THE IDENTITY OF TINZENITE WITH MANGANOAN AXINITE*

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Abstract

Tinzenite, described in 1923 as a new mineral of formula $2CaO \cdot Mn_2O_3 \cdot Al_2O_3 \cdot 4SiO_2$, is shown by *x*-ray, chemical, physical, and optical data to be manganoan axinite. More than 5% B_2O_3 was overlooked in all of the previous seven analyses of tinzenite. The existence of such axinite with CaO content greatly lower than previously known shows that the formula of axinite, usually written $HCa_2(Fe, Mn)Al_2BSi_4O_{16}$, is better written $H(Ca, Fe,Mn)_3Al_2BSi_4O_{16}$.

History of Tinzenite

Tinzenite was described by Jakob (1923) from Tinzens, Canton Graubünden, Switzerland, as a new species, with the formula, based on two analyses, $2CaO \cdot Mn_2O_3 \cdot Al_2O_3 \cdot 4SiO_2$. The mineral was described as yellow, fibrous to platy, with monoclinic symmetry, with cleavage perfect on {100}, optic plane parallel to {010}, Z=c; indices of refraction 1.693, 1.701, 1.704, with corresponding pleochroism, weak yellow green, weak green, colorless; density 3.286.

In abstracting the paper, Foshag (1925) commented that the formula given by Jakob did not include the water content, which may be essential; that recalculation of Jakob's analysis led to a formula closer to $2CaO \cdot 3(Al,Mn)_2O_3 \cdot 6SiO_2$; that the purity of the analyzed specimens was not stated; and that the exact character of this mineral (tinzenite) must be considered doubtful.

Jakob (1926) replied to this criticism by stating that the analyzed material was microscopically pure; the water (and alkalies) was not extraneous, but belonged in the constitution of the mineral; that low summations (in two of four analyses) resulted solely from the smallness of the samples analyzed; the water, most of which required strong heating to drive off, must, with the alkalies, be considered as replacing CaO, and not, as Foshag suggested, be disregarded. Jakob believed that variability in color of tinzenite, from citron yellow to orange red, is not caused by superficial alteration, but that it may be found in perfectly fresh material. Two new analyses by P. Esenwein are similar to the two made by Jakob. He concludes that variability in color may be related to oxidation states of the manganese, which present analytical methods cannot precisely define.

Tinzenite was also identified from Cassagna in Liguria, Italy, by Pel-

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* Publication authorized by the Director, U. S. Geological Survey.

loux (1934) in material which he had described some years earlier (Pelloux, 1919).

Sanero (1936) studied Pelloux's tinzenite, giving two new analyses of the Italian mineral that closely agree with the four previous analyses of tinzenite from Switzerland.

Jakob (1933) reviewed the mineralogy, especially the chemistry of tinzenite, with a fifth analysis of rose red material (formula $2CaO \cdot Mn_2O_3 \cdot Al_2O_3 \cdot 4SiO_2$), which agrees well with previous analyses of citron yellow to orange red tinzenite. He also mentions that tinzenite had been erroneously identified as zoisite (Müller, 1916; Arbenz and Tarnuzzer, 1923). This fifth analysis made on adequate "absolutely pure" material, and stated to be "absolutely reliable" (absolut zuverlässig), is cited below in analysis A, Table 2.

Winchell (1951) also refers to tinzenite as "closely related to thulite in composition and properties," and ascribes a formula $H_2Ca_3Al_4Mn_4Si_8O_{32}$.

The morphology of tinzenite has been investigated recently by Parker (1948) and Waldmann (1948), who found a triclinic symmetry and who mentioned a crystal setting showing some relation to axinite.

Strunz (1949) lists tinzenite as monoclinic with the formula $Ca\,Mn'''Al(SiO_4)_2$, with structure undetermined.

It seems strange that in all these analyses no test for boron was made, notwithstanding the close similarity of properties of the so-called tinzenite with those of axinite. The low summation in Jakob's analyses should have indicated an undetermined constituent. Jakob's interpretation of the state of oxidation of the manganese as trivalent gave him a better summation, but so much Mn_2O_3 (20%+) would hardly yield a yellow mineral with weak yellow green, weak greenish, to colorless pleochroism. One is reminded of the deep color and strong pleochroism of piedmontite with much less Mn_2O_3. It may be that the rose red and orange red varieties of the so-called tinzenite contain a small amount of Mn_2O_3.

The Identity of Tinzenite with Manganoan Axinite

The validity of tinzenite as a species was not seriously questioned until 1952, when, in the course of a study of manganese ore from Aroostook County, Maine, a special study was made of the rare manganese silicate ganophyllite, which had been found there. Among the comparative material investigated was ganophyllite from Franklin, New Jersey, which occurred in close association with a manganoan axinite, described by Palache (1935), who noted its yellow color as characteristic of axinite from this locality. He also noted a pale rose colored variety, as well as yellowish green and colorless. We prepared *x*-ray diffraction patterns of the yellow Franklin axinite (U.S.N.M. 95339) and axinite from Dauphin,

TABLE 1. *X*-RAY DIFFRACTION DATA FOR AXINITE AND TINZENITE = MANGANOAN AXINITE

Axinite*		Tinzenite = manganoan axinite†		Axinite*		Tinzenite = manganoan axinite†	
d(Å, meas.)	I	d(Å, meas.)	I	d(Å, meas.)	I	d(Å, meas.)	I
		8.83	3	2.526	3		
6.30	7	6.30	7	2.489	2		
5.87	½	5.90	2	2.474	2	2.474	3
5.15	½	5.12	2	2.444	5		
4.99	1	4.94	2	2.424	5	2.424	3
4.80	2	4.78	3			2.400	3
4.53	3	4.55	3	2.396	1		
3.99	2	3.96	3			2.368	3
		3.87	1	2.363	5		
3.80	3					2.323	2
3.68	6	3.66	3	2.318	½		
3.46	8	3.46	8	2.292	1		
3.42	½	3.42	4	2.271	3		
3.39	½					2.254	1
3.28	6	3.28	6	2.250	3		
3.23	½			2.226	1		
3.19	½					2.210	1
3.16	9	3.14	7	2.206	3		
3.08	4B	3.06	4	2.190	6		
3.02	5	3.01	5	2.179	2	2.179	4
2.998	6	2.975	7	2.163	7		
2.968	5					2.152	7
2.931	3			2.134	3B		
		2.881	6			2.126	2
2.874	3			2.060	5	2.060	4
2.839	4			2.040	5		
2.812	10	2.812	10			2.033	3
2.792	4			2.014	3B		
		2.766	2			2.008	7B
2.760	4			1.998	3B		
		2.734	2	1.989	5	1.990	2
2.667	4			1.973	½		
		2.661	3			1.967	3
2.643	4B			1.955	4		
		2.620	2			1.940	2
2.575	5			1.926	5		
2.564	6					1.923	3B
		2.553	6B	1.895	1B		

TABLE 1—*(continued)*

Axinite*		Tinzenite = manganoan axinite†		Axinite*		Tinzenite = manganoan axinite†	
d(Å, meas.)	I	d(Å, meas.)	I	d(Å, meas.)	I	d(Å, meas.)	I
		1.870	2B	1.426	3		
		1.818	2	1.420	3		
1.808	2			1.405	5B	1.403	3B
1.788	4	1 791	4B	1.374	2B		
1.744	1			1.359	4		
1.732	3	1.732	2			1.355	3
1.721	3			1.348	1B		
1.704	2	1.706	2			1.343	1
1.691	1	1.693	2			1.331	5
1.680	1			1.327	5		
1.668	4	1.668	2	1.323	3		
1.652	4	1.650	2	1.314	1B		
1.636	5					1.307	1B
		1.630	4	1.301	1		
1.623	3			1.296	1		
		1.617	3	1.288	1		
1.608	2					1.280	1B
1.597	3	1.597	3	1.273	1VB		
1.580	4			1.256	1VB		
1.570	2	1.570	3	1.242	2	1.241	2B
1.538	3			1.233	2	1.230	2B
		1.526	2B	1.225	1VB		
1.516	2B			1.215	1		
		1.505	1	1.211	1		
1.495	3					1.205	1
		1.490	2			1.195	1
1.478	2			1.190	1B		
		1.463	2B	1.175	1		
1.460	4B			1.166	1		
		1.449	2B	1.135	1B		
1.442	1			1.127	1B		
1.435	1			1.120	1B		
		1.430	2				

* Axinite from Bourg d'Oisans, Dauphine, France (U.S.N.M. C-3141) (film 7051).

† Tinzenite = manganoan axinite from Tinzens, Switzerland (U.S.N.M. R-6433) (film 6987) (analyzed sample).

France (U.S.N.M. C-3141), obtained through George Switzer, of the U. S. National Museum, and noted the evident similarity of the pattern recorded for tinzenite from Switzerland (Geiger, 1948). Thereupon we also obtained from the U. S. National Museum some type Swiss material and verified the similarity of the x-ray patterns of minerals from the

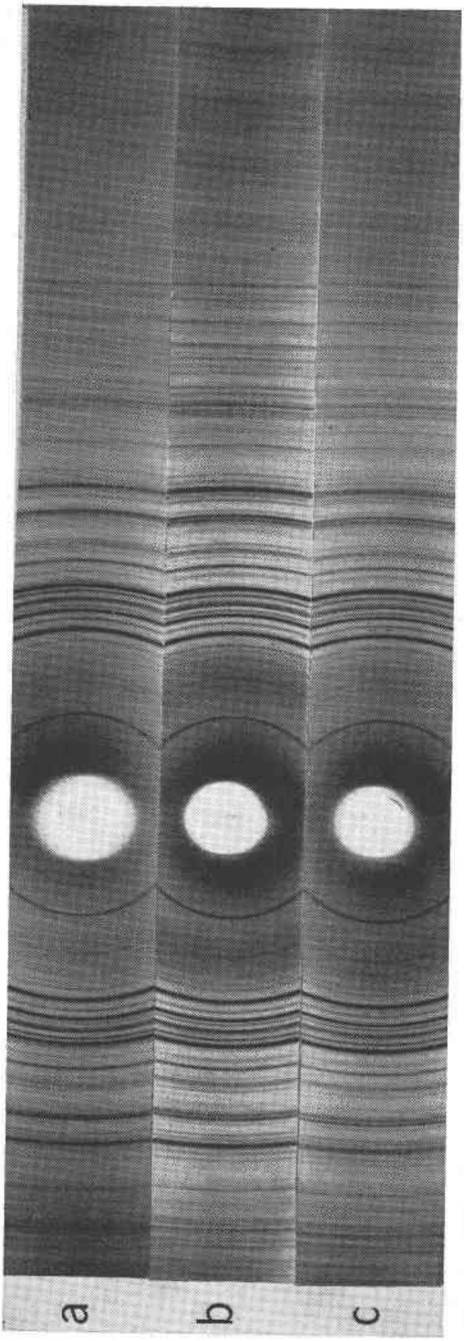

FIG. 1. a. Tinzenite = manganoan axinite from Tinzens, Switzerland (film 7077) b. Manganoan axinite from Franklin, New Jersey (film 7070) and c. Axinite from Dauphine, France (film 7067). The broken line in this pattern is attributed to a small amount of quartz.

Franklin and the Tinzens localities (Fig. 1, a, b and c). Our suspicion that a single mineral, not two, was in question was quickly verified when qualitative chemical tests, soon confirmed by spectrographic study (by E. L. Hufschmidt, of the Geological Survey), showed substantial boron in tinzenite. The complete analysis of the Tinzens mineral showed that tinzenite is manganoan axinite, and that all previous analyses of tinzenite were in error in that 5 per cent or more of B_2O_3 was overlooked. It was also an error to assume trivalent, not divalent, manganese; the oxygen assumed in this erroneous calculation masked the absence of boron, one of the major constituents. If Jakob's formula for tinzenite, $2CaO \cdot Mn_2O_3 \cdot Al_2O_3 \cdot 4SiO_2$, is doubled, and the Mn_2O_3 converted to $2MnO$, and one molecular proportion of B_2O_3 and of H_2O added, it gives the accepted formula of axinite, $4CaO \cdot 2(Mn, Fe, Mg)O \cdot 2Al_2O_3 \cdot B_2O_3 \cdot 8SiO_2 \cdot H_2O$, as suggested by Schaller (1911).

In addition to the diffraction patterns shown in Figure 1, patterns of axinite from the Toroku mine, Miyazaki Prefecture, Japan (U.S.N.M. 105575) (no chemical analysis), and "tinzenite" from the Huachuca Mountains, Arizona (U.S.N.M. 102822) (no chemical analysis), were also obtained. The patterns indicate that all five minerals are isostructural but not identical because of small differences in chemical composition. The patterns of axinite from Bourg d'Oisans, Dauphine, France, and the Toroku mine, Japan, are identical. The patterns of tinzenite from Arizona and manganoan axinite from Franklin, New Jersey, are identical and so similar to patterns of the axinites from France and Toroku mine, Japan, that measurement of their lines was not deemed necessary. *X*-ray diffraction data for axinite from Dauphine, France, and tinzenite = manganoan axinite from Tinzens, Switzerland, are shown in Table 1.

All diffraction patterns were made with North American Philips Debye-Scherrer powder cameras (114.59 mm. diameter) using the Straumanis and Wilson techniques with FeKα (Mn filter), $\lambda = 1.9373$ Å.

Calculation of the molecular ratios of Sherwood's analysis (Table 2, analysis B) gives

B_2O_3	0.96
SiO_2	8.05
Al_2O_3, Fe_2O_3	2.00
MnO, MgO, CaO, Na_2O, K_2O	6.27
H_2O+	0.97

These percentages are in fair accord with the accepted formula of axinite. (The small iron content has been assigned to R_2O_3, rather than RO, arbitrarily; but even if this were not done the ratios would still be much the same.) It may also be noted that these ratios are much closer to whole numbers than those computed from Jakob's analysis (Table 2, analysis A).

TABLE 2. ANALYSES OF TINZENITE, MANGANOAN AXINITE, AND AXINITE

	Tinzenite, Tinzens J. Jakob, analyst (Jakob, 1933)		Manganoan axinite (tinzenite) Tinzens A. Sherwood, analyst	Axinite Radautal, Harz (Fromme, 1909)	Axinite yellow, brown, Obira, Japan (Ford, 1903)	Axinite Franklin, N. J., W. E. Ford, analyst (Palache, 1935)	Axinite Kristiania, Norway (Goldschmidt, 1911)	Axinite Bourg d'Oisans Dauphine, France (Ford, 1903)
	A		B	C	D	E	F	G
B_2O_3	—		5.65	6.31	5.61	5.10	5.13	6.12
SiO_2	40.65		40.80	41.74	41.80	42.77	41.99	42.78
TiO_2	0.00		—	—	—	—	—	—
Al_2O_3	18.31		16.23	17.08	17.15	16.73	16.32	17.67
Fe_2O_3	0.03		1.59	1.87	1.11	1.03	1.62	0.99
FeO	—		—	1.35	2.84	—	—	6.02
Mn_2O_3	24.87		—	—	—	—	—	—
MnO		(22.38)	21.19	11.54	10.71	13.69	12.86	2.99
MgO	0.00		0.17	0.34	0.21	0.23	0.07	2.41
CaO	13.50		12.51	18.65	19.51	18.25	20.14	20.16
Na_2O	0.58		0.27	—	—	(CuO 0.12)	—	—
K_2O	0.48		0.13	—	—	(PbO —)	—	—
						(ZnO 1.48	0.12)	—
$H_2O+110°$	1.47		1.20	1.81	1.22	1.29	1.87	1.40
$H_2O-110°$	0.10		0.10	—	—	—	—	—
	99.99	(97.50)	99.84	100.69	100.16	100.69	100.12	100.54
Sp. Gr.	3.286			3.313	3.302	3.358	3.334	3.287

Optical properties of four of the minerals whose analyses are given in Table 2 are tabulated in Table 3.

Table 2 gives Jakob's analysis (1933) of tinzenite from Tinzens, Switzerland (A), followed by Sherwood's analysis of another specimen (U.S.N.M. R6433) of the same material from the U. S. National Museum collection (B). Analyses C, D, E, and F are of manganoan axinites from the literature, G is a low-manganese axinite.

The analyzed Tinzens tinzenite was first cleaned from a thin adherent film of dark-brown or black manganese dioxide by treatment with dilute nitric acid and hydrogen peroxide. This manganese mineral could not be identified from its diffraction pattern, which shows that it is poorly crystalline with broad lines at approximately 9.4 Å, 7.2 Å, 4.7 Å, 3.9 Å, and 2.2 Å.

The analysis of the Tinzens specimen was supplemented by spectrographic determinations by Helen W. Worthing, of the U. S. Geological Survey, as follows:

More than 10%	Al Mn Si
1.0–10%	Ca B
0.1–10%	Fe Mg
0.01–0.1%	Ni Sr Ba
0.001–0.01%	Ga V Ti Y Zr Cr Cu
0.0001–0.001%	Be Yb

TABLE 3. COMPARISON OF OPTICAL PROPERTIES OF TINZENITE WITH THOSE OF MANGANOAN AXINITE

	Tinzenite			Manganoan axinite						
	A (B)			C		D	E		F	
α	1.693			1.681		(No optics recorded by Ford)	1.684		1.679	
		β-α	0.008		0.007			0.008		0.006
β	1.701			1.688			1.692		1.685	
		γ-β	0.003		0.003			0.004		0.013
γ	1.704			1.691			1.696		1.698	
		γ-α	0.011		0.010			0.012		0.019
2V	63°									
	Color yellow					yellow brown	yellow		yellow	

The indices of refraction of tinzenite are slightly higher than those reported for any axinite, as would be expected because of the lower CaO content and higher MnO content. Winchell (1951) cites as maximum values for the indices of refraction of axinite 1.690, 1.698 and 1.704.

COMPOSITION OF AXINITE

W. T. Schaller (whose interest in this study is gratefully acknowledged) suggested (Schaller, 1911) that the amount of CaO in axinite may be constant because most of the analyses depart but slightly from 20 per cent CaO, regardless of considerable reciprocal variation in percentages of FeO and MnO. Those analyses, made prior to 1911, in which the percentages of CaO departed considerably from 20 per cent were rejected at that time by Schaller as being of questionable accuracy. However, his suggestion is invalidated by recognition of the identity of tinzenite, which contains much less than 20 per cent CaO, with axinite.

Likewise Gädeke (1938), in discussing the relations of iron and manganese in axinite, states that the manganese almost entirely ("fast ausschliesslich") replaces divalent iron and not calcium. He plots the variations of the mean refractive index (the average of the three) for five selected axinites that contain from 0.33 per cent to 12.86 per cent of MnO. The graph shows a linear variation. However, tinzenite so plotted does not fall on his curve at all, but this variation may be ascribed to the low CaO.

A tabulation of 53 analyses of axinite (all that have been recorded, including those of tinzenite) shows (Fig. 2) that there is a serial variation in CaO extending from 12 to perhaps 30 per cent, with a very marked clustering close to 20 per cent. Nearly two-thirds of all the analyses lie between 19 and 21 per cent CaO. The range, however, is both below and above 20 percent.

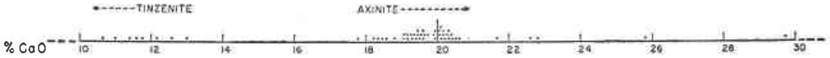

FIG. 2. Serial variation in CaO content of axinite (including tinzenite, i.e., manganoan axinite).

The formula of axinite, therefore, should not be written as $HCa_2(Fe, Mn)Al_2BSi_4O_{16}$, with calcium constant, but as $H(Ca, Fe, Mn)_3Al_2BSi_4O_{16}$. Whether a calcium-free axinite or an iron- and manganese-free axinite will be found remains to be seen.

Peacock (1937) made an exhaustive study of the crystallography of axinite, in which he assigned as the contents of the unit cell 2 moles of composition $HBAl_2Ca_2(Mn, Fe)Si_4O_{16}$. He also accepts the established formula of axinite with Ca in fixed ratio, and assumes that Mn and Fe are present in equal atomic proportions, to give a molecular weight of 569.5. Of course, he was not concerned in the problem under consideration.

The crystal structure of axinite has been worked out by Ito and Takeuchi (1952) on axinite from Obira, Japan, with composition given as $H(Fe_{0.3}Mn_{0.7})Ca_2Al_2BSi_4O_{16}$.

A recent paper by Simonen and Wiik (1952) describes two axinites, one from Jokoinen, southwest Finland, and the other from Petsamo, U.S.S.R. that are remarkably high in FeO (9.36% and 9.56% respectively) and notably low in MnO (0.69% and 0.75% respectively); MgO on the other hand is very high for axinite (1.59% and 1.19%). These writers accept Peacock's unit-cell content $H_2B_2Al_4Ca_4(Mn, Fe)_2Si_8O_{32}$ and give a triangular diagram of the FeO:MnO:MgO ratios of some 19 axinites. They show that whereas pure Mg-axinite does not exist, Fe- and Mn-axinites do. By pure, however, they signify a molecule with 4 fixed atoms of Ca and 2 of Fe+Mn. However, as we have shown, considering tinzenite as manganoan axinite broadens the picture considerably, and the variation to be considered is not Simonen and Wiik's ternary, but a fourfold Ca-Fe-Mn-Mg.

There are two analyses reported in the literature with extremely high CaO content, 25.84 per cent and 29.70 per cent. Both have questionable features and probably should not be accepted as valid. The first one, of a Swedish axinite cited by Hintze (1897), was made by Hisinger in 1826 and is obviously defective. No B_2O_3 or ferrous iron is determined. In view of the inadequacy of analytical methods 130 years ago with regard to complex borosilicates, we may well disregard this analysis.

The second more recent analysis, of axinite from Radautal, Harz, was published by Luedecke (1889); Dana (1892) gives the same analyses with, however, a somewhat different set of figures (i.e., CaO 30.21%). Confusion arises in Dana's using Luedecke's calculated, not actually determined, composition. Luedecke noted that the formula based on his analysis departs widely from formulas of all previously identified axinite. One may infer that the axinite was imperfectly separated from other calcium silicate minerals—augite, garnet, and wollastonite—accompanying it.

These uncertainties, however, do not exist in the low CaO (tinzenite) range, where the analyzed material was sufficiently homogeneous and the critical analysis dependable.

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