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TEPHROITE FROM FRANKLIN, NEW JERSEY*

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ABSTRACT

A study of tephroite specimens from Franklin and Sterling Hill, New Jersey showed in all of them the presence of thin sheets of willemite believed to be a product of exsolution. These sheets are oriented parallel to the {100} and {010} planes of tephroite with the *a* and *c* axes of tephroite and willemite parallel. It is believed that little zinc remains in the tephroite structure and that much of it reported in chemical analyses has been contributed by intergrown willemite. This conclusion is supported by experiments synthesizing tephroite. The indices of refraction and *d* spacing of {130} vary as would be expected with changes in amounts of MgO, FeO and CaO.

INTRODUCTION

Tephroite, Mn_2SiO_4, a member of the olivine group, was described as a new mineral from Sterling Hill by Breithaupt in 1823. A chemical analysis of the original material was published by Brush (1864) together with several additional chemical analyses of tephroite made by others. These analyses report ZnO in varying amounts which Brush attributed to invariably associated zincite. Palache (1937) did not agree with Brush and stated " . . . that the molecular ratios in some analyses more nearly satisfy the orthosilicate formula when zinc is regarded as essentially a part of the mineral rather than as a constituent of mechanical inclusions." The present study was undertaken for the purpose of investigating the variations in the properties of tephroite with changes in chemical composition, particularly the effect of zinc. Relationships were not expected to be simple for analyses show, in addition to ZnO, variable amounts of MgO, FeO, and CaO.

DESCRIPTION OF THE SPECIMENS

For this study 27 specimens in the Harvard collection labelled *tephroite* and *roepperite* were assembled. Several additional specimens were kindly made available by Mr. John L. Baum of the New Jersey Zinc Company and Mr. John Albanese of Union, New Jersey.

The name *tephroite* was given to the original material because of its gray color (from the Greek—*ash-colored*) but only six of the specimens studied were gray; thirteen were reddish brown; four rose-red. Roepperite is black. It was also considered for it has been described as a variety of tephroite containing notably high amounts of FeO and ZnO. Of

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the four roepperite specimens available, three proved to be black willemite.

When examined microscopically, most tephroite is seen to contain minute inclusions. These inclusions have been studied by Metsger, Tennant and Rodda (1958) who conclude they are franklinite and are responsible for the color variation. Black franklinite is present in roepperite and red franklinite (spinel) is present in the red tephroite. " . . . paler shades of gray and flesh pink . . . are due to the sparse scattering of inclusions." It has previously been thought that zincite inclusions were responsible for the red coloring. However, in some tephroite specimens flakes of both red zincite and black franklinite are present associated with willemite sheets and elongated parallel to the *c* axis of the tephroite.

Portions of all the specimens gave under ultra violet light the characteristic greenish luminescence of willemite. Some of this fluorescence resulted from massive willemite intergrown with the tephroite but much of it seemed to be coming from the tephroite itself. Closer examination showed thin fluorescing sheets of colorless willemite lying along the $\{100\}$ and $\{010\}$ planes of the tephroite. Sections normal to these two directions, $\{001\}$, show the traces of the sheets intersecting at right angles (Fig. 1). Under magnification more and thinner sheets become visible forming a minute crosshatched pattern. This is best observed in thin section where it is seen that the willemite sheets although discontinuous are all crystallographically oriented with the *c* axis of willemite parallel to the *c* axis of the tephroite host, Fig. 2. The major and most continuous willemite sheets are irregularly spaced and may have a thickness as great as 0.10 mm. The lesser sheets are much less continuous with thickness ranging from 0.05 mm. to less than 0.005 mm. A similar intimate intergrowth of willemite with glaucochroite was reported by O'Daniel and Tscheischwili (1944).

The cleavage of tephroite is given as $\{100\}$ and $\{010\}$, the directions of the interlayered sheets of willemite. On most of the Franklin tephroite when examined in detail these directions of breaking do not yield plane surfaces but are striated in a direction parallel to the *c* axis; an observation early made by Brush (1864). They appear to be more a parting than a cleavage, separating easily along the planes of the major willemite sheets. On most specimens it is impossible to develop a cleavage between these parting planes and in thin section no cleavage cracks are visible between the willemite layers. Small transparent crystals of Franklin tephroite show no cleavage parallel to $\{100\}$ or $\{010\}$ but a good $\{001\}$ cleavage.

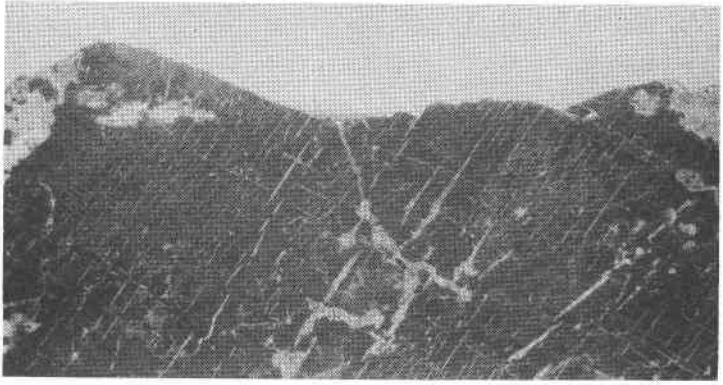

FIG. 1. Polished surface of tephroite crystal cut nearly normal to the *c* axis. Photographed under ultraviolet light with fluorescing willemite recorded as light lines and areas. Full scale.

In addition to the parallelism of the *c* axes of the tephroite and the included willemite there is a parallelism of other axial directions. *X*-ray rotation photographs were taken of the willemite with the rotation axes perpendicular to the sheets. One set of sheets, parallel to {100} of tephroite, yields 13.97 Å as the identity period (a_0 of willemite); the other set of sheets at right angles and parallel to {010} of tephroite

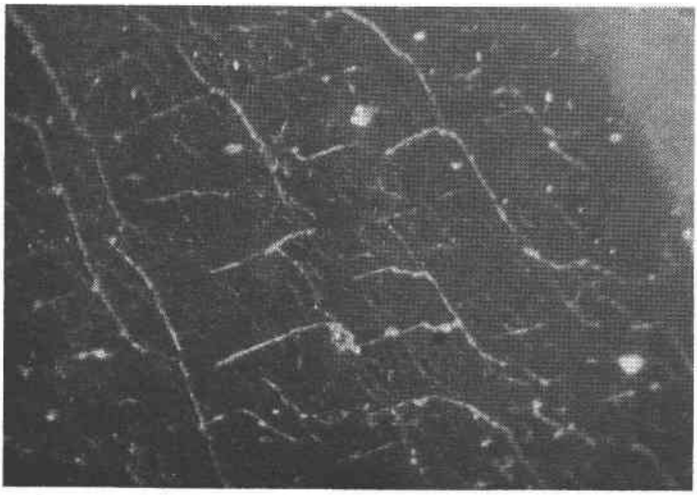

FIG. 2. Photomicrograph of tephroite thin section cut nearly normal to the *c* axis. Crossed nicols. Light lines are willemite. Area: 2×1.7 millimeters.

yields 24.20 Å as the identity period. For the willemite $c_0 = 9.35$ Å. The axial dimensions of the willemite and tephroite thus compare as follows:

Tephroite	$a_0 = 4.87$ Å	$b_0 = 10.64$	$c_0 = 6.23$
Willemite	$a_0 = 13.97$ Å	$\perp(10\bar{1}0) = 24.20$	$c_0 = 9.35$

For willemite Bragg and Zachariasen (1930) give $a_0 = 13.96$ Å, $c_0 = 9.34$. The closest structural correspondence of the two sets of dimensions is found in the values for c_0, for $3 \times c_0$ of tephroite is 18.69 Å, nearly equal to $2 \times c_0$ of willemite, 18.70 Å.

The constant orientation of the willemite with respect to the tephroite host as well as the intimate intergrowth strongly suggest that the willemite is a product of exsolution. Moreover, it is almost certain that much of the zinc reported in chemical analyses was contributed by willemite.

CHEMICAL COMPOSITION

Palache (1937) lists 13 chemical analyses of tephroite from Franklin and Sterling Hill. All of these show the presence of FeO (3.33% max.), and all but the earliest two MgO (15.9% max.) and ZnO (18.90% max.). CaO (2.70% max.) is present in six analyses. With the possibility of so many elements substituting for manganese in the tephroite structure, it at first appeared a hopeless task to correlate in any significant manner the physical constants with chemical composition.

Of the 13 specimens represented by the analyses given by Palache (1937, p. 77) only one (number 11) was available for study. This is a reddish-brown tephroite with abundant interlaminated sheets of willemite. The analysis made by L. H. Bauer (No. 1, Table 1) gives ZnO = 12.15%. With the thought that willemite may have contributed much of the zinc to the analysis, a magnetic separation was made on minus 325 mesh material. Tephroite is slightly magnetic, willemite non-magnetic. After many passes through the Frantz isodynamic separator, even the most magnetic material was far from being free of willemite as shown by inspection under the microscope and ultra-violet light, and the presence of willemite lines in an *x*-ray powder photograph. An analysis of this admittedly contaminated sample by Mr. Jun Ito gave 6.1% ZnO, approximately one half of that reported in the earlier analysis. With zinc present in the unseparated willemite as well as in the franklinite of the coloring inclusions, the amount in the tephroite structure must be considerably less. Could this mean that zinc is a negligible variant in the composition of tephroite?

Of the 27 specimens studied, one was selected for a complete analysis. This was of a large reddish brown tephroite crystal from which only the coarse associated willemite had been separated. The analysis, No. 2,

Table 1, compares very favorably with several earlier analyses reported by Palache (1937). Partial analyses were made of seven other tephroite specimens from Franklin and Sterling Hill and one of roepperite. In these zinc is not reported since willemite and probably franklinite was present in all and its determination would not have been significant. For comparison a partial analysis of tephroite from Långban containing no zinc was also made. In most of these analyses the chief oxide other than MnO is MgO and thus most of the specimens belong essentially to the series Mg_2SiO_4-Mn_2SiO_4. Glasser and Osborn (1960) point out that a continuous solid solution series exists between Mg_2SiO_4 and Mn_2SiO_4.

TABLE 1. ANALYSES OF TEPHROITE*

	1	2	3	4	5	6	7	8	9	10
SiO_2	29.53	30.17								
ZnO	12.15	10.22								none
MnO	43.64	49.57	36.09	32.82	58.42	53.18	46.19	51.31	28.68	55.65
MgO	9.64	4.92	15.28	15.76	2.40	1.07	8.72	2.66	5.65	10.75
FeO	4.41	3.94	1.26	1.40	0.79	0.78	1.90	0.29	24.28	0.09
CaO	—	0.05	0.63	0.10	0.05	4.40	tr	2.81	tr	1.10
Ig. loss	—	1.00								
	99.37	99.87								
Molecular ratio MnO:MgO										
MnO	72.02	85.13	57.29	55.92	93.26	96.58	75.29	91.64	74.27	74.64
MgO	27.98	14.87	42.71	44.08	6.74	3.42	24.71	8.36	26.73	25.36

* 1. Harvard No. 105489 Reddish-brown tephroite, Franklin, in Palache (1937) L. H. Bauer, analyst.
Analyses 2–10 Jun Ito, analyst.
2. Harvard No. 105617 Reddish-brown tephroite, Franklin
3. Hancock Coll. (Harvard) Pink tephroite crystals, Sterling Hill
4. Harvard No. 85551 Reddish brown crystals, Sterling Hill
5. Rowe Coll. (Harvard) Gray tephroite, Franklin
6. Harvard No. 33651 Gray tephroite, Franklin
7. Harvard No. 105490 Reddish brown tephroite, Franklin
8. Harvard No. 19574 Gray tephroite, Franklin
9. Bauer Coll. (Harvard) Black Roepperite, Franklin
10. Harvard No. 106580 Gray tephroite, Långban, Sweden

SYNTHESIS

In an effort to determine the extent of the solid solubility of zinc in tephroite a series of crystalline substances in the system $MnO \cdot MgO \cdot ZnO \cdot SiO_2$ were synthesized. The method of dry fusion following closely that used by Snow (1943) is briefly as follows: Reagent grade chemicals were used—silicic acid and the carbonates of the metals. Amounts of the reagents proportional to the stoichometric mole per cents were ground together in an agate mortar. The mixture placed in a platinum crucible was then heated at 950° C. in a stream of nitrogen for 90 minutes. The sintered oxides were then removed from the furnace and reground to insure thorough mixing. This powdered material was divided into two halves, pressed into pellets and returned to the furnace in separate crucibles where it was heated at 1250° C. for 90 minutes in a stream of nitrogen. One portion was then removed and cooled quickly in air. The other portion remained in the furnace which was cooled at the rate of 20° C. per hour to 950° C. At this temperature the furnace was turned off and allowed to cool to room temperature.

The first synthesis was of Mn_2SiO_4. This was followed by other runs in which increasing amounts of ZnO were introduced with proportionally less MnO. MgO in varying amounts was introduced in several runs. Data obtained on the slowly cooled material are summarized in Table 4. The x-ray powder data obtained on the slowly cooled and rapidly cooled products were the same within the limits of error. However, the indices of refraction of the slowly cooled material containing zinc were all slightly higher than the corresponding rapidly cooled portion. The maximum difference in refractive index was 0.014.

X-RAY INVESTIGATION

X-ray Weissenberg photographs were taken on a crystal of tephroite supplied by Mr. Albanese. This crystal, transparent and nearly colorless, was one of five in a cavity in franklinite-willemite ore from Franklin. The largest of these crystals was 2 millimeters long. Spectroscopic analysis showed less than 1.0% ZnO and less than 0.5% MgO, FeO, CaO. It appeared to be very similar to crystals described by Gordon (1922) and others analysed by L. H. Bauer and reported by Palache (1928). In Bauer's analysis MgO = 0.46, ZnO = 1.53, FeO = 0.31%. The unit cell dimensions were determined as $a_0 = 4.871$ Å, $b_0 = 10.636$, $c_0 = 6.232$. These are all slightly larger than those given for tephroite from Franklin by O'Daniel and Tscheischwili (1944), which were $a_0 = 4.86$ Å, $b_0 = 10.62$, $c_0 = 6.22$, but almost identical with those reported by Strunz (1957). The axial ratios $a_0 : b_0 : c_0 = 0.458 : 1 : 0.586$. Palache (1937) gives the morphological axial ratios $a : b : c = 0.461 : 1 : 0.589$. The specific gravity of these crystals, the only tephroite studied which it is felt is sufficiently free of mechanical inclusions to give a significant determination, is 4.10 measured on the Berman balance. The calculated specific gravity of Mn_2SiO_4 for the measured cell dimensions is 4.15. It is also interesting to note that these crystals show a good {001} cleavage but no {100} or {010} cleavage.

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR SYNTHETIC TEPHROITE
Filtered copper radiation with quartz standard

hkl	*d* obs.	I	*hkl*	*d* obs.	I
020	5.301	15	131	2.611	70
110	4.431	5	112	2.572	90
021	4.044	20	041 200	2.440	15
101	3.830	5			
111	3.624	6	210	2.307	15
002	3.116	14	140	2.335	20
130	2.867	100	211	2.200	18
022	2.688	10	132	2.101	5
040	2.660	30	113 222	1.811	35

X-ray study of the other natural and synthetic tephroite was confined largely to recording of powder diffraction data. In Table 2 the *d* spacings of synthetic Mn_2SiO_4 are given. It will be noted in Table 2 that the line of greatest intensity ($d=2.867$) is given by the plane (130). Yoder and Sahama (1957) presented a determinative curve for olivine (forsterite-fayalite) based on the position of this (130) reflection which is of high intensity and varies linearly throughout the series. Sahama and Hytönen (1958) also used this (130) *d* spacing to distinguish between members of the monticellite-kirschsteinite series. In all the manganese bearing olivines (130) is also a high intensity reflection and was thus chosen as the structural parameter to measure in the present study.

The data were recorded using a Norelco Geiger-counter diffractometer with a scan speed of $\frac{1}{4}°$ per minute and a chart speed equal to 2 inches per degree 2θ. Finely ground samples, mixed with quartz to about 20% of their volume, were made into pressed mounts. The position of the copper Kα $(10\bar{1}1)$ reflection for quartz ($2\theta=26.664°$) was used to correct the measurements of the (130) reflection of the tephroite.

The values of d_{130} for the analyzed tephroites are given in Table 3 and for the synthesized tephroite in Table 4. Both are plotted in Fig. 3 as a function of the MnO:MgO ratio.

REFRACTIVE INDICES

The indices of refraction of material labelled "tephroite" from Franklin and Sterling Hill show a considerable variation reflecting compositional difference. The β refractive indices of analyzed tephroites obtained using sodium light are given in Table 4 and are plotted in Fig. 3 as a function of the ratio of MnO:MgO. The β refractive indices of synthetic products containing MgO given in Table 4 are also plotted in Fig. 3.

TABLE 3. X-RAY MEASUREMENTS AND REFRACTIVE INDICES OF NATURAL TEPHROITE*

	MnO:MgO		β index	d_{130}
1	72.02	27.98	1.775±0.001	2.840±0.001
2	85.13	14.87	1.795	2.850
3	57.29	42.71	1.739	2.829
4	55.92	44.08	1.743	2.827
5	93.26	6.74	1.800	2.861
6	96.58	3.42	1.791	2.871
7	75.07	24.93	1.775	2.844
8	91.64	8.36	1.790	2.868
9	74.72	26.73	1.804	2.840
10	74.64	25.36	1.768	2.848
11	98.12	1.88	1.803	2.863

* Numbers 1–10 correspond to analyses of Table 1. Number 11 is tephroite from Antarctica described by Mason (1959) and loaned by him for this study.

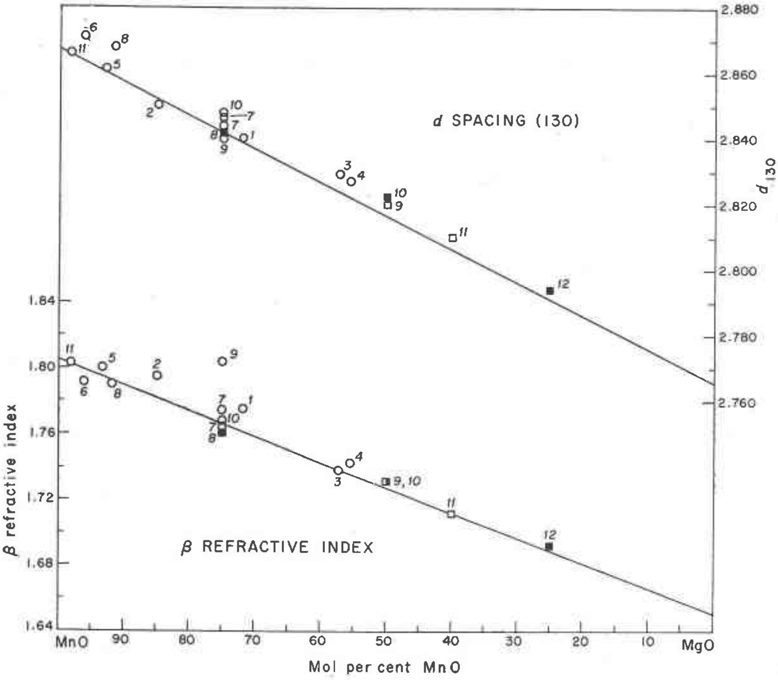

FIG. 3. Plot of d_{130} spacing and refractive index of tephroite plotted against mol per cent MnO. Circles represent natural tephroite; squares represent synthetic tephroite. Open squares—no zinc in starting material; solid squares—zinc present in starting material. Curves are drawn assuming a linear variation between Mn_2SiO_4 and Mg_2SiO_4 for d_{130}, and refractive indices.

DISCUSSION OF RESULTS

In Fig. 3 are plotted the d_{130} spacings and β refractive indices of synthetic and analysed natural tephroite against mol per cent of MnO. The curves are drawn as straight lines assuming linear variations between the fictive end points. For tephroite $d_{130}=2.867$ Å, $\beta=1.805$; forsterite $d_{130}=2.766$ Å (Yoder and Sahama, 1957), $\beta=1.651$ (Larsen and Berman, 1934).

The departure of the plotted points from both curves is believed due largely to the presence of cations other than Mn^{++} and Mg in the A position of A_2SiO_4. For Fe_2SiO_4 (fayolite) $d_{130}=2.833$ Å (Yoder and Sahama, 1957) and $\beta=1.886$ (Larsen and Berman, 1934). Thus Fe^{++}, when substituting for Mn^{++}, tends to slightly lower the d_{130} spacing and to raise the refractive index. For $CaMgSiO_4$ (monticellite) $d_{130}=2.934$ Å (Sahama and Hytönen, 1958) and $\beta=1.651$. Calcium has the effect when substituting for Mn^{++} of increasing the d_{130} spacing and decreasing the refractive index. The effect of the presence of Fe^{++} is shown most strikingly in specimen No. 9 (roepperite) with 24.28 wt. per cent FeO, and to a lesser extent in Nos. 1 and 2. Specimen No. 6 (4.40 wt. per CaO) shows the increase of d_{130} and decrease of β index with appreciable calcium.

TABLE 4. *X*-RAY MEASUREMENTS AND REFRACTIVE INDICES OF SYNTHETIC TEPHROITE, A_2SiO_4

	Mol Per Cent of A Cation			β index	d_{130}
	Mn	Zn	Mg		
1	100			$1.805^{\pm 0.001}$	$2.867^{\pm 0.001}$
2	95	5		1.803	2.863
3	90	10		1.804	2.861
4	85	15		1.803	2.860
5	80	20		1.802	2.860
6	75	25		1.802	2.860
7	75		25	1.764	2.847
8	60	20	20	1.760	2.842
9	50		50	1.732	2.820
10	45	10	45	1.731	2.822
11	40		60	1.712	2.810
12	20	20	60	1.693	2.794

The position of the plotted points in Fig. 3 for both refractive index and d_{130} for natural tephroite are essentially what would be expected from the compositions without consideration of zinc. One can thus conclude that zinc, if at all significant, plays a very minor role.

Consideration of the data given in Table 4 indicates that the solid solubility of zinc in tephroite is limited. The zinc that enters the lattice has little or no effect on the refractive index, but appears to have a slight effect on the structure as shown by the reduction of the *d* spacing of (130). Additions of 5, 10, and 15 mol per cent of ZnO to the starting mixture show a progressive, though slight, decrease in this spacing of the crystalline products. Greater amounts of ZnO show no effect. Unfortunately it is impossible to tell how much of the available zinc substituted for manganese in the tephroite and how much formed the separate phase, Zn_2SiO_4. Willemite lines were detectable on all diffractometer recordings in which the starting material for the synthesis contained more than 5 mol per cent ZnO. A separate phase of lower refractive index ($n=1.69$) was also observed optically. It seems reasonable to conclude that up to a certain amount the more zinc available, the more will be taken into the tephroite structure though even at low concentrations all of it is not accommodated. The experiments indicate that certainly not more than 10% and probably less than 5% of zinc substitutes for manganese. The slight effect of the presence of zinc is shown in the two pairs of synthetic products 7–8 and 9–10. One member of each pair contained ZnO, the other none, the ratio of MnO:MgO remaining the same; yet the indices of refraction and the d_{130} spacings are closely similar.

Although it is possible to identify a tephroite and a willemite phase in the synthesized material, there was no indication in the fine grained crystalline aggregates of any ordered arrangement between them as in natural tephroite. It was thus impossible to tell by observation whether they formed simultaneously or that the willemite was exsolved on cooling. Although the *d* spacing of (130) was essentially the same in both quenched and slowly cooled samples, the index of refraction of the quenched material was consistently lower. For example for run No. 4, $\beta=1.804$ slowly cooled and $\beta=1.790$ on the quenched sample. There is thus indication that there has been unmixing on slow cooling.

The greatest amount of zinc reported in a tephroite analysis by Palache (1937) is 18.9 wt. per cent ZnO. This, approximately 22 mol per cent of the manganese, might be assumed as the maximum amount of zinc present in the structure at high temperature. If exsolution has indeed taken place, zinc must have been in 6-coordination. With separation of willemite on cooling, the zinc is in the more comfortable situation of 4-coordination. That only small amounts of zinc are accommodated in the crystal structure of tephroite is consistent with the general observations on the geochemistry of zinc. Newmann (1949) points out that in all the common zinc minerals with the exception of smithsonite, zinc is in 4-coordination. He further states that if it entered into common structures in 6-coordination it would be camouflaged in the ferromagnesian minerals. Ridge (1952) in discussing the geochemistry of the ores of Franklin remarks, "If the zinc reported by the chemical analyses in tephroite is really in the crystal lattice and is not present as submicroscopic inclusions of zincite, it seems almost certain that the zinc is present as the unusual Zn^2 in 6-coordination."

CONCLUSIONS

The oriented intergrowth of willemite in tephroite speaks eloquently for its origin as a product of exsolution. With the slow cooling of natural tephroite the unmixing of Zn_2SiO_4 may have been nearly complete. Most certainly one can conclude that it contains much less zinc than has been reported in many chemical analyses. The variations that exist in the properties of tephroite result, therefore, from the substitution of Mg, Fe^{++}, and Ca for Mn^{++} rather than from the substitution of Zn.

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