

## STUDIES ON TUNELLITE (STRONTIUM BORATE) MINERAL

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**SUMMARY.** — In these studies, the physical, chemical and mineralogical properties of the tunellite found associated with the boron mines in Turkey, which have long been known, have been investigated and the chemical composition determined. The thermal decomposition of tunellite mineral has been studied both by dynamic and static methods. The results obtained with the methods above were checked with those obtained by Röntgenographic analysis and with the DTA studies.

As a result of these studies, it has been observed that the tunellite mineral was transformed into veatchite mineral, after losing 4 molecules of its crystal water.

### INTRODUCTION AND HISTORY

Boron minerals which are gaining ever-increasing importance in the world industry occur widespread in the northwest part of Turkey. Boron occurrences of the country are generally located in the vicinity of Bigadiç, Balıkesir, Mustafakemalpaşa, Emet and Eskişehir. Borate ores encountered in these mines are generally, ulexite and colemanite. The reserves and the grade of the ore are considered favorable for economic production.

Associated with the colemanite and ulexite produced from these mines, some other boron minerals are also found and the most important of these are inyoite, meyerhofferite, tertschite and howlite. These secondary minerals are locally found interbedded in the clay seams, as thin beds or nodules.

In some mines, a new mineral, showing the composition of strontium borate, is found in association with colemanite and ulexite; this new mineral, which sometimes shows a prismatic structure, is also found to occur closely mixed with clay having bentonite texture. This mineral, which at present has no economic value for Turkey, is tunellite.

Tunellite was first described by R.C. Erd in 1957 from borate deposit in California, U.S.A. Erd, found tunellite within the greenish-black-colored montmorillonite clay associated with polymorph minerals, such as inderite and kurnacovite.

Hydrothermal origin is accepted for the above-referred minerals.

These minerals in many deposits are mixed with realgar and orpiment and show a reddish to yellowish color.

In fact there are only very few minerals containing SrO and H<sub>2</sub>O in addition to B<sub>2</sub>O<sub>3</sub>. Most widely known types of this mineral are tunellite and veatchite. Although these two minerals generally occur together and are strikingly similar regarding their composition, they have totally different lattice structures.

Tunellite also occurs associated with nobleite, having the formula of  $\text{CaO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ .

The analysis of the tunellite mineral, which was first discovered in the U.S.A., gave the following results (V. Morgan):

|                        |         |
|------------------------|---------|
| $\text{B}_2\text{O}_3$ | 53.70 % |
| $\text{SrO}$           | 27.71 % |
| $\text{H}_2\text{O}$   | 18.71 % |

These results correspond to the formula of  $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . The SrO content of the tunellite mineral is sometimes replaced by the BaO at a ratio of 15 %.

Researches on the crystal structure of tunellite mineral showed that this mineral is a member of the borate series having the formula of  $M^{+2}\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ , where for tunellite  $M = \text{Sr}$  and  $X=4$ .

The crystal lattice of the tunellite mineral is monoclinic, as is the case with most boron minerals.

J.R. Clark showed that veatchite is the accessory mineral of tunellite. Veatchite is also a member of the  $M^{+2}\text{O} \cdot 3\text{B}_2\text{O}_3 \cdot \text{XH}_2\text{O}$ . But here the  $X$  will be 2 for the veatchite mineral.

«p. veatchite» is the dimorph of the veatchite mineral.

Tunellite is found in the borate deposit occurring in the Göcenoluk locality 20 km SW of the town Seyitgazi, Eskişehir. The tunellite samples studied are collected from the above-referred deposits and are in the form of very pure crystals.

## METHODS AND APPARATUS

### I. METHODS OF ANALYSIS

A.  $\text{B}_2\text{O}_3$  determination. — The  $\text{B}_2\text{O}_3$  content of the original and calcinated tunellite samples is determined as follows:

1. Volumetrically by using the acid extraction method.
2. Gravimetrically by using Chapin distillation method.

B. SrO determination:

1. Gravimetric determination of the remaining  $\text{SrSO}_4$  obtained as a result of the evaporation process of the pulverized sample with HF and  $\text{H}_2\text{SO}_4$ .
2. Complexometric determination of the SrO content by using the n/10 EDTA solution and Phthaleinpurpur indicator.

C. Determination of the crystal water. — The crystal water content of the mineral is determined as the glow loss using 1.0000 gr sample. Very finely ground tunellite sample was heated at 750-780°C for approximately 7-8 hours. The loss of weight indicates to the crystal water content of the sample. For the determination of the crystal water content of the tunellite sample this method is successfully employed. For colemanite mineral, However, the method in question does not seem applicable, since loss of weight will occur due to explosions and attendant scattering around of the sample upon heating.

## II. DEHYDRATION AND THERMOGRAVIMETRIC ANALYSIS

Two methods are employed in the dehydration of the sample:

- A. Static method,
- B. Dynamic method.

*A. Static method.* — In this method the sample is heated at given temperatures until attaining a constant weight. Following this, the sample is cooled and weighed. Thus, the thermal decomposition and the dehydration data of the samples at given temperatures are obtained.

Normal (standard) muffle furnaces, which can be adjusted to a constant temperature as long as desired, are used in this method.

*B. Dynamic method.* — In this method the sample is weighed automatically at regular intervals at temperatures increased linearly. In dynamic method, Guichar's thermal hydrostatic balance is used. In our studies, automatic thermogravimetric balance is used.

Apparatus used in thermogravimetric analysis consists of a cylinder-shaped vertical electric furnace and a balance to weigh automatically the crucible suspended in the furnace. The rise of temperature in the furnace is adjusted to the rate of 60°C/h by a variac.

Platinum crucible containing very finely pulverized sample (1.0000 gr) is suspended in the furnace. The weight change of the sample is recorded graphically by a recorder as the temperature of the furnace is increased 60°C/hour. The graph obtained thus represents the loss of weight % - temperature.

Using the same apparatus, dehydration (decomposition) curves of the sample at constant temperatures can also be obtained. The graph recorded automatically in these studies will show the loss of weight % - period (minutes).

## III. DIFFERENTIAL THERMAL ANALYSIS

The dehydration and the decomposition of the sample at temperatures raised linearly, is due to heat exchange.

In parallel to the dynamic method studies using thermogravimetric analysis apparatus, differential thermal analyses are conducted.

The apparatus employed in this study consists of a cylinder-shaped horizontal furnace, a pyrometer consisting of Pt/Pt-Rh thermo-couples and microampere galvanometer (or a recorder).

The sample to be studied is placed into the furnace together with an inert substance. The rise of temperature selected for this procedure is 10°C/minute.

The endothermic and exothermic peaks produced as a result of the thermal dehydration and decomposition of the sample upon heating are recorded automatically by a recorder.

## IV. X-RAY ANALYSIS

For the study of the original and dehydrated forms of pulverized tunellite mineral, standart (normal) X-ray equipment is employed. Powder diffraction method is used in this study. The diagrams are recorded automatically by a recorder.

## CONCLUSION

## I.

*a. Composition.* — The analysis of the pure tunellite crystals collected from the above-referred deposits gave the following composition:

|         |                               |
|---------|-------------------------------|
| 26.76 % | SrO                           |
| 53.25 % | B <sub>2</sub> O <sub>3</sub> |
| 19.98 % | H <sub>2</sub> O              |

The formula suggested for this mineral based on the data obtained is SrO·3B<sub>2</sub>O<sub>3</sub>·4H<sub>2</sub>O or SrB<sub>6</sub>O<sub>10</sub>.

In the formula SrO·3B<sub>2</sub>O<sub>3</sub>·4H<sub>2</sub>O, the theoretical percentage of the components constituting the composition are calculated to be:

|         |                               |
|---------|-------------------------------|
| 26.95 % | SrO                           |
| 54.31 % | B <sub>2</sub> O <sub>3</sub> |
| 18.71 % | H <sub>2</sub> O              |

The following analytical results are given for the same mineral by V. Morgan and J.R. Clark:

|         |                               |
|---------|-------------------------------|
| 27.71 % | SrO                           |
| 53.70 % | B <sub>2</sub> O <sub>3</sub> |
| 18.71 % | H <sub>2</sub> O              |

The discrepancy observed between the results obtained is due to the irregularity of the water mole coefficient in the M<sup>+</sup>O·3B<sub>2</sub>O<sub>3</sub>·XH<sub>2</sub>O formula.

It has been shown that the tunellite samples on which various studies are conducted do not contain CaO, MgO, Na<sub>2</sub>O, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The same situation is also clearly reflected in the X-ray diagrams. The characteristic X-ray diagram of the original tunellite sample, employing X-ray powder diffraction method, is represented in Figure 1.

*b. Mineralogical and physical properties.* — The mineralogical characteristics of the tunellite mineral studied are given below:

|                              |  |
|------------------------------|--|
| <b>Cell content</b> .....    | <b>4 (SrO·3B<sub>2</sub>O<sub>3</sub>·4H<sub>2</sub>O)</b> |
| <b>Impurities</b> .....      | <b>BaO (maximum 0.15 %)</b>                                |
| <b>Color</b> .....           | <b>colorless, transparent</b>                              |
| <b>Crystal pattern</b> ..... | <b>monoclinic</b>  |
| <b>Density</b> .....         | <b>2.39 gr/cm<sup>3</sup></b>                              |
| <b>Cleavage</b> .....        | <b>100</b><br><b>001</b>                                   |
| <b>Hardness</b> .....        | <b>2.5</b>   |

Upon heating tunellite mineral in a closed vessel, scaly cleavages are formed and a silvery color is observed. Upon continuing the heating, the mass becomes white. At 780°C, the sample is sintered and after 800°C it melts. The substance thus obtained is anhydrous veatchite—not tunellite mineral.

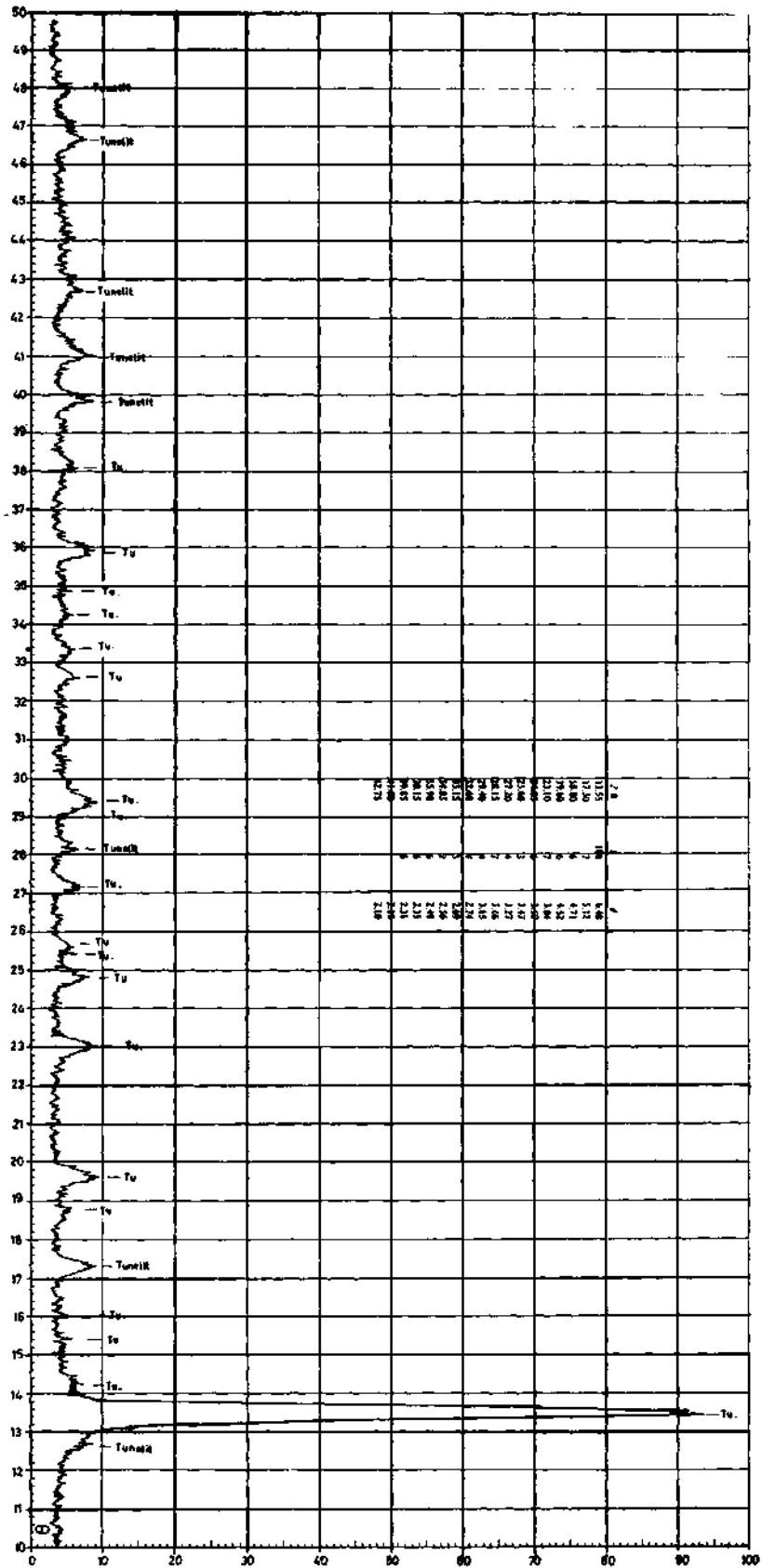


Fig. 1 - Powder diffraction X-ray diagram of original tunellite mineral at ordinary temperatures.

The color change of the tunellite crystal (pulverized) upon heating is very interesting:

|                |                              |
|----------------|------------------------------|
| at 200°C ..... | white                        |
| at 250°C ..... | slightly tan                 |
| at 300°C ..... | slightly tan                 |
| at 350°C ..... | slightly increased tan color |
| at 400°C ..... | slightly increased tan color |
| at 450°C ..... | tan color                    |
| at 500°C ..... | tan color                    |
| at 550°C ..... | tan color                    |
| at 600°C ..... | tan color                    |
| at 650°C ..... | very deep tan color          |
| at 700°C ..... | color bleaches rapidly       |
| at 750°C ..... | white                        |

The color change observed, is due to the modification of the mineral structure upon heating. It is clearly understood that the tunellite mineral will undergo a modification of structure on heating.

*c. Chemical properties.* — Pulverized and coarse crystalline forms of tunellite mineral dissolve in strong inorganic acids rapidly (HCl, H<sub>2</sub>SO<sub>4</sub>, etc.) without any trace. The rise of temperature has a positive influence on the dissolution process.

Tunellite mineral dissolves in concentrated alkali solutions (NaOH, KOH, etc.), but this time a gelatinous precipitate is formed.

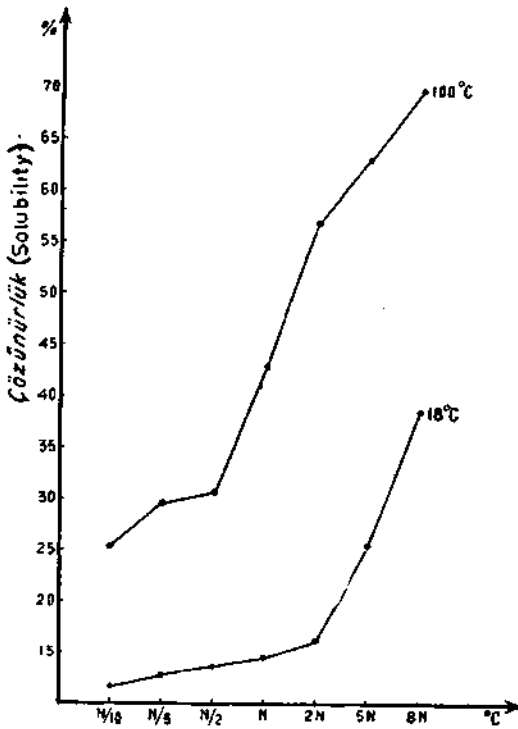


Fig. 2

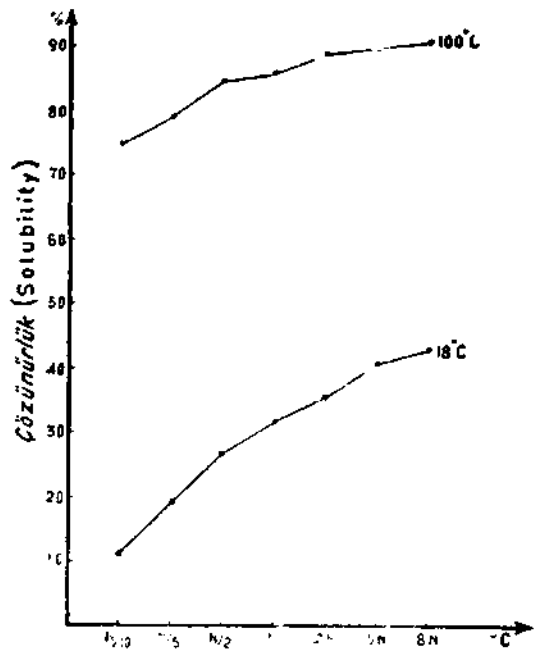


Fig. 3

The solubility of the original tunellite mineral in NaOH solutions showing various concentrations at ordinary temperature (18°C) and 100°C is studied and the graph obtained is presented in Figure 2.

The solubility of the dehydrated (i.e. anhydrous) tunellite sample, at ordinary temperature (18°C) and 100°C in NaOH solutions, proved that the solubility degree of this sample differs from that of original tunellite sample studied under the same conditions. The graph showing the solubility of the dehydrated tunellite mineral is given in Figure 3.

## II. DEHYDRATION OF TUNELLITE MINERAL

1.0000-gr portion of tunellite mineral is taken at each time and is, heated at temperatures of 50°C intervals for 5 hours, up to 750°C, and the loss of weight is measured by static method. The upper limit of dehydration is 750°C. The sample starts sintering above 750°C and no weight losses are observed. The graphs showing the temperature—weight loss and temperature—loss of water obtained through static methods at temperatures between 50-750°C are given in Figure 4.

The dehydration process is rather rapid until 250°C at which temperature 2.5 moles of water are removed and from this temperature on the process is slowed down.

The last mole of water contained in the structure is removed at relatively high temperatures, 350°-625°C, and it takes some time. This in turn indicates that the last mole of water is closely bound to the structure.

The dehydration of the tunellite mineral is also studied employing dynamic methods. The graph obtained by thermogravimetric balance and showing the weight losses of the tunellite mineral heated at temperatures increased linearly is given in Figure 5.

In this graph it is obvious that the first 3 moles of water are easily removed from the structure at temperatures up to 350°C. The last mole of water is removed in the temperature range between 350-625°C and this takes some time. After 625°C, the sample is converted into veatchite and is not tunellite any more. This transformation will be explained in detail in the section on X-ray diagrams.

The dehydration of the tunellite mineral at constant temperatures is studied in order to evaluate the results obtained by static and dynamic methods and also to establish the intermediate products of borate hydrates formed at certain temperature intervals.

For this procedure, 2.0000 grams of pulverized tunellite sample weighed with precision are heated to a constant weight at a series of selected temperatures. The loss of weight during this procedure is recorded automatically by a recorder on the thermogravimetric balance.

The period-water loss % (mole of water loss) graphs obtained for the tunellite mineral at a temperature range between 150-750°C are shown in Figures 6, 7, 8, 9,10,11,12, 13 and 14.

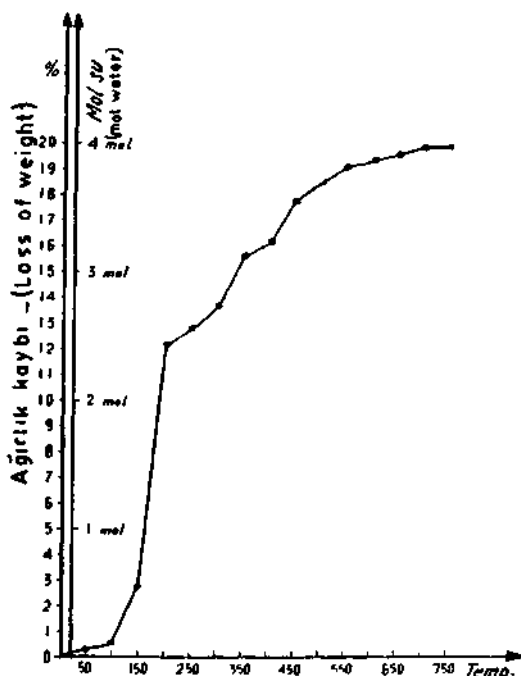


Fig. 4

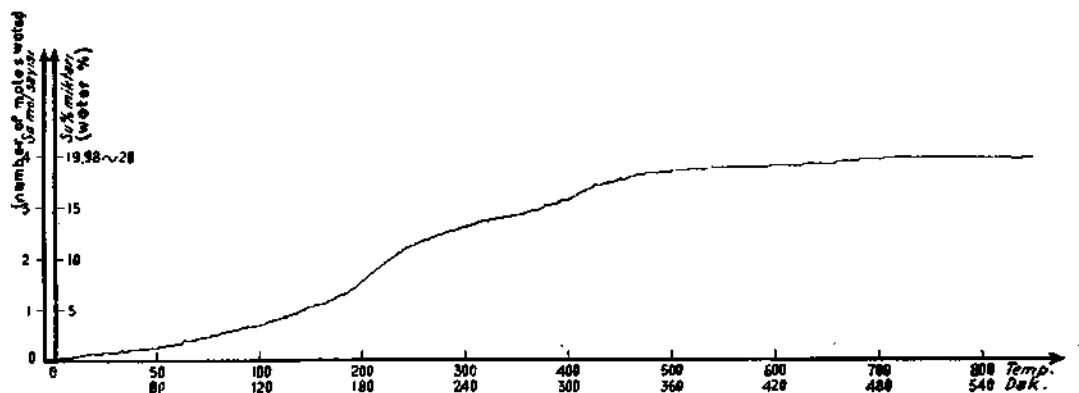


Fig. 5

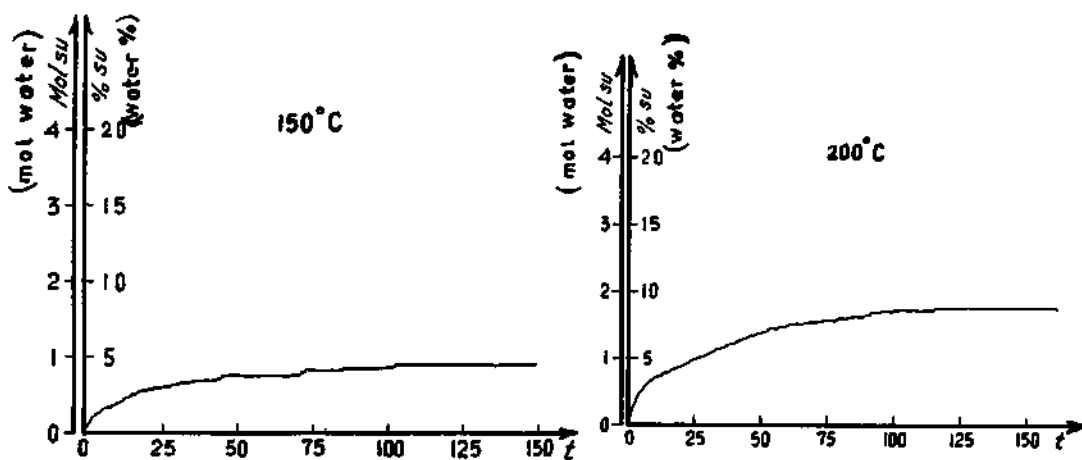


Fig. 6

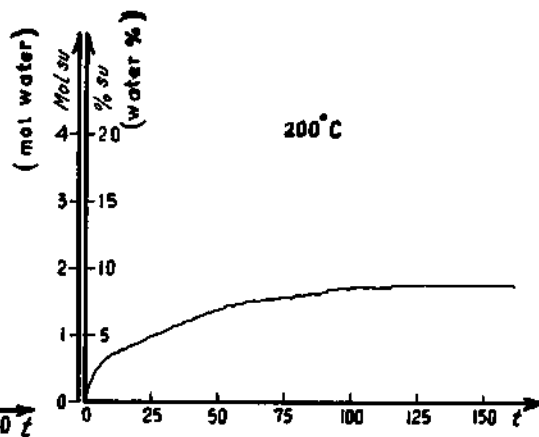


Fig. 7

No records on the occurrence in nature of intermediate products of borate hydrates, obtained at temperatures indicated above, are available in literature. Tunellite and veatchite minerals occur in nature, their formula being  $\text{SrO} \cdot 3\text{B}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ . Although these two minerals are very similar in regard to their composition, they are in fact fundamentally different regarding their structure.

### III. DIFFERENTIAL THERMAL ANALYSIS

To obtain further physical and chemical data on the structure of the tunellite mineral studied, differential thermal analysis of this mineral is done. The diagram obtained is presented in Figure 15.

In Figure 15, the DTA diagram and the diagram on the thermogravimetric analysis are presented together. Thus it becomes possible to follow the dehydration and the change of structure of the tunellite mineral more clearly.

In the DTA diagram two endothermic and one exothermic peaks are observed. The first endothermic peak represents the removal of the first 2 moles of water while the second endothermic peak indicates that the third mole of water is removed. The exothermic peak produced at 700°C,



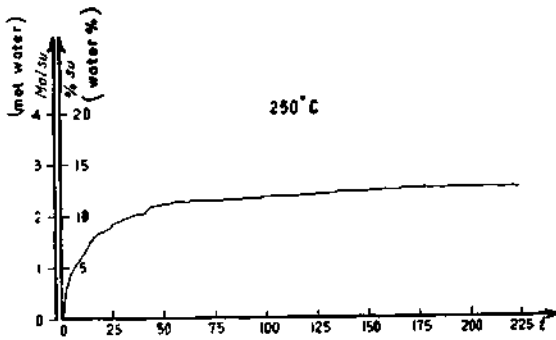


Fig. 8

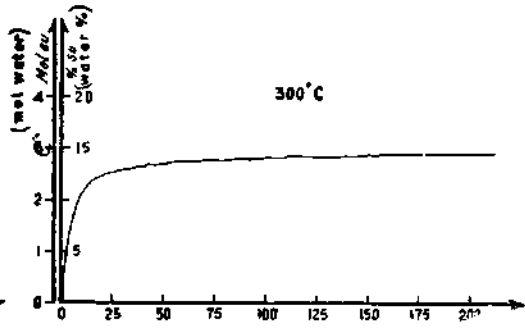


Fig. 9

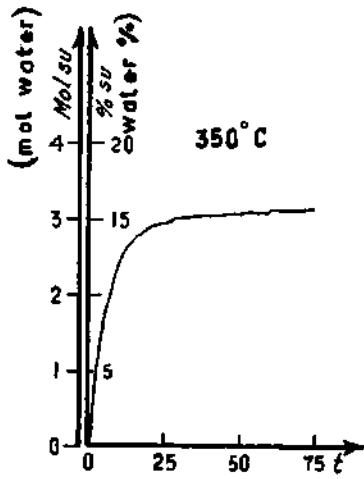


Fig. 10

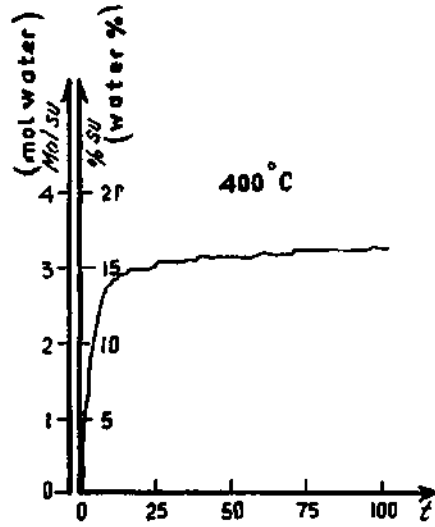


Fig. 11

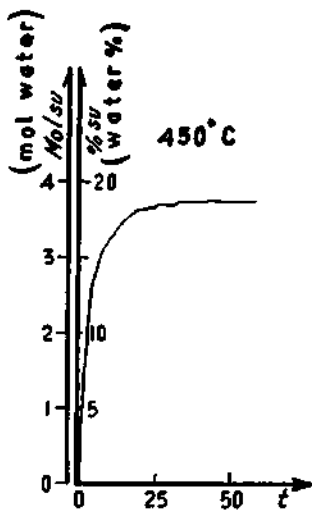


Fig. 12

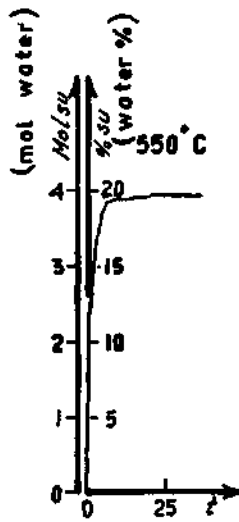


Fig. 13

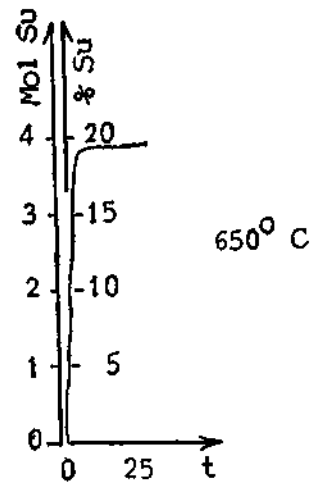


Fig. 14

shows that the tunellite mineral is converted into veatchite upon modification of structure rather than indicating that the fourth mole of water is removed. The last mole of water, which is the construction water of the mineral, will not be thrown out since it necessitates the decomposition of the crystal lattice. Although an endothermic peak is produced as a result of the dehydration of the fourth mole of water, the thermic variances destruct each other and a relatively low exothermic peak is produced at the temperature range between 475-700°C due to the fact that the modification of structure takes place exothermically at temperatures above 475°C.

The sample starts melting at 780°C.

In fact the transformation of the tunellite mineral into veatchite, upon heating to remove the last mole of water is well represented in the X-ray studies.

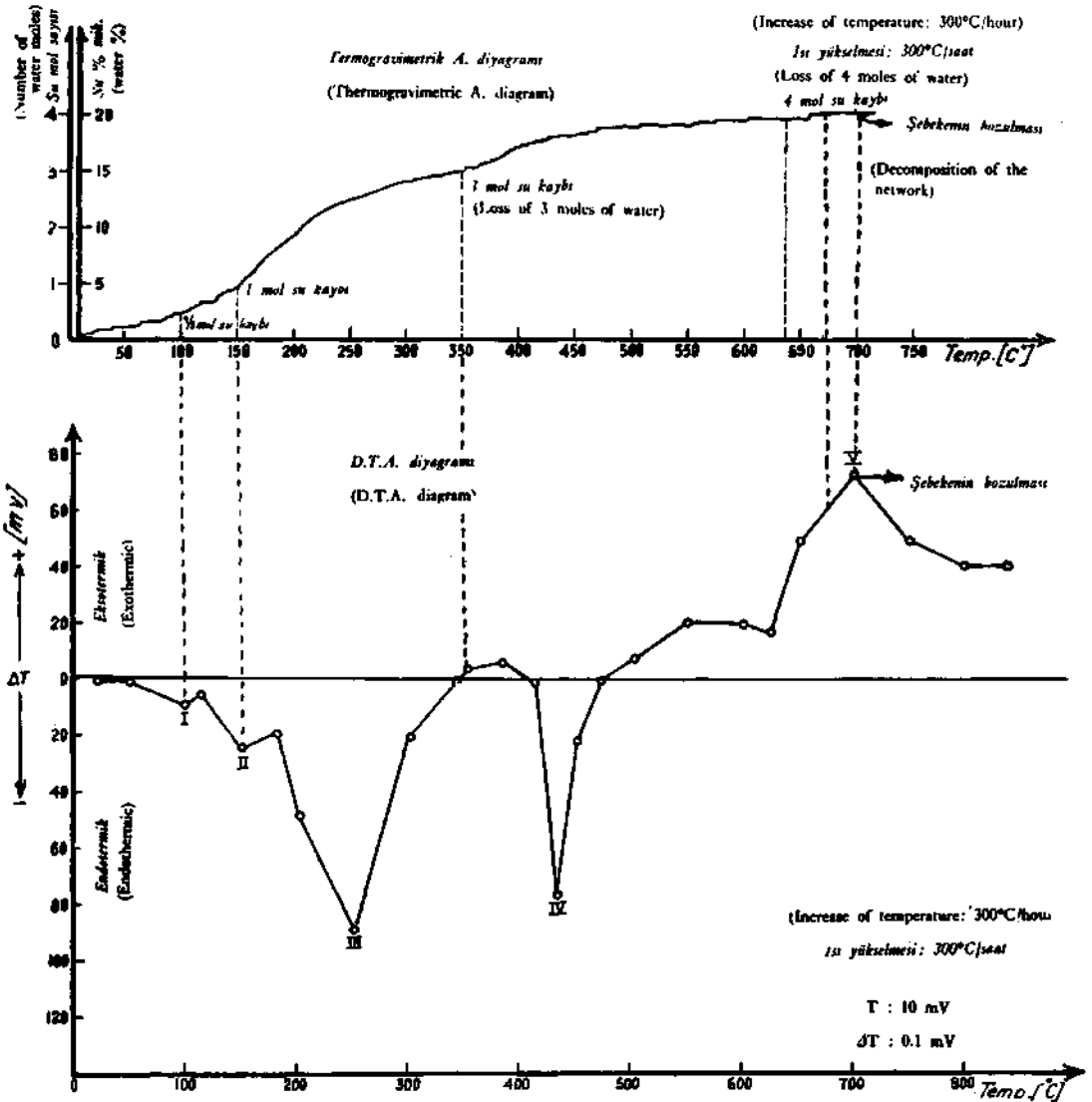


Fig. 15

## IV. X-RAY STUDY OF THE DEHYDRATION PROCESS

In Section I, where the physical properties of the tunellite mineral are given, it was also stated that the color of the samples used in dehydration studies darken upon heating at various temperatures. This darkening of color reaches its maximum degree at 600°C, and upon raising the temperature, the color showing an abrupt change becomes white again (at 700°C). The thermochromy of the tunellite mineral is due to structural modifications in parallel to heat effects.

X-ray studies of the tunellite mineral, using Debye-Scherrer powder diffraction method, is carried out to find out the thermochromy and the structural modifications of the mineral during dehydration and results obtained are represented in a diagram.

Characteristic diagram of the tunellite mineral at ordinary temperature is obtained (Fig. 1). In this diagram the peak produced around 2 $\theta$ :13.40 characterizes the tunellite mineral.

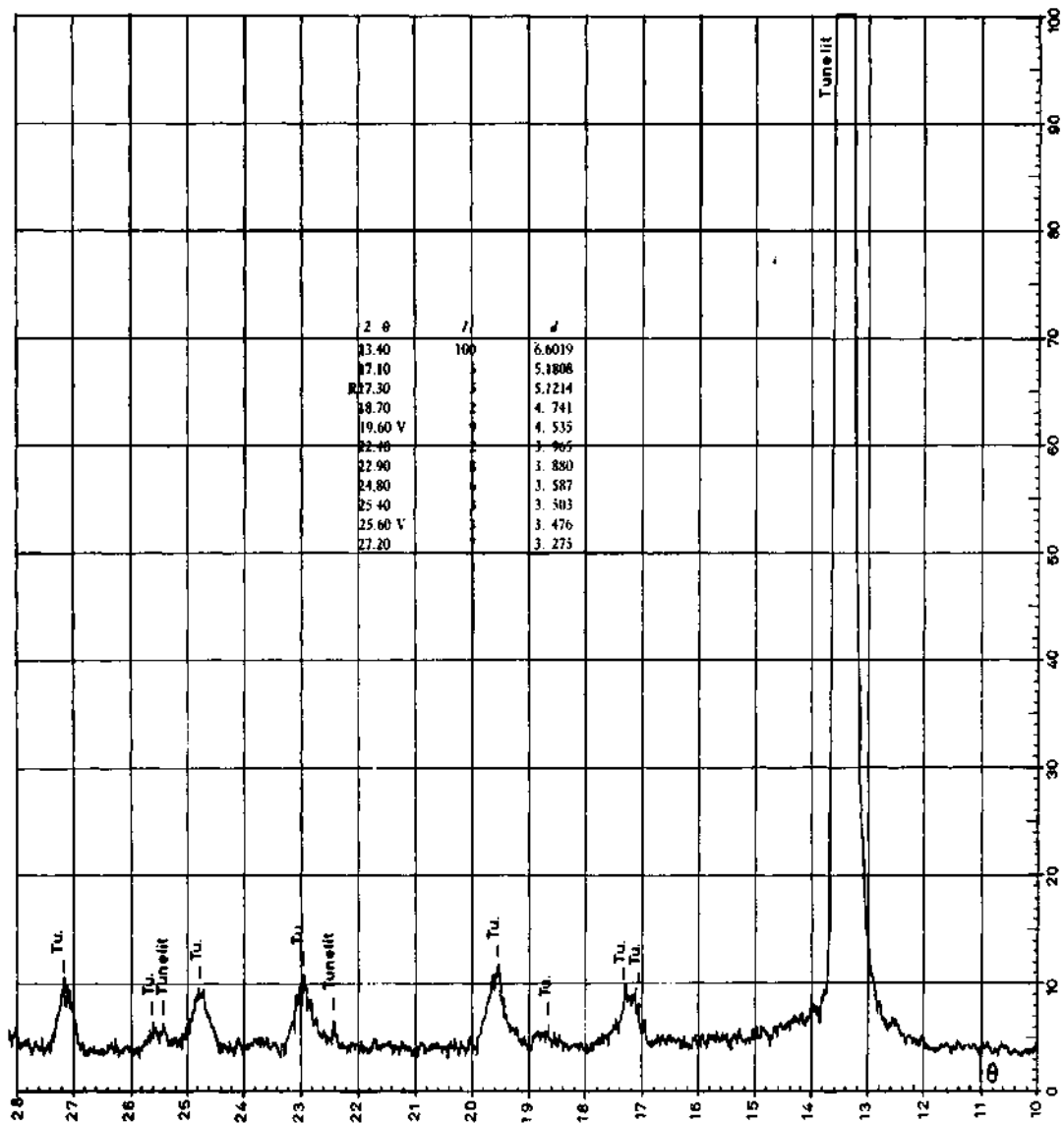


Fig. 16 - X-ray diagram of tunellite mineral at 100°C.

On the diagram it is observed that several other peaks having various  $\theta$  values and relatively low intensities are also present.

Following this, the tunellite minerals were heated separately at various temperatures and then cooled for 24 hours in order to have complete crystal formation and were very finely ground.

Tunellite samples were subject to heating at the following temperatures respectively: 100°, 150°, 200°, 250°, 300°, 350°, 400°, 450°, 500°, 600°, 725°, and 800°C. The diagrams obtained are presented in Figures 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26 and 27.

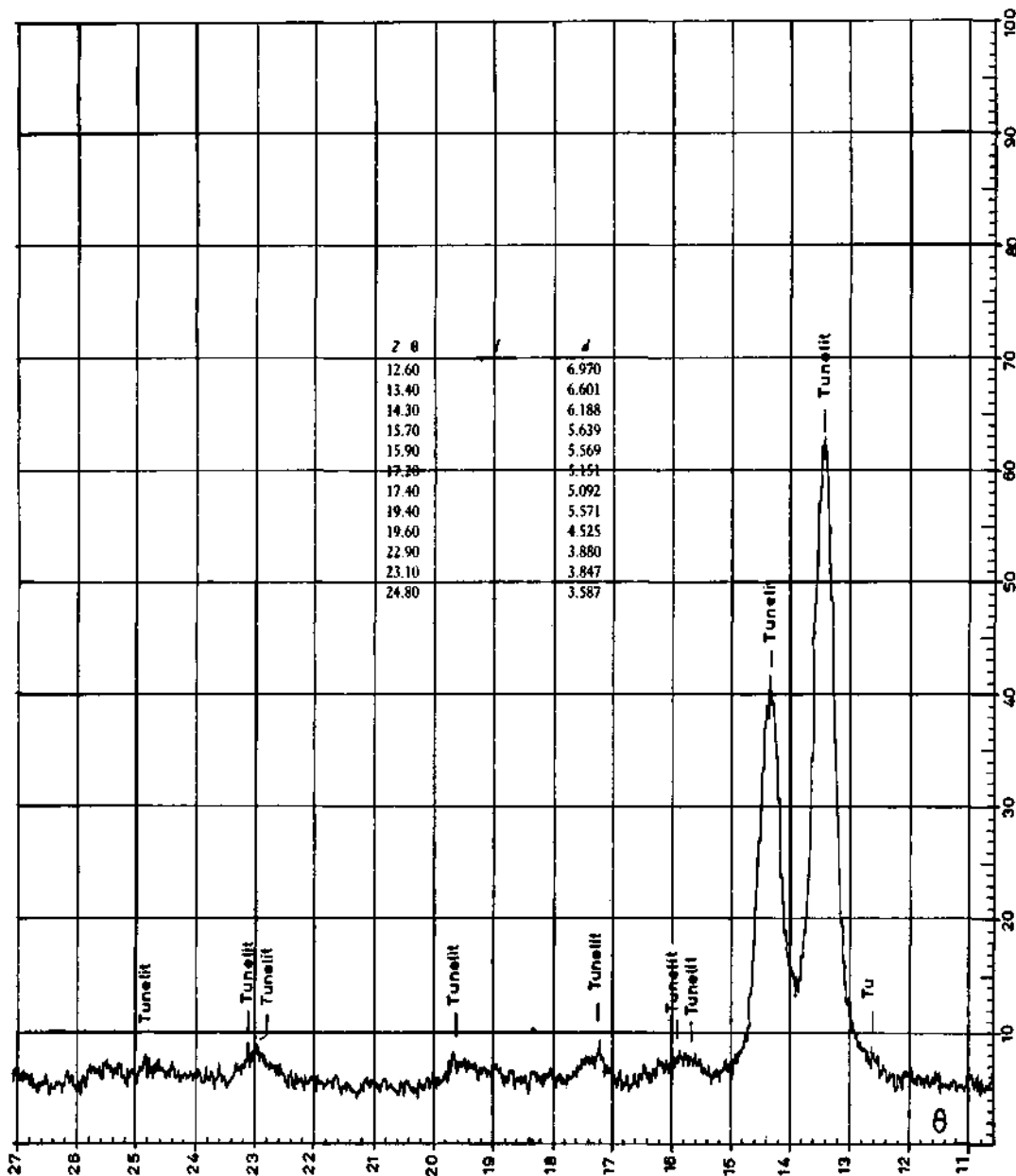


Fig. 17 - X-ray diagram of tunellite mineral at 150°C.

Close investigation of the graphs showed that the crystal cells expand due to heat absorption as a result of raising the temperature; furthermore the diffraction capacity of the X-rays is due to resulting surface modifications. This is represented in the diagrams for temperatures 150°C and 200°C (Fig. 17 and 18).

The peak produced at 20:13.50 has completely disappeared at 450°C. It is obvious that a considerable change took place in the crystal cell lattice which characterizes the crystal.

The crystal exhibits a complete structural decomposition at 600°C.

At 400-625°C, where the last mole of water which is closely bound to the crystal lattice is dehydrated, the reflex of the last X-ray diffraction peaks produced in the diagram on original tunellite mineral is zero. As the last mole of water is removed, the crystal lattice undergoes a complete decomposition and the original structure, as a result of an exothermic reaction, is converted into veatchite or p-veatchite.

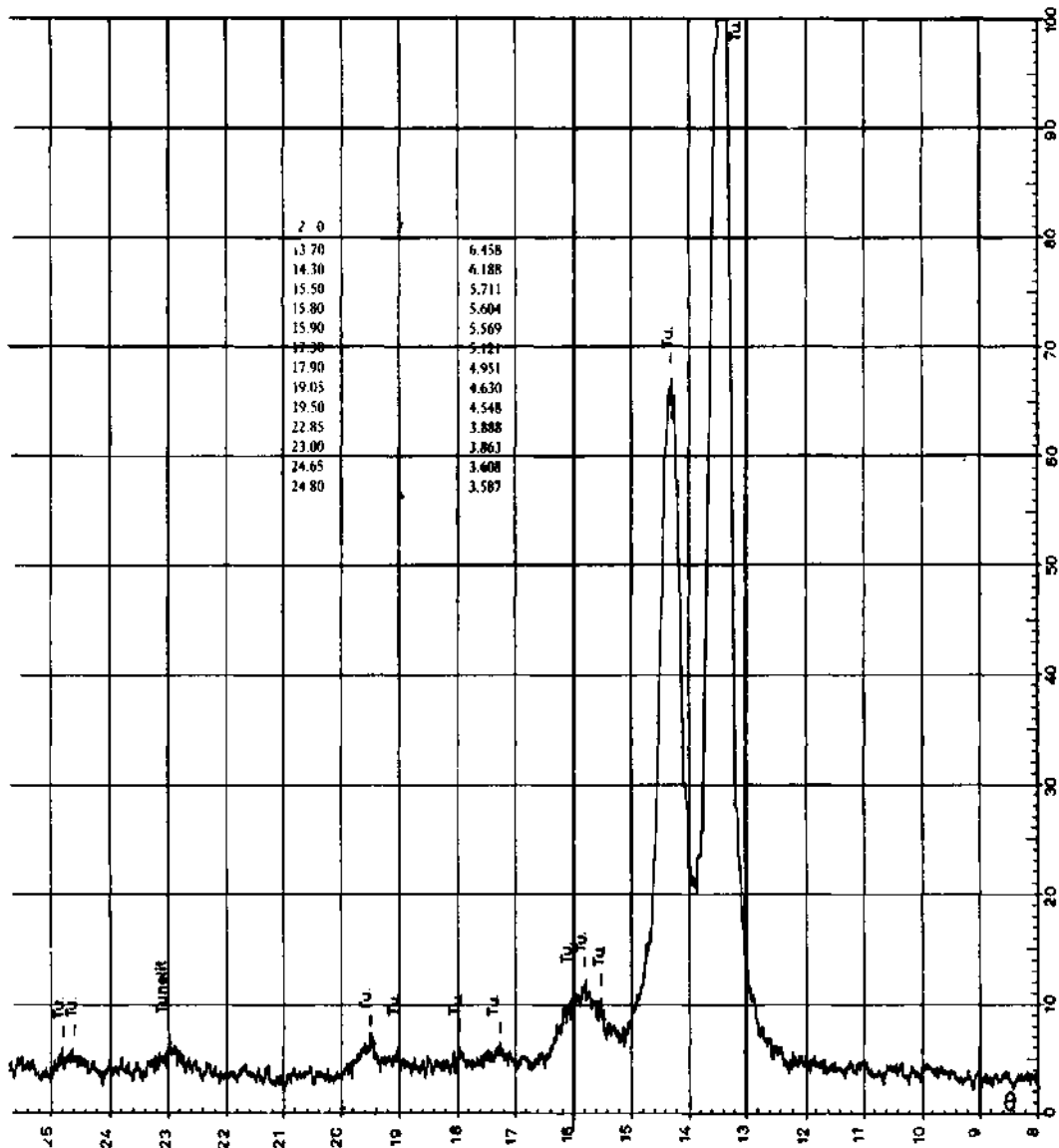


Fig. 18 - X-ray diagram of tunellite mineral at 200°C.

The X-ray diagram at 725°C, indicates that the crystal lattice is completely changed (Fig. 26). The mineral, completely dehydrated at this temperature, gives a diagram very similar to that of the diagram obtained for veatchite by X-ray study.

A new crystal lattice, resembling the anhydrous veatchite lattice is formed in the sample heated at 800°C. The lattice formed, however, is not in its final form, so it presents some variations compared to the lattice assigned to veatchite in literature.

CONCLUSION AND DISCUSSION

The tunellite occurrences of Turkey in the area described previously do not appear to be of economic interest.

The results obtained from the analysis showed that this new boron mineral recently discovered in Turkey is a member of the  $M^{+2}O \cdot 3B_2O_3 \cdot XH_2O$  series and that the  $M = Sr$  and  $X = 4$ . Thus the new mineral discovered is proved to be tunellite.

The dehydration studies of tunellite mineral using various methods showed that the first 3 moles of water contained are easily removed from the structure. The removal of the last mole of water necessitates relatively high temperatures (350-625°C) and also takes some time.

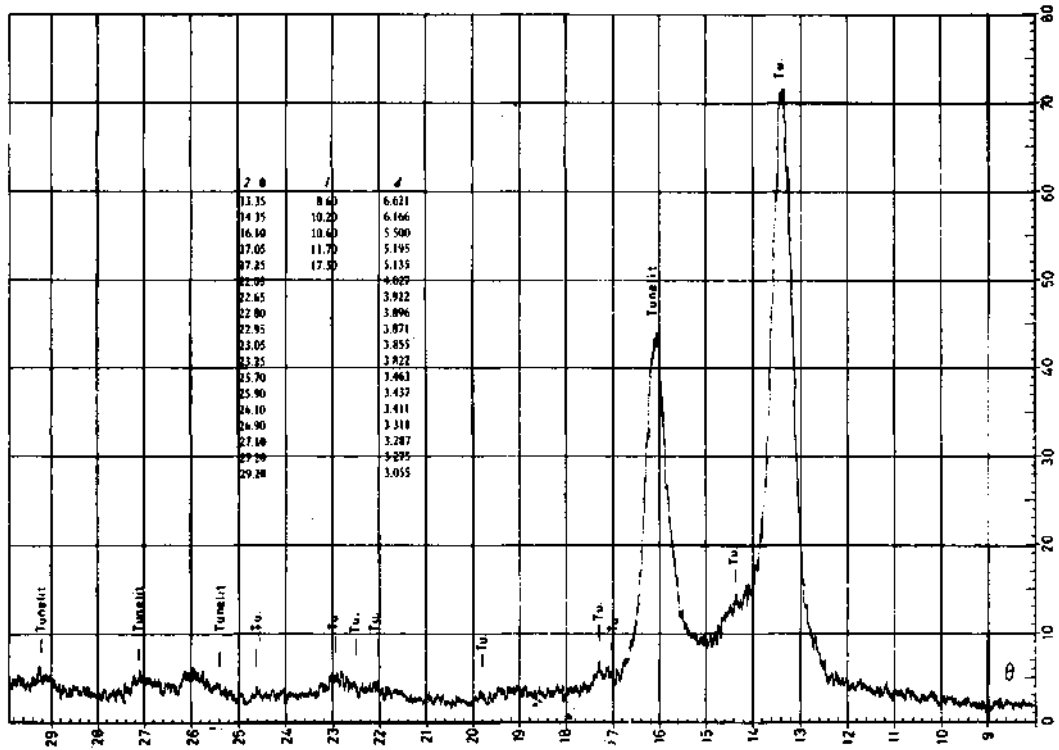


Fig. 19 - X-ray diagram of tunellite mineral at 250°C.

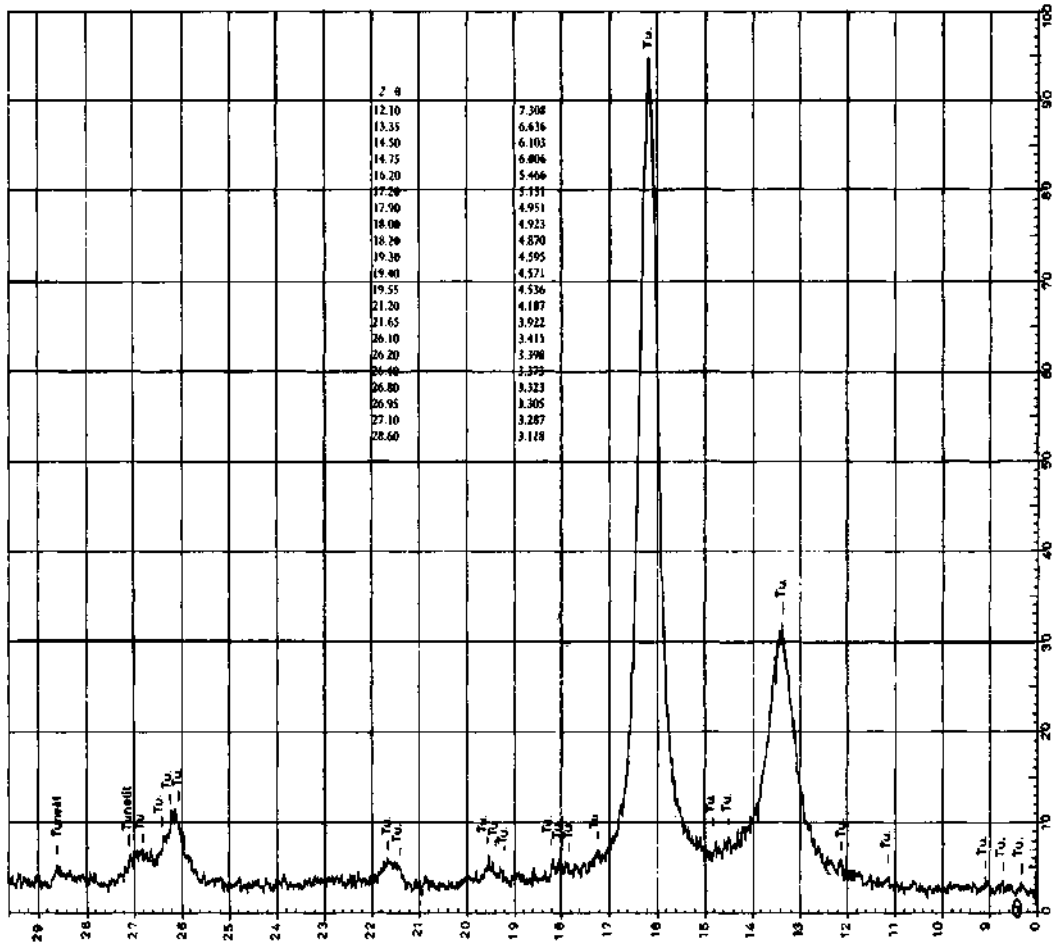


Fig. 20 - X-ray diagram of tunellite mineral at 300°C.

The dehydration of the mineral is also studied with DTA studies. The DTA studies showed that the mineral undergoes a structural modification upon the removal of the last mole of water.

X-ray studies showed that the structural modification takes place. Another fact revealed by the x-ray studies is that the original tunellite mineral is converted into anhydrous veatchite upon such dehydration process.

Translated by: Filiz E. DİKMEN

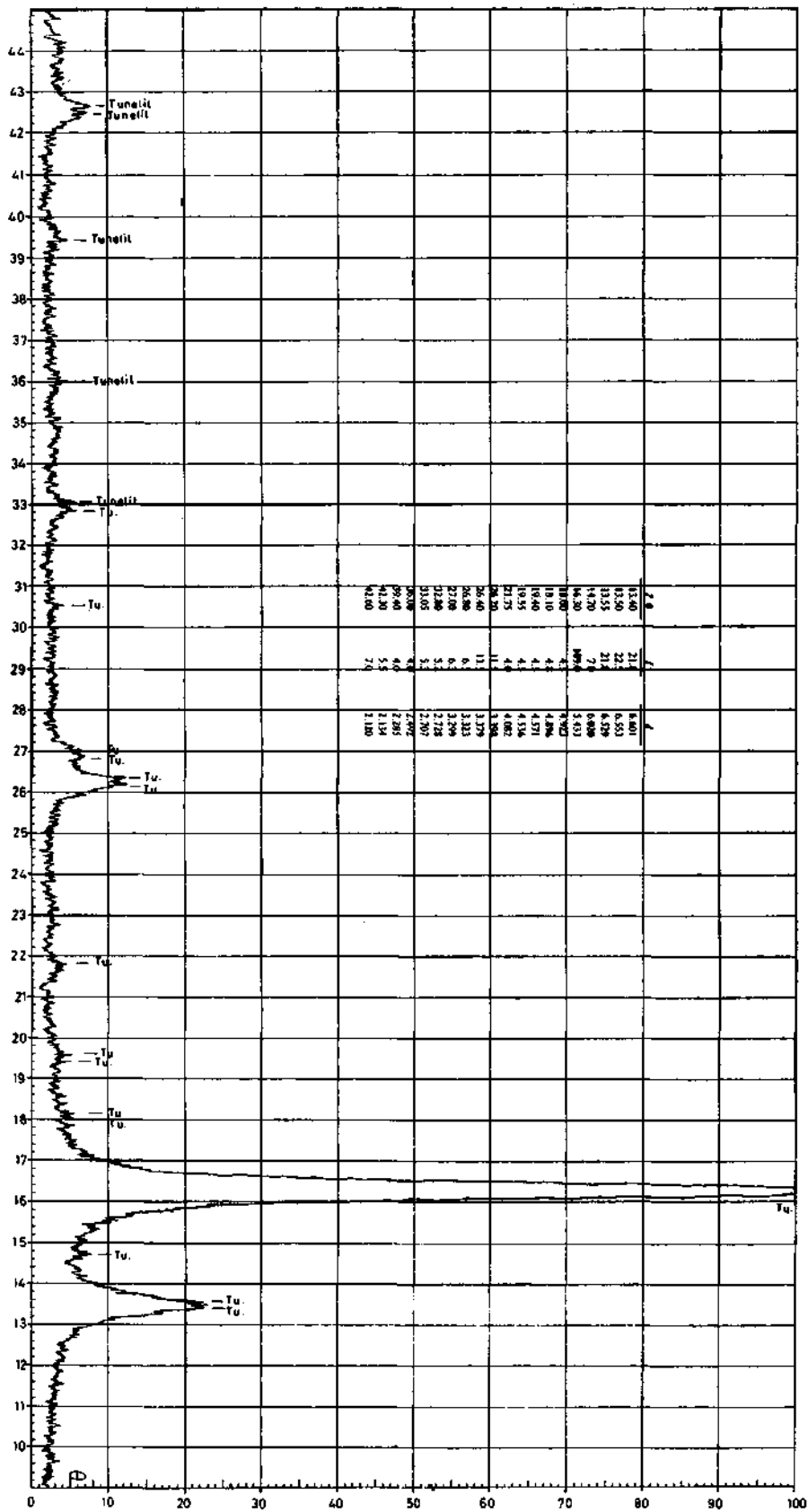


Fig. 21 - X-ray diagram of tunellite mineral at 350°C.



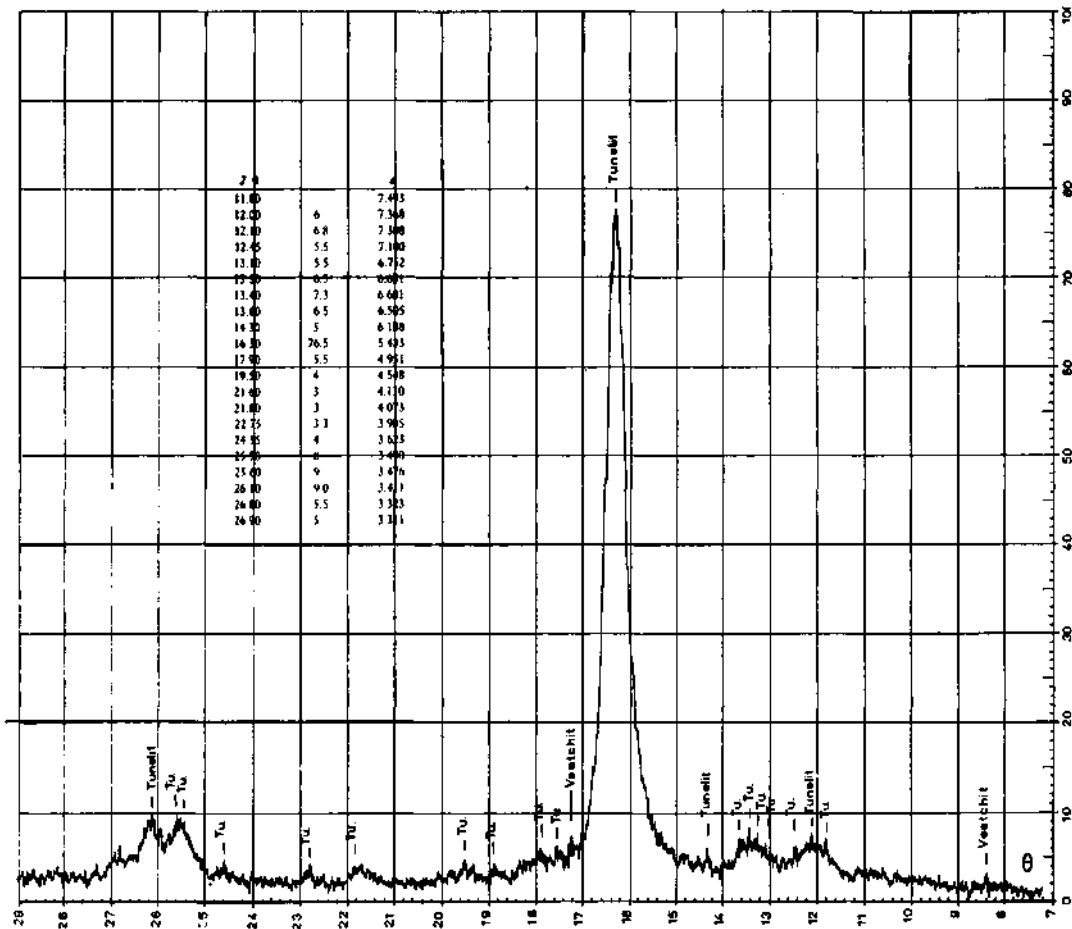


Fig. 22 - X-ray diagram of tunellite mineral at 400°C.

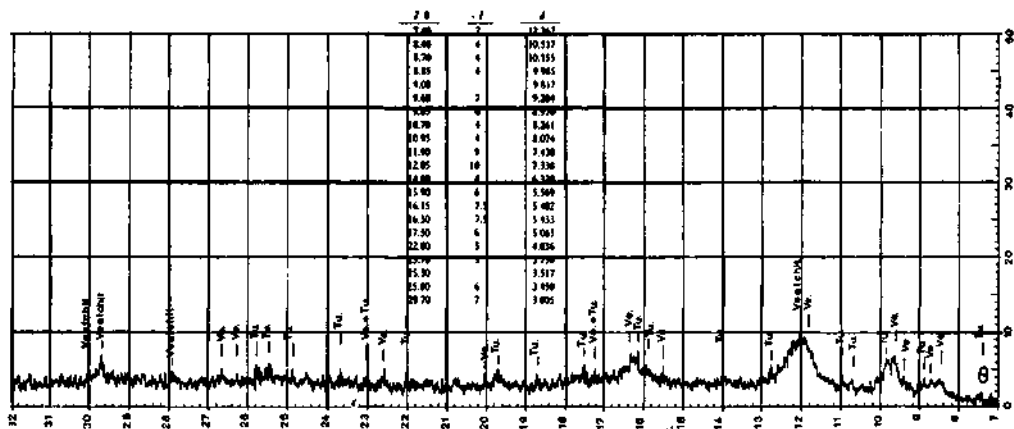


Fig. 23 - X-ray diagram of tunellite mineral at 450°C.

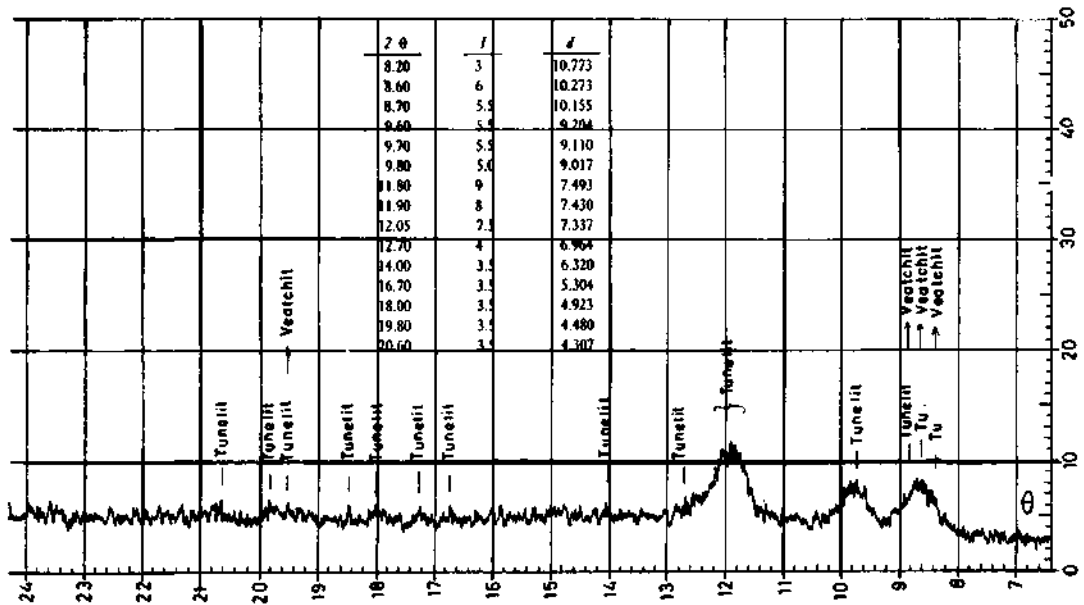


Fig. 24 - X-ray diagram of tunellite mineral at 500°C.

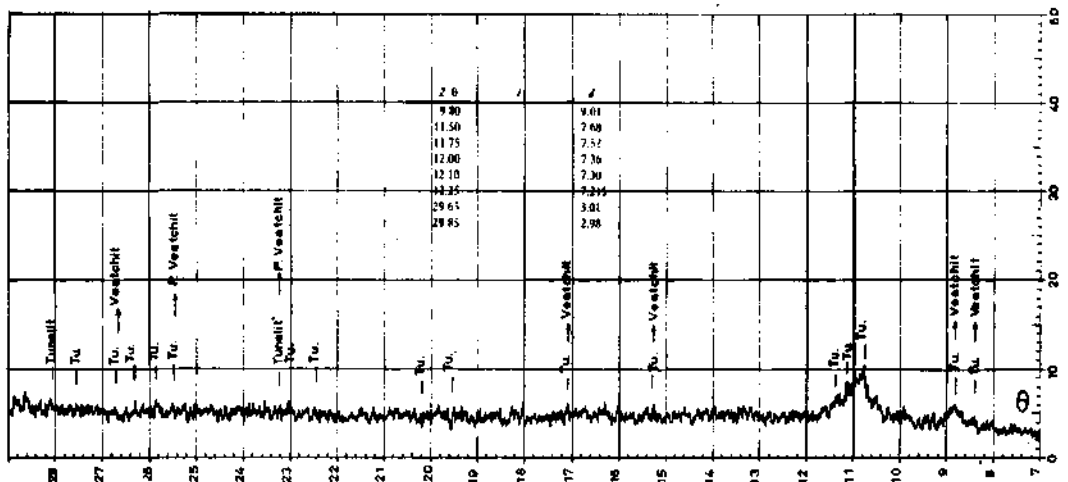


Fig. 25 - X-ray diagram of tunellite mineral at 600°C.

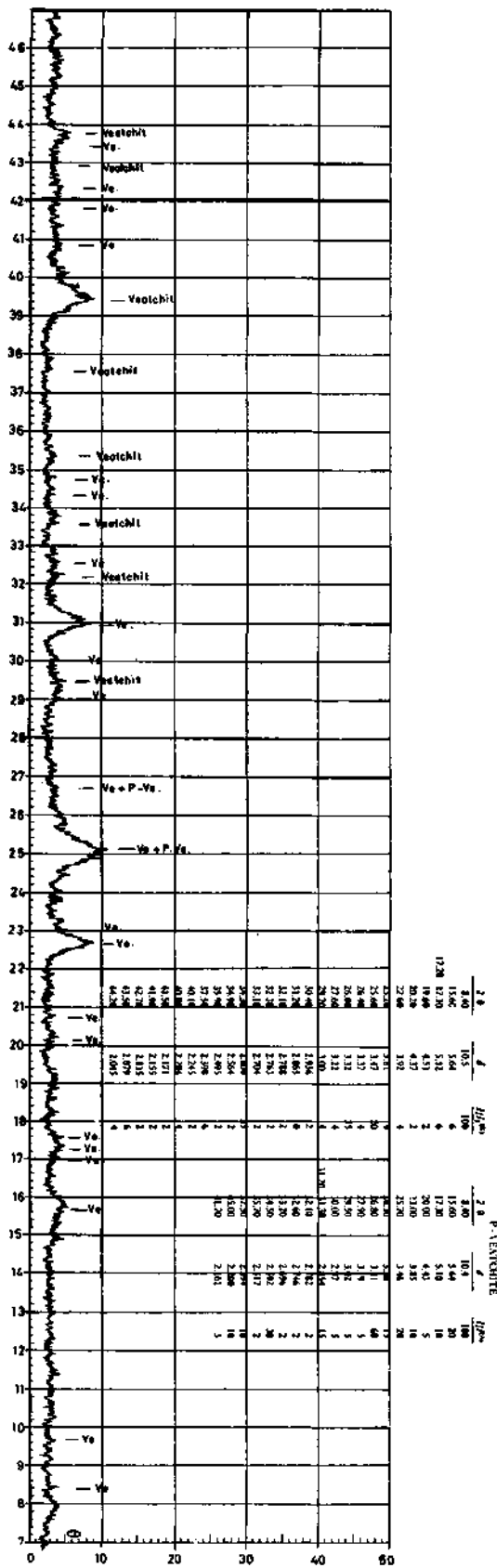


Fig. 26 - Diagram showing the transformation of original tunellite into veatchite and P-veatchite at 725°C.

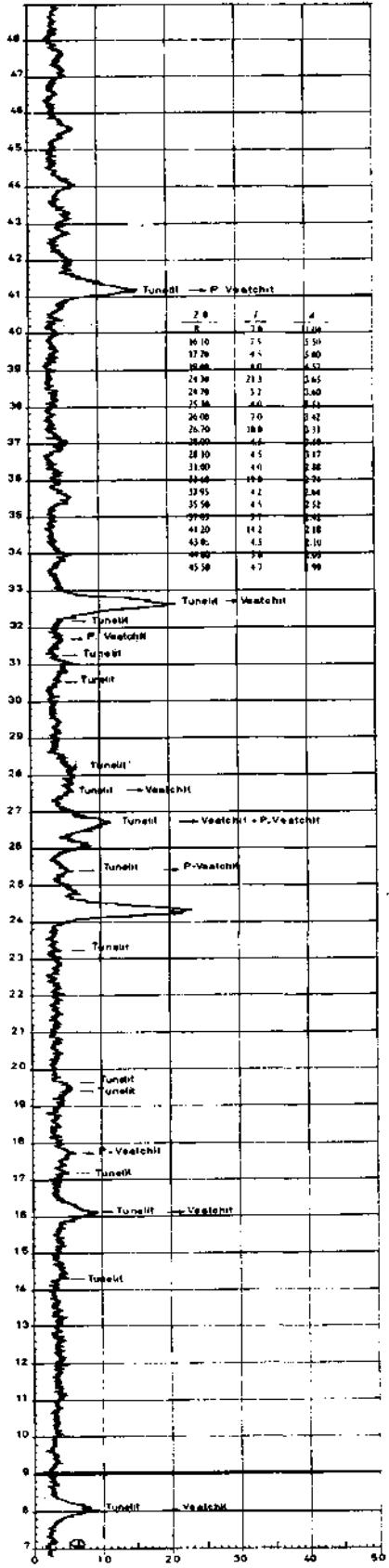


Fig. 27 - X-ray diagram of tunellite mineral at 800°C.

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