemanite in basic media and its calcination curve.

Thus, from this study, it may be concluded that although the rate of solubility of the mineral in CO_2-containing medium, at lower calcination temperatures, is relatively higher, the difference between the rates of solubility disappears with increasing calcination temperatures.

Furthermore, it cannot be said that temperature alone affects the rate of solubility of colemanite. However, as shown in the graph of Figure 7, the solubility of colemanite in a media with and without CO_2 reaches the maximum value between 350-400°C, when the mineral structure undergoes complete decomposition.

This is a very important point since the product obtained at the same calcination temperature in tests, carried out previously, proved to be highly active in terms of solid-phase chemical reactions (8)

6. Solubility in boric acid (H_3BO_3)

To establish the reversibility of solubility of colemanite in CO_2-containing water, which is expressed, in general, by the following equation

$$xCaO.yB_2O3.zH_2O+xCO_2+nH_2O \qquad xCaCO_3+2yH_3BO_3+[(z-3y)+n]H_2O$$

as described at the beginning of this article ("Studies on Solubility"), l.000gr of sample, weighed prior to each test, was dissolved in H_3BO_3 solutions of various degrees of concentration. For these tests time and temperature were taken at variable parameters. The results obtained are given in Table 8.

Values given in Table 8, relate to tests carried out for 30 minutes. However, in another test, with the time set at 60 minutes, no important changes were observed.

The figures given in the table show that the degree of cencentration of the boric acid clearly affects the rate of solubility of the tested material.

It should, further, be noted that the pH values of the resulting solutions are much higher compared to the pH of the solvents used in the tests. The difference between the pH values of the solutions (and the solvents) being in the range of 2.0-2.5, is due to the presence of Ca++ ions in the solution, liberated from the calcite phase.

With the increase of the solvent temperature to 50°C, the rate of solubility of the marble (calcite) mineral in boric acid, was affected negatively, i.e the rate of solubility was considerably lower compared to the rate of solubility at room temperature. This is best illustrated in Table 9, where the rate of solubility of the calcite mineral in boric acid at 50°C is given.

It should, nevertheless, be noted that the solubility of colemanite mineral is directly proportional to temperature.

In other tests carried out, parallelly, precipitated $CaCO_3$ and limestone of known composition were used. However, the results were not very different from those obtained for calcite (marble).

Table 8 - Solubility of calcite in H_3BO_3

H_3BO_3 concentration (gr/100 ml water)	pH		Amount of dissolved sample (%)	Contents in solution	
	Solvent	Solution		CaO (mg)	$CaCO_3$ (mg)
1	4.9	7.2	4.41	26.67	44.00
2	4.4	6.85	7.91	44.30	79.00
3	4.0	6.70	12.92	72.90	130.00
4	3.8	6.48	18.07	102.63	183.00
Saturated	3.8	6.55	15.07	85.27	152.00

Table 9 - Solubility of calcite in H_3BO_3 at 50°C

H_3BO_3 concentration (gr/100 ml water)	pH		Amount of dissolved material (%)	Contents in Solution	
	Solvent	Solution		CaO (mg)	$CaCO_3$ (mg)
1	4.9	7.00	3.66	20.75	37.00
2	4.4	6.70	6.40	35.89	64.00
3	4.0	6.55	9.69	54.39	97.00
4	3.8	6.35	14.97	83.56	149.00
Saturated	3.8	6.50	11.65	65.61	117.00

CONCLUSIONS

I. It was determined that the solubility of colemanite mineral in CO_2-containing water is relatively higher when the sample is in calcined form as compared to the colemanite in its original form, and the maximum solubility of B_2O_3 takes place at temperatures between 450-600°C. At this temperature interval, colemanite appears in the form of an anhydrite calcium borate having a composition of $2CaO.3B_2O_3$. In this case, the geological formation of the colemanite mineral may be explained as follows:

As is known, the boron elements are of magmatic origin. After the solidification of the initial magma, the subsequent, relatively more acidic portion of the magma, penetrates through interstices and fissures the previously crystallized mass of the initial magma, thus forming the first boron minerals, such as tourmaline, axinite and other silicate minerals containing boron (17).

As concerns the primary boron minerals thus formed, they were subsequently dissolved in CO_2-containing water, giving off their B_2O_3 content. On its way, the CO_2-containing water reacted, whenever encountered with the $CaCO_3$, $MgCO_3$, $FeCO_3$ and similar minerals, which were dissolved and converted into bicarbonates. In this way, lakes were formed in favorable drainage basins by the water containing soluble salts, e.g. H_3BO_3 and $Ca(HCO_3)_2$, and the subsequent evaporation that takes place in these lakes may have led to the formation of hydroborate minerals of known composition.

The increases in temperature of CO_2-containing water increases the speed of solubility, thus accelerating the formation of minerals such as described above.

It is known that boron minerals generally occur in beds of Cenozoic age, where the occurrence of volcanic rocks is also common. These volcanic rocks — mostly represented by dacites and andesites—are overlain in their upper layers by altered limestones which, subsequent to their dissolution, as described above, may have assimilated the boron minerals in the form of calcium components.

From stratigraphical viewpoint, the uppermost part of the boron deposits is represented by limestone, followed by marls, volcanic clay, basal marls, volcanic tuffs and andesites.

Water containing boric acid, which derived from the dissolution of the boron element contained in the volcanic masses, can be found in some areas even today. Typical example of such hot springs, is the «soffioni» near Toscana, Italy (29).

The formation of hydrothermal boron minerals (e.g. colemanite, pandermite, ulexite, etc.) was completed during Tertiary (17).

Figures 8, 9, 10 and II clearly show that colemanite and other boron minerals (in particular ulexite) occur in the Neogene areas.

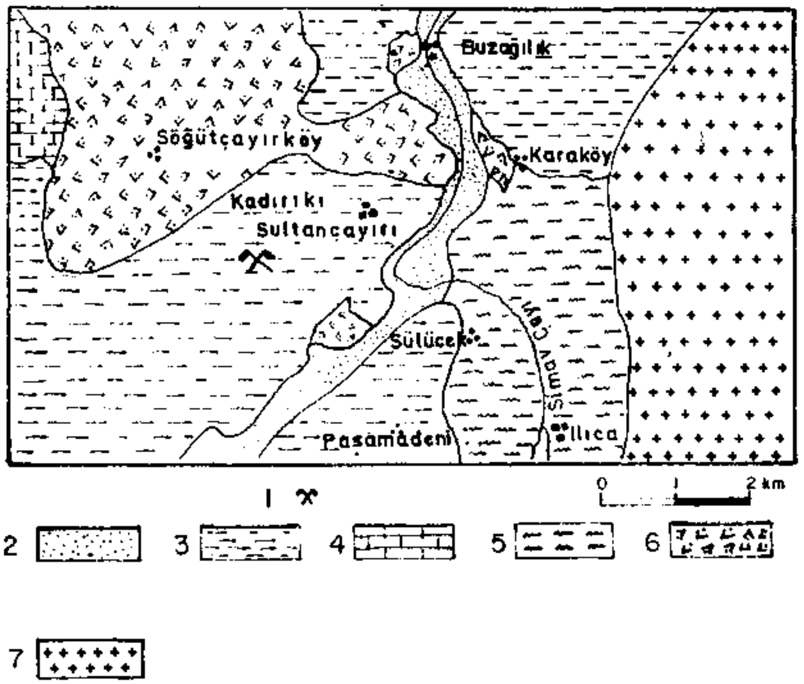

Fig. 8 - Geological sketch map showing the pandermite ore occurrence in the vicinity of Sultançayırı (23*a*).

1 - Mine; 2 - Alluvium; 3 - Neogene; 4 - Limestone; dolomitic marble; 5 - Crystalline schist; 6 - Basalt, andesite, dacite, rhyolite; 7 - Granite.

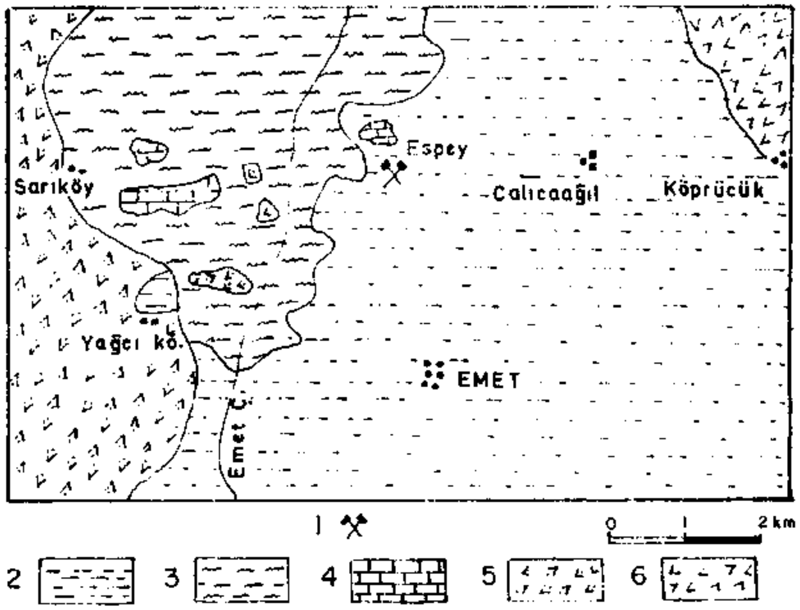

Fig. 9 - Geological sketch map showing the colemanite ore occurrence in the vicinity of Emet (23*b*).

1 - Mine; 2 - Neogene; 3 - Micaschist; 4 - Marble; 5 - Dacite; 6 - Andesite.

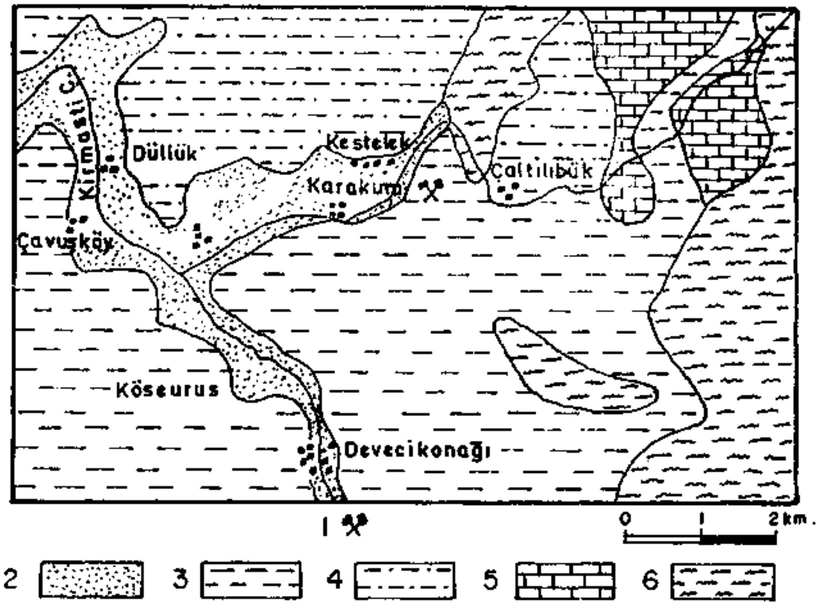

Fig. 10 - Geological sketch map showing the colemanite ore occurrence in the vicinity of Kestelek (23c).

1 - Mine; 2 - Alluvium; 3 - Neogene; 4 - Miocene; 5 - Grey limestone of Middle Triassic age; 6 - Serpentine.

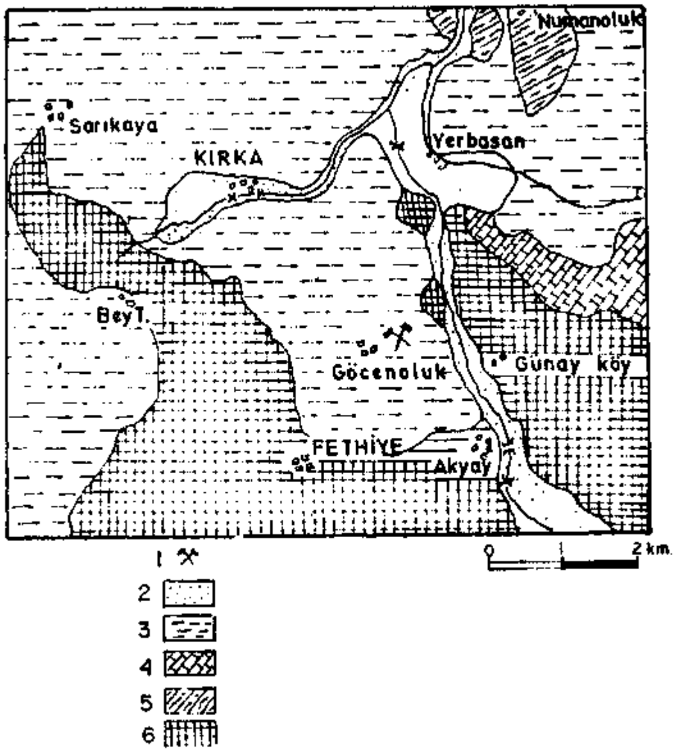

Fig. 11 - Geological sketch map showing the colemanite ore occurrence in the vicinity of Göcenoluk (23d).

1 - Mine; 2 - Pleistocene-Holocene, alluvium; 3 - Neogene; 4 - Permo-Carboniferous and Mesozoic recrystallized limestones; 5 - Permo-Carboniferous and Mesozoic, green schists; 6 - Neogene, mostly, represented by effusive rhyodacitic rocks.

2. Throughout geological ages, the hydrated boron minerals, formed in the manner described above, dissolved again as a result of being in continuous contact with the CO_2-containing waters, and their B_2O_3 content was replaced by CO_2. In conclusion, it may be stated that this process led to the formation of boron minerals observed especially in the vicinity of Kestelek, where along with the boron ores (a sort of coarse sandstone) some formation locally called «kefeki» were discovered.

Boron minerals (in particular colemanite) being in contact with the CO_2-containing water have been, with time, entirely converted into calcite ($CaCO_3$). It should, however, be noted that although ordinary calcite normally has hexagonal system, calcite resulting from the above-described process has monoclinal structure, which fact leads us to assume that the boron minerals occurring in Kestelek, are actually only pseudomorph calcite.

3. Solubility tests carried out in basic medium in CO_2-containing water also contribute to the understanding of the reactions taking place during the production of borax ($Na_2B_4O_7$ IOH_2O) from colemanite (and other calcium borate minerals as well).

4. It was further proved that, under favorable conditions, H_3BO_3 can be produced from calcium borate ores using only CO2 and H_2O.

5. Provided that the tests are performed in a stable medium, the reaction expressed as

$$xCaO.yB_2O_3.zH_2O+xCO_2+nH_2O \qquad xCaCO_3+2yH_2BO_3+[(z-3y)+n]H_2O$$

may be reversible with time. It should, however, be noted that when the CO_2-containing water, acting as a solvent in this process, is continally refreshed the above reaction may work entirely in favor of the right-hand side.

Manuscript received January 26, 1977

Translated by : Filiz DİKMEN

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