

TUNELLITE, A NEW HYDROUS STRONTIUM BORATE FROM THE SARIKAYA BORATE DEPOSITS IN TURKEY

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SUMMARY. — *Tunellite* which is a hydrous strontium-borate mineral with the composition $\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$ was discovered in the borate deposits of Sarıkaya (Kırka), located in the center of Eskişehir-Afyon-Kütahya triangle. Sarıkaya borate deposits differ from the others in their mineralization and origin. There are also other Na-, Na-Ca-, Ca-, Mg-Ca- and Mg-borate minerals encountered beside *tunellite*, such as *borax*, *ulexite*, *kurnakovite*, *colemanite*, *inderite*, *inderborite*, *meyerhofferite* and *inoite*.

Microscopic, chemical and X-ray diffraction studies were made of the various samples collected from the deposits. The results are in accordance with those of Erd *et al.* (1961) who worked on the *tunellite* of Kramer and Death Valley.

The *tunellite* of Sarıkaya has a secondary origin. Burial of deposits by young sediments caused a rise in the temperature and pressure. Therefore the activity of capillary water decreased. This factor along with enrichment of Sr^{++} in some places led to forming of *tunellite* from highly hydrous borates.

INTRODUCTION

Tunellite was first discovered in 1957 by Erd in the samples collected from Jenifer mine at Kramer borate deposits of California (Erd *et al.*, 1961). Preliminary studies of *tunellite* showed that its optical properties were quite similar to those of *hydroboracite* ($\text{MgCaB}_6\text{O}_{11} \cdot 6\text{H}_2\text{O}$). No X-ray diffraction studies were carried out at this stage. Later Morgan (*in* Erd *et al.*, 1961) worked on samples from the same mine and determined the chemical formula of *tunellite* to be $\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$. McAllister encountered the same mineral in 1959 at Furnace Creek deposits of Death Valley, California. X-ray diffraction studies were made of these samples by Clark (*in* Erd *et al.*, 1961) and the results showed that *tunellite* is a new borate mineral isomorphous with *nobleite* ($\text{CaB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$).

Tunellite has not been observed anywhere other than California. It was found by the author who studied the borate deposits of Sarıkaya, Turkey (Baysal, 1968; 1969; 1970; 1972).

Sarıkaya borate deposits are Na-borates and have been studied by the author since 1968. These deposits are located in the center of Eskişehir-Afyon-Kütahya triangle in large reserves and will have a high production capacity in the future. Therefore it is necessary, here, to give information about the genesis and occurrence of these deposits and especially about *tunellite*. The author has collected his studies and his conclusions since 1968 in «A mineralogical study and genesis of Sarıkaya (Kırka) Borate deposits (Baysal, 1972).

Samples from Sarıkaya borate deposits collected in the field and also taken from the cores have been studied systematically under the microscope and by chemical and X-ray diffraction methods. Doing so the mineralogy and the genesis of the deposits have been understood clearly. Geological, petrographical and geochemical aspects have also been determined in general. Detailed geochemical study is being carried out by the author.

Sarıkaya borate deposits are located in the lacustrine-volcanic sedimentary facies of Neogene. Lithologically and stratigraphically five different facies are seen in Neogene:

- | | | |
|-----------------------------|---|------------|
| (5) Upper calcareous series | } | — Pliocene |
| (4) Clay-marn series | | |
| (3) Borate series | | |
| (2) Marn-clay series | | |
| (1) Lower calcareous series | — | Miocene |

There must have been a connection between the origin of these series and the volcanic events because tuffaceous layers are observed both in the borate series and in the marl-clay, clay-marl series.

Sarıkaya borate deposits differ from the other borate deposits of Turkey because Na-, Na-Ca-, Mg-, Ca-, Mg-Ca- and Sr-borate minerals all occur together. Below is a list according to the abundance of these minerals:

<i>Borax</i>	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
<i>Ulexite</i>	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
<i>Kurnakovite</i>	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
<i>Colemanite</i>	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
<i>Tunellite</i>	$\text{SrB}_6\text{O}_{10} \cdot 4\text{H}_2\text{O}$
<i>Inderite</i>	$\text{Mg}_2\text{B}_6\text{O}_{11} \cdot 15\text{H}_2\text{O}$
<i>Inderborite</i>	$\text{MgCaB}_6\text{O}_{11} \cdot 11\text{H}_2\text{O}$
<i>Meyerhofferite</i>	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 7\text{H}_2\text{O}$
<i>Inyoite</i>	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 13\text{H}_2\text{O}$

Of these minerals *borax*, *kurnakovite*, *inderite* and *inderborite* have first been observed in Turkey in Sarıkaya borate deposits (Baysal, 1968; 1969; 1970; 1972). Especially *tunellite*, *inderborite*, *kurnakovite* and *inderite* are very rare in the world. Only *tunellite* was studied in this paper. A series of papers about the others will be published in the future.

Exhalations containing sodium, magnesium and boric acid and coming from the Miocene faults mixed directly into the Neogene lakes along with volcanic ash and mud. These volcanic activities continued during Pliocene.

Borax which constitutes the essential part of the deposits along with *ulexite*, *kurnakovite*, *inderite* and *inyoite* were deposited chemically as primary minerals in the lakes and formed the Sarıkaya borate deposits of exhalative-sedimentary origin. *Borax* was deposited in the deep parts of the lakes whereas *ulexite* was deposited in the shallow regions. On the other hand, *kurnakovite* and *inderite* were deposited mainly in the late stages of deposition. *Inyoite* is very rare.

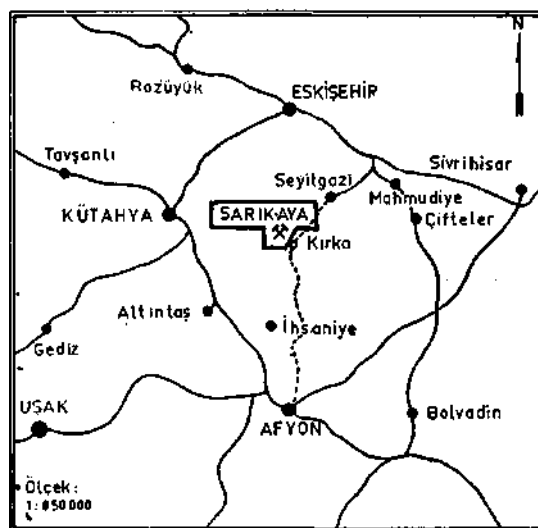


Fig. 1 - Location of Sarıkaya borate deposits.

Burial of the deposits by young sediments, temperature, pressure, mixing of circulating waters and dehydration of primary borates caused a change in the composition of capillary water and indirectly in the hydrostatic pressure. Under these new physical and chemical conditions some primary borates became unstable and turned into secondary borates, such as *ulexite*, *colemanite*, *meyerhofferite*, *inderborite* and *tunellite*.

Accompanying the forming of primary borates, pyroclastic material in lake waters became partly hydrolized because of its fine grain size and its thermodynamically unstable glassy structure in the basic media. As a result silica, Mg and partly Al in the lake waters took part in the forming of Mg-montmorillonite of the argillaceous rocks in spite of low temperature and pressure.

The excess of silica remaining from the synthesis of Mg-montmorillonite took part in the deposition of siliceous limestones. Argillaceous rocks and the limestones which formed after the borate deposits became dolomitic under early diagenetic conditions.

Tunellite of Sarkaya, of which we have tried to make a summary so far, does not have any important economic values in the present but it is the most common mineral after *borax*, *ulexite*, *kurnakovite* and *colemanite*. *Tunellite* occurs in different places of the borate deposits, especially at the floor and on the ceiling, in the rhythmic clay and in marl with *ulexite* and sometimes with *kurnakovite* and *indente*. *Tunellite* was found in abundance in the drills K-5, K-10 and S-2, it was not so abundant in drills K-6 and K-7. *Tunellite* was not encountered in the other drills or in the excavated cover. It was also found in abundance in the Kuşkaya gallery and in galleries 1, 8 and 5 of the Turkish Borax Mining Company and also in front of the pit number 3 (see Baysal, 1972).

MINERALOGY

The structural and chemical formulas of *tunellite* are $\text{Sr} [\text{B}_6\text{O}_9 (\text{OH})_2] \cdot 3\text{H}_2\text{O}$, $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ respectively. It occurs with *ulexite*, *kurnakovite* and *inderite* in nodular form and as idiomorph crystals. The nodules have irregular shapes and diameters from a few millimeters to 3-4 centimeters. They have deformation and slippage planes parallel to the cleavage. Idiomorph *tunellite* crystals are in the form of flakes and plates 2-3 centimeters in length. Crystals grow on {100}, {111}, {011}, {110} and {001} faces (Fig. 2). {100} is the most prominent face and it is a cleavage plane. The cleavage is very good and the mineral can be broken into planes and flakes parallel to {100}. It is often seen that many idiomorph *tunellite* crystals display displacements and accordion-like cracks parallel to the cleavage plane. These features resemble mineral aggregates grown parallel to one another. There is always some clay and marn

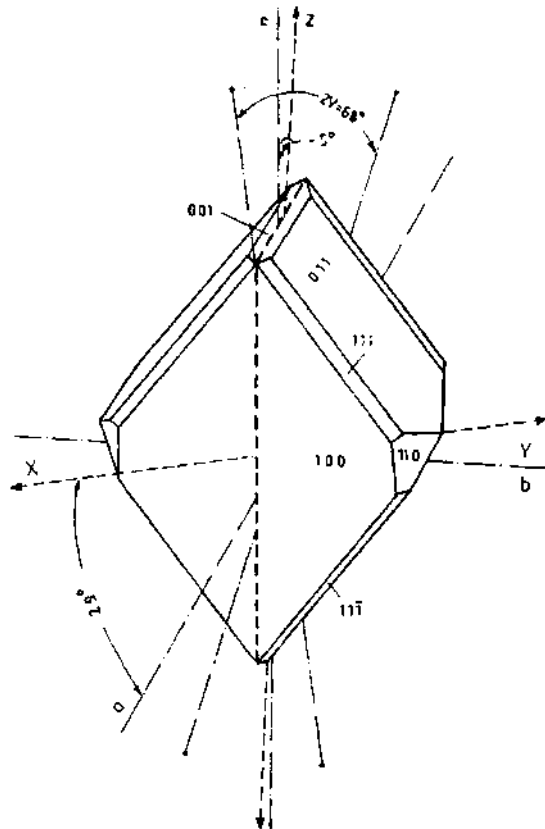


Fig. 2 - Optical orientation of tunellite.

intermixed with these slippage planes. Water is taken up by these clay layers and subjects the mineral to pressure. Again, accordion-like cracks form on the cleavage faces when the crystals are slightly heated.

Pure *tunellite* crystals are colorless and transparent. {100} faces display perfect cleavage and pearly luster. On the other faces glassy luster is more prominent. Some *tunellite* crystals appear gray-white and milky, due to the presence of interlayered clay, and some are silver-white because of slight dehydration. Thin plates of the crystals resemble muskovite and are elastic. {0k1} faces of *tunellite* crystals have lines parallel to {001}.

Tunellite is monoclinic. Its structure was determined by Clark (1964) and differs from the other polyborates in that it contains $[B_6O_9(OH)_2]^{2-}$ polyanions. Optical properties of *tunellite* of Sarikaya were determined under microscope and by the use of universal stage. Its refracting indices were measured under Na-light. The results are in quite good agreement with those of Erd and his colleagues. Table 1 lists the crystallographical, optical and physical properties of *tunellite* determined by Erd *et al.* (1961).

Table - 1

Crystallographic, optical and physical data of tunellite

Cell contents	4 $[SrO \cdot 3B_2O_3 \cdot 4H_2O]$
Crystal system	Monoclinic
Space group	$P2_1/a$
a_0	$14.36 \mp 0.05 \text{ \AA}$
b_0	$8.19 \mp 0.02 \text{ \AA}$
c_0	$9.93 \mp 0.02 \text{ \AA}$
β	$113^\circ 55' \mp 10'$
Cell volume	1068 \AA^3
Density (measured)	2.40 ∓ 0.01
n_x	1.519 ∓ 0.003
n_y	1.534 ∓ 0.002
n_z	1.569 ∓ 0.002
2V (calculated)	68°
Dispersion	$r_{\Delta v}$, weak
Optical orientation	$X_{\Delta a} = 29^\circ$ $Y = b$ $Z_{\Delta c} = -5^\circ$
Cleavage	$\{100\}$ perfect $\{001\}$ indistinct
Hardness	2.5

No alterations were observed in these *tunellite* samples from drill core's. However, samples from old galleries and pits often display chalk-like specks on the cleavage faces. These crystals look much like muscovite, are silver-white in color and they probably formed by dehydration of *tunellite* exposed to weathering. To prove this hypothesis fresh *tunellite* crystals were heated and the crystals first became silver white and then turned into earthy masses resembling white chalk. Again the *tunellite* crystals in these masses were broken off along the cleavage planes due to swelling of the interlayered clay.

CHEMICAL COMPOSITION

A chemical analysis was made of a pure, colorless and transparent *tunellite* crystal. 0.5 gm of the sample was dissolved in HCl and was neutralized by NH₄OH. Enough H₂SO₄ was added to precipitate all of strontium. Methanol of the same volume was put into this solution and the latter was left overnight, during which a SrSO₄ precipitate formed. This was filtered, washed, dried and weighed again. B₂O₃ was determined by titration with NaOH and manitol. Water was determined by loss on ignition of 1 gram samples. Spectral analysis showed that the sample contains 0.04 % Ca, 0.03 % Ba and 0.01 % Mg.

Table 2 gives the results of the chemical analysis done by the author, in comparison with that of native and synthetic *tunellite* (Erd *et al.*, 1961), and theoretical chemical composition of *tunellite*.

Table - 2

Chemical composition of tunellite

	1	2	3	Theoretical composition
SrO	26.85	27.71	27.02	26.94
B ₂ O ₃	54.16	53.70	52.88	54.32
H ₂ O	18.90	18.71	20.04	18.74
Total :	99.91	100.12	99.94	100.00

1 - Chemical composition of *tunellite* from Sarıkaya borate deposits (the author).

2 - Chemical composition of *tunellite* from Kramer (Erd *et al.*, 1961).

3 - Chemical composition of synthetic *tunellite* (Erd *et al.*, 1961).

X-RAY DIFFRACTION ANALYSIS

X-ray diffraction analyses of a few samples of *tunellite* were made to check the results of microscopic and chemical study. The apparatus used was a General Electric X-Ray Diffractometer 700. One of the diagrams with the characteristics d-spaces is given in Figure 3. Intensities are given in logarithmic scale because the apparatus was calibrated prior to the analyses.

Results of the X-ray diffraction analyses are also in agreement with those of Erd *et al.* (1961), who worked on both the native and the synthetic *tunellite* (see ASTM 14-616). Data in Table 3 is included here for the purpose of comparison.

Table - 3
X-ray diffraction data for tunellite

SARIKAYA (KIRKA)		DEATH VALLEY* (CALIFORNIA)		SYNTHETIC COMPOUND*		
<i>I</i>	<i>d</i> _{hkl}	<i>I</i>	<i>d</i> _{hkl}	<i>I</i>	<i>d</i> _{hkl}	<i>hkl</i>
				1	9.10	001
7	6.970	4	6.97	24	6.97	110
8	6.789	7	6.78	11	6.79	201
100	6.573	100	6.57	100	6.57	200
8	6.194	3	6.21	15	6.21	111
5	5.230	2	5.215	2	5.231	211
9	5.136	8	5.138	32	5.135	210
5	4.757	1	4.745	11	4.750	202
14	4.529	11	4.525	18	4.529	002
				8	4.112	020
5	3.960	< 1	3.969	3	3.969	012
		1	3.914	8	3.922	120
13	3.858	9	3.867	21	3.867	310
5	3.731	< 1	3.743	8	3.743	021
5	3.655					312
13	3.590	8	3.592	9	3.596	401
		1	3.513	17	3.517	221
						220
6	3.473	2	3.484	16	3.484	112
5	3.407	1	3.399	3	3.399	402
13	3.290	5	3.286	2	3.288	400
		2	3.175	8	3.175	202
7	3.169					311
		< 1	3.113			321
		< 1	3.059	9	3.106	222
12	3.048	7	3.045	19	3.046	410
						022
6	3.021	5	3.028	18	3.025	003
5	2.986	2	2.993	10	2.996	320
5	2.945	1	2.954	7	2.952	313
6	2.894	1	2.898	9	2.898	322
		1	2.887	11	2.887	403
6	2.840	1	2.840	11	2.840	013
4	2.802			6	2.804	112
7	2.754	3	2.751	3	2.751	401
				4	2.722	413
8	2.694	4	2.696	8	2.697	421
						511
		< 1	2.673	3	2.673	130
						512
6	2.614			13	2.619	131
		1	2.509			031
						422
6	2.567	1	2.565	7	2.566	411
						223
6	2.530	< 1	2.536	6	2.536	420
						231
				6	2.514	312
						222
15	2.501	8	2.503	11	2.505	131
		< 1	2.479	4	2.479	323
8	2.383	3	2.388	4	2.390	510
				3	2.375	
11	2.353	5	2.359	5	2.361	
5	2.316			6	2.320	
14	2.265	6	2.266	13	2.266	
14	2.204	7	2.202	8	2.204	
		2	2.190	2	2.191	
				4	2.176	
5	2.146	< 1	2.141	7	2.143	
8	2.121	2	2.119	19	2.120	
		1	2.101	11	2.102	
6	2.075	< 1	2.071	11	2.073	
7	2.051	2	2.051	11	2.051	
6	2.033	2	2.024	13	2.026	
5	1.983	< 1	1.981	4	1.983	
10	1.948	4	1.948	7	1.948	
8	1.935	2	1.931	6	1.931	
8	1.906	2	1.905	6	1.896	
4	1.839		4	4	1.885	
				1	1.858	
5	1.822	< 1	1.819	3	1.821	
6	1.803	1	1.802	4	1.804	
				2	1.789	
				1	1.772	
4	1.766			1	1.761	
7	1.746	1	1.744	3	1.745	
5	1.712					
				2	1.708	
7	1.642					
7	1.563					
6	1.504					
5	1.439					
4	1.336					
3	1.309					
3	1.296					
2	1.246					
3	1.235					
3	1.196					
3	1.193					

* From Erd et al. (1961).

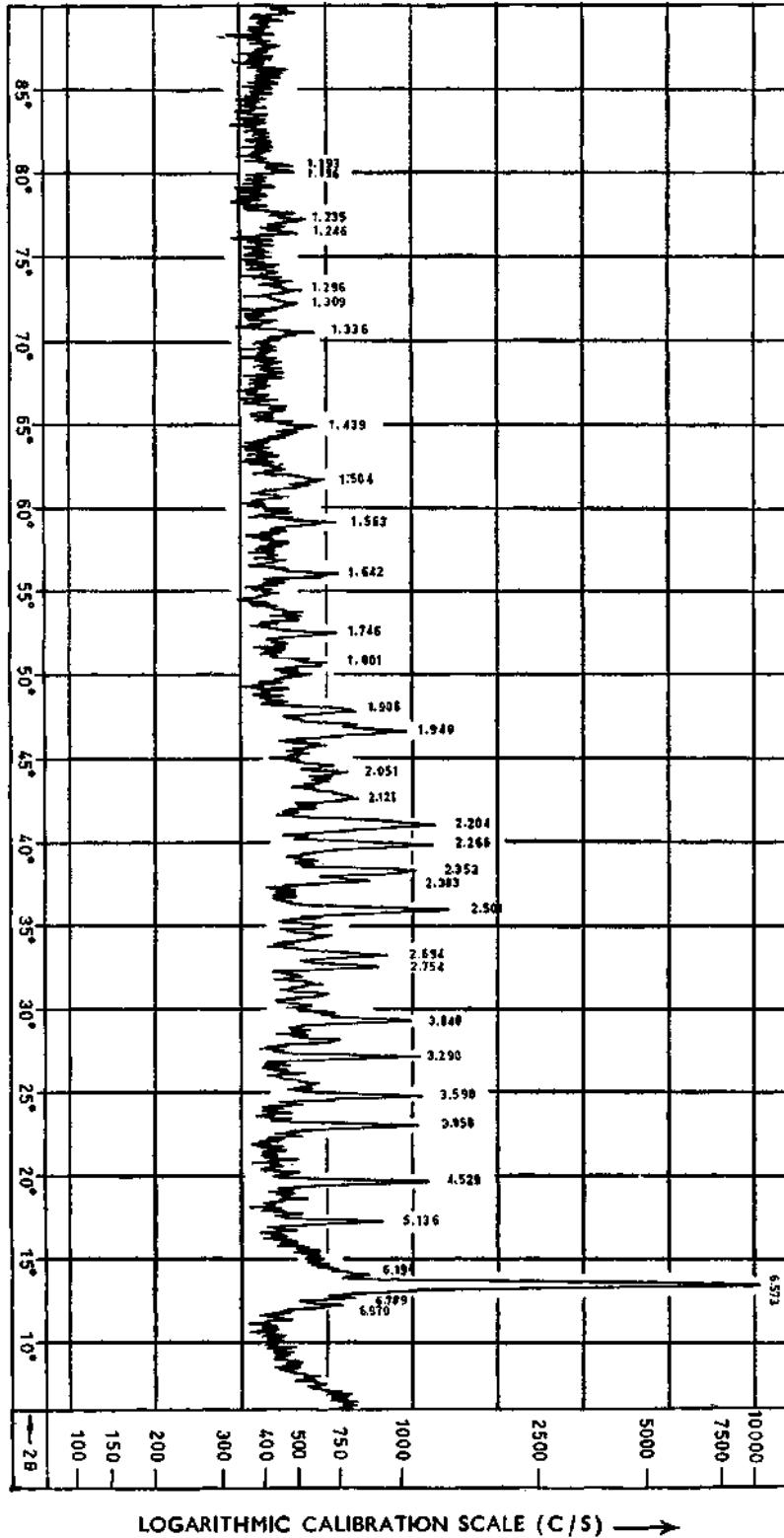


Fig. 3 - X-ray diffraction diagram of tunellite from Sarıkaya borate deposits.
 Rad.: $\text{CuK}\alpha$; Filter: 2 layers nickel; Diffractometer: beam slit 3° ; Soller=medium; Time constant:
 approx. 2 sec.; Log 10-10000; Scan: $2^\circ/\text{min.}$; Target angle: 4° ; Chart speed: 12/hr; KVP: 45; MA: 5.

ORIGIN

Experiments have shown that the types of polyanions and polyborates present in the borate solutions are dependent on the following factors: the PH the temperature, the concentration of the solution and the presence of some cations (Christ *et al.*, 1967; Valyashko & Wlassowa, 1969; Baysal, 1972). For example in the lakes containing Na and Ca, hydrous Na-, Na-Ca- or Ca-borates form depending on the concentration of Na and Ca. If, on the other hand, Mg⁺⁺ and Sr⁺⁺ are abundant the kind of borates which will form depend on the $[Ca^{++}] / [Mg^{++}]$ and $[H_2O]$ or $[Ca^{++}] / [Sr^{++}]$ and $[HaO]$.¹ Experiments, thermodynamic and geochemical principles along with the observations at numerous evaporite deposits have shown that under surface temperatures the most hydrous borate of each series is chemically precipitated first. To put it differently, under surface conditions the borates that are precipitated as primary minerals in the lake waters are the most hydrous members of their series (Muessig, 1959; Christ *et al.*, 1967; Özpeker, 1969; Baysal, 1972). Indeed, in Sarıkaya deposits, *borax*, which is the essential mineral and the most hydrous member of its series, is a primary mineral.

The only Sr-borate mineral of Sarıkaya deposits is *tunellite* ($SrB_6O_{10} \cdot 4H_2O$). No literature was found about the stability conditions for this mineral. Crystal structure of *tunellite* is the same as that of *nobleite* ($CaB_6O_{10} \cdot 4H_2O$), and also their crystallographical, optical and physical properties are the same. A high hydrous type of *tunellite* $SrB_6O_{10} \cdot 5H_2O$ was synthetically made by Gode and Kesans (cit. in Erd *et al.*, 1961). The formula and the crystal structure of this mineral resemble very much those of *goverite* ($CaB_6O_{10} \cdot 5H_2O$). Considering these similarities, the author came to the conclusion that *tunellite* probably formed, as *nobleite*, after the deposits were buried by young sediments. Because it is thermodynamically and geochemically impossible for *tunellite* to form under surface conditions, on the contrary it is possible that *tunellite* forms, as seen in Figure 4, from a higher hydrous borate mineral of its series, such as *nobleite* (Ca-borate) by hydration or metasomatism. No concrete conclusions can be drawn, however, because neither *nobleite* nor *goverite* was found in Sarıkaya borate deposits.

The author thinks that the activity of the capillary water decreased due to the rising temperature caused by the burial

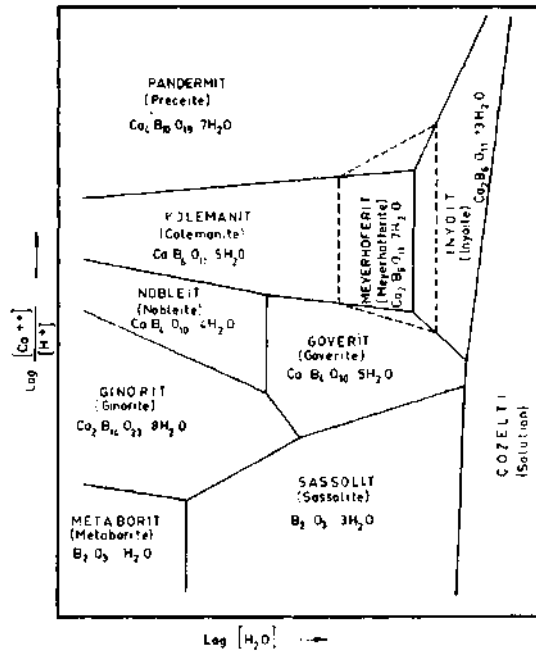


Fig. 4 - Schematic plot of the phase relations in the system $4CaO \cdot 5B_2O_3 \cdot 7H_2O - B_2O_3 \cdot H_2O - H_2O$. The solids are in equilibrium with saturated solution; brackets denote activities; the dashed lines enclose metastable fields. System is closed with respect to boron and open with respect to the cations and H_2O . As drawn, 1 unit along the $\log (H_2O)$ -axis is equal to 10 units along the $\log ([Ca^{++}]/[H^+])$ -axis.

Ascale of this kind is in accordance with the fact that $\log (H_2O)$ can vary only over a fraction of the range of $\log ([Ca^{++}]/[H^+])$

(From C.L. Christ; A.H. Truesdell & R.C. Erd, 1967).

of deposits by young sediments. It can be seen in Figure 4 that this lower activity corresponds to *nobleite*. Meanwhile concentration of Sr^{++} in capillary water containing borate polyanions increased in places. As a result idiomorph *tunellite* crystals or nodules, similar to the *ulexite* concretions, formed in the argillaceous rocks (see Baysal, 1972). The fact that *tunellite* almost always occurs with or in the secondary *ulexite* concretions proves this hypothesis mentioned above.

The strontium which takes part in the forming of *tunellite* is either given off by hydrolization of pyroclastic material or came with the volcanic exhalations and was enriched in the pores of argillaceous rocks. The second alternative seems to be more probable because *tunellite* is almost always encountered near the fault zones of argillaceous rocks where volcanic exhalations came to the surface. On the other hand the strontium that is given off by hydrolization of pyroclastic material must also be considered. Because it is known that pyroclastic material mixed into the lake waters by volcanic activities is rich in volcanic glass dust, has fine grain size and its glassy structure is thermodynamically unstable. These factors combined with the basic character of the media ($\text{pH} > 8.5$) causes the pyroclastic material to become highly hydrolized and dissolved. Chemical analyses have also shown that argillaceous rocks contain trace amounts of SrO (see Baysal, 1972). As a conclusion it can be said that the necessary strontium for *tunellite* came with volcanic exhalations and was in part supplied by the hydrolized pyroclastic material.

Manuscript received May 27, 1972

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