

Properties of the Al-Fe-Mn epidotes

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Summary. Natural Al-Fe-Mn epidotes are divided into Al-Fe and Al-Fe-Mn series.

In the Al-Fe series, *a*, *b*, and *c* increase steadily over the range 0 to 0.9 Fe³⁺ per formula unit, and more slowly at higher Fe contents. Index variation diagrams show the reverse trend, with indices increasing moderately fast over the range 0 to 0.85 Fe, and faster at higher Fe contents.

In the Al-Fe-Mn series, *b* increases almost linearly over the range of (Fe, Mn) contents, with Mn causing a larger increase than Fe, whilst *a* and *c* increase over the range 0 to 0.9 (Fe, Mn), and then decrease. This curious behaviour is accounted for by the application of crystal field theory. The indices increase linearly over the range 0.8 to 1.5 (Fe, Mn), the optic axial angle depending on (Fe, Mn) content and the ratio Mn/(Fe, Mn).

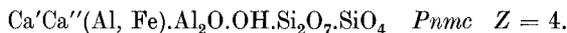
Thermal and mechanical properties (conductivity, thermal expansion, specific heat, compressibility, and hardness), electromagnetic properties (dielectric constants, conductivity, magnetic susceptibility), and thermodynamic data (*S*) are also summarized, and estimates given where experimental data are not available.

THE minerals of the Al-Fe-Mn epidote system may be divided into two series, each having both orthorhombic and monoclinic members, namely the Al-Fe series (zoisite, clinozoisite, epidote), and the Al-Fe-Mn series (thulite, piemontite, withamite). The composition ranges and defining properties of the varieties that form the Al-Fe and Al-Fe-Mn series are shown in fig. 1.

The structure of monoclinic Al-Fe epidote (0.97 Fe) was described by Ito, Morimoto, and Sadanaga (1954), and that of zoisite by Fesenko, Rumanova, and Belov (1955). The epidote structure is based on chains of AlO₆ and AlO₄(OH)₂ octahedra, sharing edges, and stretched along the *b* axis. The chains are linked by SiO₄ and Si₂O₇ groups, which are in turn bound by (Al, Fe) in 6 coordination, and by Ca in two types of 6 to 10 coordinated site. Most of the iron (about 0.85 out of 0.97) is in the 'between-chain' site. Two oxygens and two hydroxyls per unit cell are not linked to Si, but to the Al of the AlO₄ and AlO₃OH chains, so that the structural formula of epidote may be written:



Zoisite is similar, except that (on the view of Ito, 1950) the twinning operation relating the structures of epidote and zoisite causes the chains to have the overall composition $(Al_2O_7OH)_n$ rather than $(AlO_4)_n$ plus $(AlO_3OH)_n$ so that the formula becomes:



Detailed descriptions of the octahedral sites will appear elsewhere (Burns and Strens, *unpub.*), and it will suffice to say here that there are

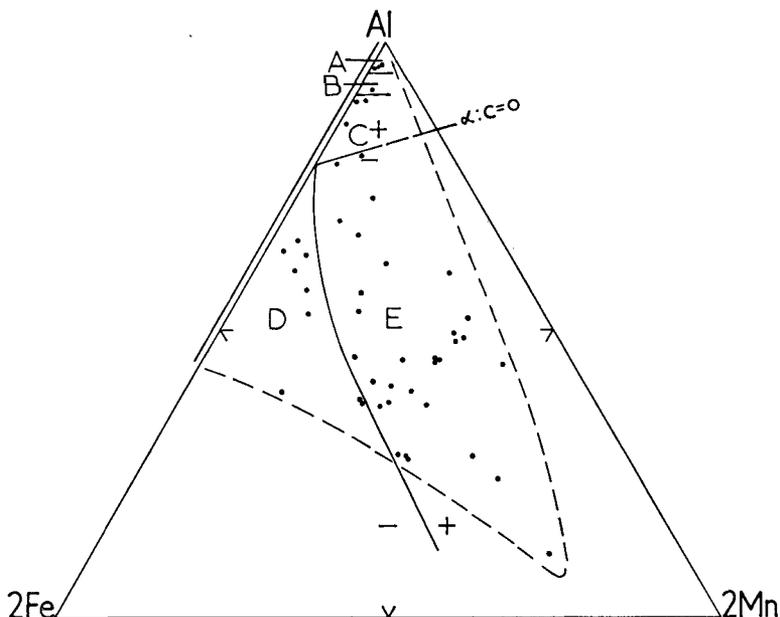


FIG. 1. The Al-Fe-Mn epidote system: A orthorhombic, O.A.P. (optic axial plane) (100); B orthorhombic, O.A.P. (010); C monoclinic, optically positive, O.A.P. (010), $\alpha:c$ positive; D monoclinic, optically negative, O.A.P. (010), $\alpha:c$ negative; E monoclinic, optically positive, O.A.P. (010), $\alpha:c$ negative; ● analyses of natural minerals; — approximate boundary of stable compositions.

three types of octahedral site in epidote (two in zoisite) denoted Al, AlO, and AlOH, corresponding to the 'between-chain' and chain AlO_6 and $AlO_4(OH)_2$ octahedra respectively. The Al and AlOH sites are tetragonally distorted (c/a 0.95), with the c axes of the octahedra making angles (projected on (010)) of $+92^\circ$ (Al) and $+62^\circ$ (AlOH) with the c -axis of the mineral. The AlO site is more regular, with a slight orthorhombic distortion.

Because of the differing degrees of distortion of the sites, and the different orientations of the symmetry elements of the sites relative to the unit-cell edges, the orientation and magnitude of the optical vectors are sensitive to the distribution of an ion, as well as to the amount of that ion. An epidote of fixed composition can thus have a range of properties, corresponding to the range of possible distributions.

Very marked site preferences are shown by trivalent Fe, Mn, and Cr ions, and Burns and Strens have made the following assignments on the basis of X-ray and optical data and crystal field predictions:

Fe, Al > AlO > AlOH; Mn, Al \simeq AlOH > AlO; Cr, AlO > Al \simeq AlOH. They were able to account for the absorption spectra, composition ranges, and indicatrix orientations of Al-Fe, Al-Fe-Mn, and Al-Fe-Cr epidotes in terms of these preferences.

Conventions. The optic axial angle is given as $2 V_\alpha$ throughout, so that common epidote has $2 V < 90$. Compositions are given as the number of Fe or Mn atoms per formula unit of $\text{HC}_{a_2}M_3\text{Si}_3\text{O}_{13}$, although it is sometimes convenient to refer to the Al, Fe, and Mn end-members, denoted Cz, Ps, and Pm respectively. Note that 1 wt. % $(\text{Fe, Mn})_2\text{O}_3$ is very nearly equivalent to 2 % (Ps, Pm) or to 0.06 (Fe, Mn).

Unit cell dimensions and composition

Seki (1959) established the relationship between cell dimensions and composition using both orthorhombic and monoclinic Al-Fe epidotes with 0 to 1.1 Fe, finding a steady increase in all dimensions, which became less rapid at Fe contents above 0.9. Myer (1965) presented further data for ten monoclinic Al-Fe epidotes with 0.16 to 0.99 Fe, and determined also b for two glaucophane-schist epidotes and an iron-rich (1.05 Fe) mineral, whilst Ernst (1964) determined the cell dimensions of five glaucophane-schist epidotes. Myer's data are probably the most accurate, and have been given the greatest weight in fig. 2.

In epidotes containing significant amounts of Mn, b is distinctly longer, and a and c are distinctly shorter than in the most iron-rich Al-Fe epidotes (table I and fig. 2). The volume plot is roughly linear over the whole range of (Fe, Mn) contents. The contraction of a and c with increasing Mn content is most unexpected when the 20 % difference in radius of Al and Mn is considered, but the application of crystal field theory suggests an explanation: Jahn-Teller distortion of the AlOH site by Mn^{3+} should reduce the Mn-O₃ distance, whilst increasing Mn-O₆ and Mn-O₁₀, thus stretching the chains. This would cause a and c to shorten, just as the diameter of a rubber cylinder is reduced by axial tension.

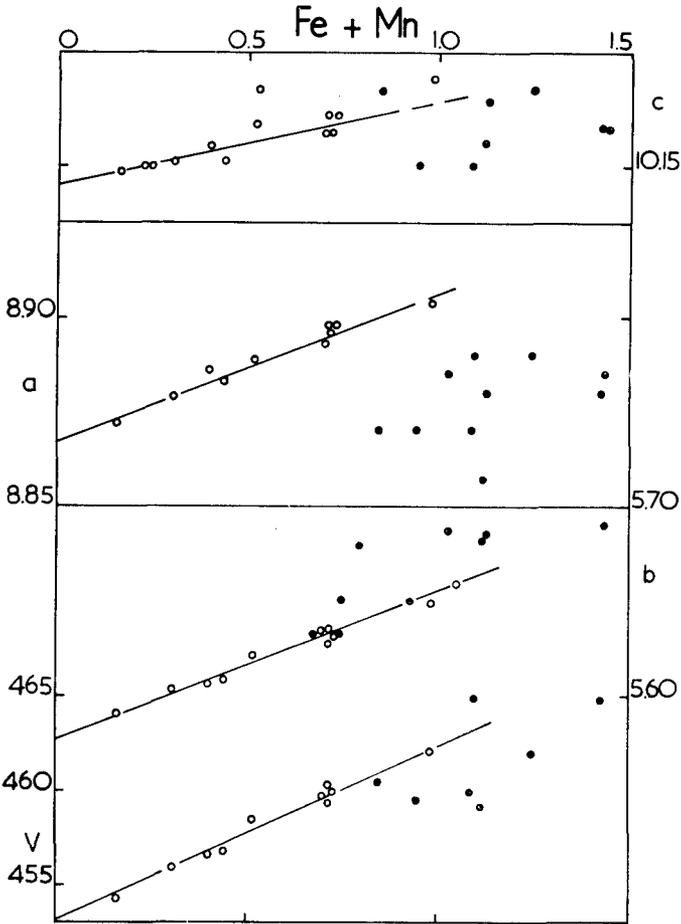


FIG. 2. Variation of a , b , c , and V with Fe (o) and Fe+Mn (●) in the Al-Fe and Al-Fe-Mn series, using the data of Ernst (1964) and Myer (1965) for the Al-Fe series, and the values in table I for the Al-Fe-Mn minerals. Note the tendency for a and c to decrease and b to increase relative to the Al-Fe trend in minerals containing Mn: this is probably due to Jahn-Teller distortion of the Al and AlOH sites by Mn(III).

Variation of optical properties in the Al-Fe series

Two features of the variation diagram (fig. 3) require comment: firstly, the indices (especially α) of epidotes with iron contents above 0.85 break away from the line representing the effect of Fe entering the Al site as significant amounts of iron start to enter the chain sites: secondly, the α

and γ indices extrapolated from the region 0.2 to 0.9 Fe cross near 0.18 Fe, accounting for the rotation of the indicatrix about $\beta = b$ [010] in iron-poor clinozoisites (Orlov, 1926; Zambonini, 1920; Johnston, 1949; De Rudder and Beck, 1963).

TABLE I. Unit cell dimensions of Al-Fe-Mn epidotes

	<i>a</i>	<i>b</i>	<i>c</i>	β	<i>V</i>	Fe	Mn	No.
Strens, this paper	—	5.632	—	—	—	0.61	0.08	1
„	—	5.632	—	—	—	0.61	0.13	2
„	—	5.650	—	—	—	0.39	0.38	3
„	—	5.679	—	—	—	0.21	0.59	4
Ernst, 1964	8.87	5.65	10.17	115.5	460.4	0.54	0.31	5
Strens	8.87	5.650	10.15	115.4	459.5	0.71	0.24	6
„	8.885	5.687	—	—	—	0.30	0.73	7
Marmo <i>et al.</i> , 1959	8.87	5.66	10.15	115.4	459.9	0.64	0.45	8
„	8.89	5.67	(10.22)	115.6	(464.8)	0.40	0.70	9
Strens	8.86	5.681	10.156	115.4	461.8	0.41	0.72	10
„	8.88	5.685	10.167	115.4	463.6	0.41	0.72	11
Marmo <i>et al.</i> , 1959	8.89	5.67	10.17	115.5	461.9	0.62	0.63	12
Nayak and Neuvonen, 1964	8.88	5.66	10.16	115.5	460.9	0.68	0.75	13
Strens	8.885	5.690	10.160	115.4	464.0	0.66	0.78	14

1. U.C.13607, withamite: anal. Dr. B. W. Evans.
2. U.C.13608, withamite: anal. Dr. B. W. Evans.
3. Piemontite, Mautia Hill, Tanganyika: presented by Dr. D. McKie, anal. J. H. Scoon.
4. U.C.13610, piemontite: anal. Dr. B. W. Evans.
6. Withamite, Llano, Texas: presented by Dr. S. E. Clabaugh, anal. R. G. J. Strens.
7. U.C.13612, piemontite, St. Marcel: anal. Dr. B. W. Evans.
10. Långban 1, piemontite: presented by Dr. B. Lindqvist, anal. Dr. B. W. Evans.
11. Långban 2, piemontite: presented by Dr. B. Lindqvist, anal. Dr. B. W. Evans.
14. Piemontite, Chikla: presented by Dr. S. A. Bilgrami, anal. Dr. B. W. Evans.

The development of the α - and β -zoisite orientations can also be explained if α -zoisite is regarded as the iron-rich form, contrary to previous assumptions, but further data are required to resolve this problem (cf. Myer, 1966). Extinction angle ($\alpha:c$ [001]) and $2V$ show an initial rapid change at low iron contents, when a given increment of iron causes a larger relative change in the ratio of the partial birefringences than is the case at high iron contents. Relatively steady values of $\alpha:c$ and $2V$ are attained at iron contents above 0.85 (fig. 4).

Absorption (*D*-line) is $\gamma > \beta > \alpha$. Dispersion of the optic axes is $r > v$ in most zoisites, $r < v$ in some zoisites and in clinozoisite, and $r > v$ in epidote (Johnston, 1949; Francis, 1958; Malmqvist, 1929). Dispersion of the bisectrices is $r < v$ in epidote (Malmqvist, 1929).

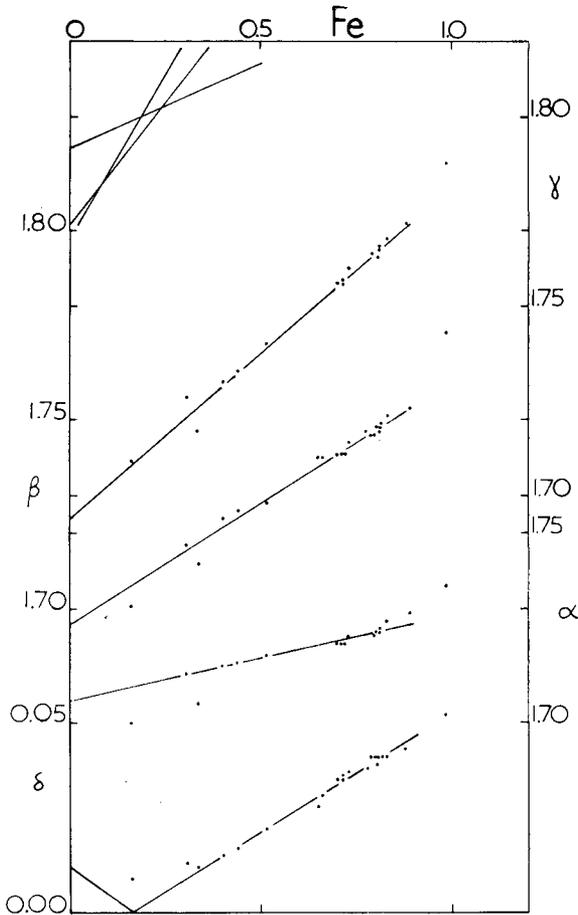


FIG. 3. Variation of α , β , γ , and $\gamma-\alpha$ in the Al-Fe series using the data of Tempel (1938), Strens (1964), and Myer (1965) for hydrothermal and metasomatic epidotes. The break in slope at $\text{Fe} \approx 0.85$ is best seen in the α curve. The behaviour of the indices at low iron contents is shown in the inset (top left; vertical scale doubled).

Crossed axial plane dispersion would be expected in zoisite and iron-poor clinozoisite in view of the very small partial birefringences, and this may be the origin of the anomalous colours often shown by these minerals.

Variation of optical properties in the Al-Fe-Mn series

There is a linear relationship between composition and indices over the range 0.8 to 1.5 (Fe, Mn), though the data show a wide scatter (table II

and fig. 5). The effect of Mn alone was obtained by subtracting from the index of a piemontite the index of an epidote having the same iron content (from fig. 3) and plotting the resulting values against Mn content. The slopes so found were identical with those of fig. 5, indicating that the Mn/(Fe, Mn) ratio has little effect on the indices, and justifying the

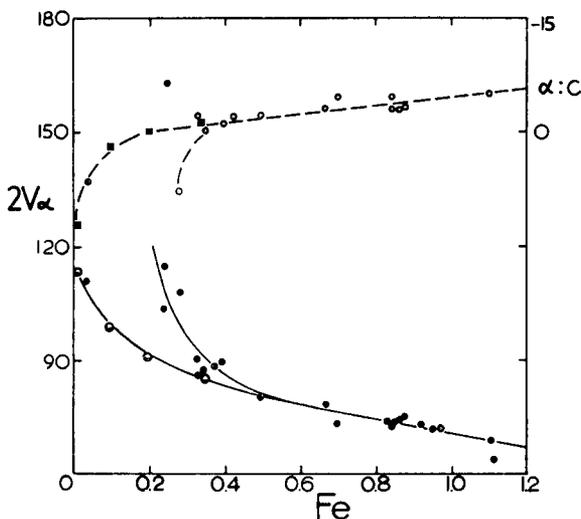


FIG. 4. Variation of $\alpha:c$ (\circ , \blacksquare) and $2V_\alpha$ (\bullet and \ominus) in the Al-Fe series, using the data of Malmqvist (1929, table 33) and Johnston (1949, point at 0.27 Fe, $\alpha:c = +7^\circ$). At low iron contents the values of $\alpha:c$ and $2V$ for hydrothermal minerals (\circ and \bullet) differ markedly from those for high index epidotes (\blacksquare and \ominus). This is because the index variation curves for high index minerals do not cross at low iron contents, as do those for the hydrothermal epidotes (fig. 3, inset). For further $\alpha:c$ data, which could not be plotted as they were unaccompanied by Fe contents, see Orlov (1926) and Johnston (1949).

treatment of (Fe, Mn) as a single component (in fact $2V_\alpha$, which is sensitive to small changes in the ratio of $(\gamma-\beta)$ to $(\beta-\alpha)$, changes appreciably with Mn/(Fe, Mn) ratio (fig. 7), but the effect is outweighed by other sources of scatter and cannot be detected on the variation diagrams). The extinction angle continues to increase from the maximum of -5° reached in the Al-Fe series, to about -13° in the Goldongri mineral with 1.45 (Fe, Mn).

The absorption scheme (*D*-line) is $\gamma > \beta > \alpha$, but the axes of the absorption ellipsoid are far from coinciding with those of the indicatrix (Malmqvist, 1929). This scheme is considerably modified at other

TABLE II. Optical properties of some Al-Fe-Mn epidotes, $\lambda = 5892 \text{ \AA}$ (Na D-line)

No.	Author	Fe	Mn	α	β	γ	δ	$2V_{\alpha}$	$\alpha:c[001]$
1	Morton, 1963	0.45	0.17	—	1.730	—	0.028	107	—
2	Hutton, 1938	0.67	0.06	1.733	1.750	1.762	0.029	78	-1
3	Tsuboi, 1936	0.64	0.21	1.730	1.7455	1.765	0.035	82	—
4	Morton, 1963	0.67	0.19	—	1.749	—	—	76	—
5	Malmqvist, 1929	0.55	0.38	1.740	1.752	1.779	0.039	93	-3.1
6	Guild, 1935	0.23	0.73	1.732	1.750	1.778	0.046	—	—
7	Malmqvist, 1929	0.30	0.71	1.7455	1.7636	1.8059	0.0604	111.8	-5.4
8	Short, 1933	0.28	0.75	1.7385	1.7649	1.7985	0.0600	110.5	—
9	Marmo <i>et al.</i> , 1959	0.40	0.70	1.742	1.767	1.805	0.063	99	—
10	Marmo <i>et al.</i> , 1959	0.64	0.45	1.751	1.781	1.812	0.061	94	—
11	Malmqvist, 1929	0.39	0.71	1.746	1.776	1.793	0.047	93	-3
12	Hutton, 1940	0.59	0.61	1.754	1.772	1.795	0.041	95	—
13	Oito, 1935	0.53	0.68	1.751	1.783	1.833	0.082	100.5 calc.	—
14	Hirowatari, 1956	0.92	0.30	1.743	1.779	1.808	0.065	83	—
15	Marmo <i>et al.</i> , 1959	0.62	0.63	1.756	1.783	1.823	0.067	108	—
16	Malmqvist, 1929	0.51	0.76	1.7495	1.7821	1.8318	0.0823	99.4	-6.6
17	Nayak, 1963	0.68	0.75	1.768	1.803	1.843	0.075	92 calc.	'38''
18	this paper*	0.66	0.78	1.772	1.813	1.860	0.088	92 calc.	—

* Piemontite, Chukla: presented by Dr. S. A. Bilgrami, anal. Dr. B. W. Evans.

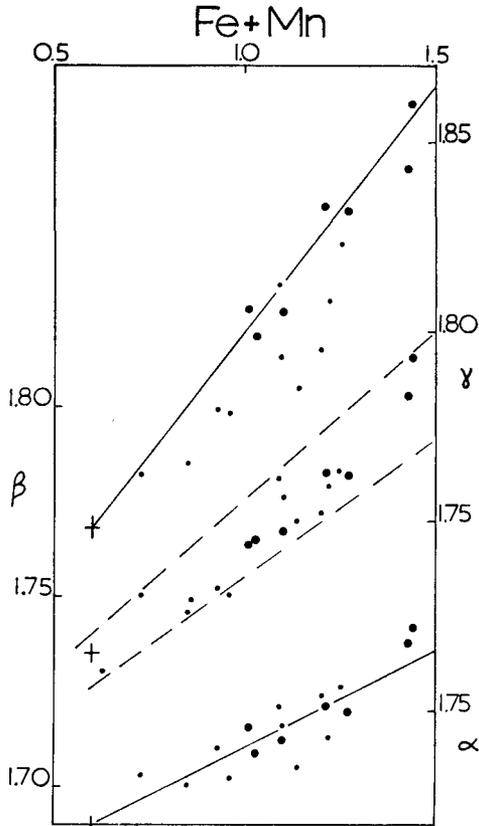


FIG. 5. Variation of indices in the Al-Fe-Mn series. The larger symbols denote points which, in the writer's judgement, ought to be given the greatest weight (see Appendices II and III). Crosses indicate the indices of Al-Fe epidotes with 0.6 Fe (from fig. 3). To a first approximation, any index of an Al-Fe-Mn epidote can be represented in the form $n = a + b(\text{Fe, Mn})_{\text{Al}} + c(\text{Mn})_{\text{AlOH}}$, assuming all Fe in the Al site, and no (Fe, Mn) in the AlO site. In general, since $(\text{Mn})_{\text{AlOH}}/(\text{Fe, Mn})_{\text{Al}}$ increases with total (Fe, Mn), and $c > b$, the variation curves should be concave towards the top left-hand corner of the diagram, but straight lines have been drawn here in view of the wide scatter of points. However, α apparently turns up, and hence $(\gamma - \alpha)$ turns down, at high (Fe, Mn) contents (fig. 7). There is, of course, no unique curve relating n and (Fe, Mn) for the general case in which the Mn/(Fe, Mn) ratio and the distribution of Fe and Mn between the sites are unspecified: the lines shown are for 'average' Mn/(Fe, Mn) ratios and distribution coefficients, with allowance made in weighting points and drawing the lines for the probable nature of the experimental errors (Appendix II).

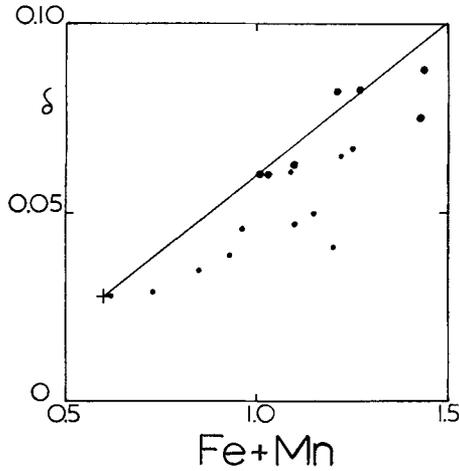


FIG. 6. Variation of birefringence in the Al-Fe-Mn series. The line is $(\gamma-\alpha)$ taken from fig. 5. The cross denotes $(\gamma-\alpha)$ for Al-Fe epidote with 0.6 Fe (fig. 3).

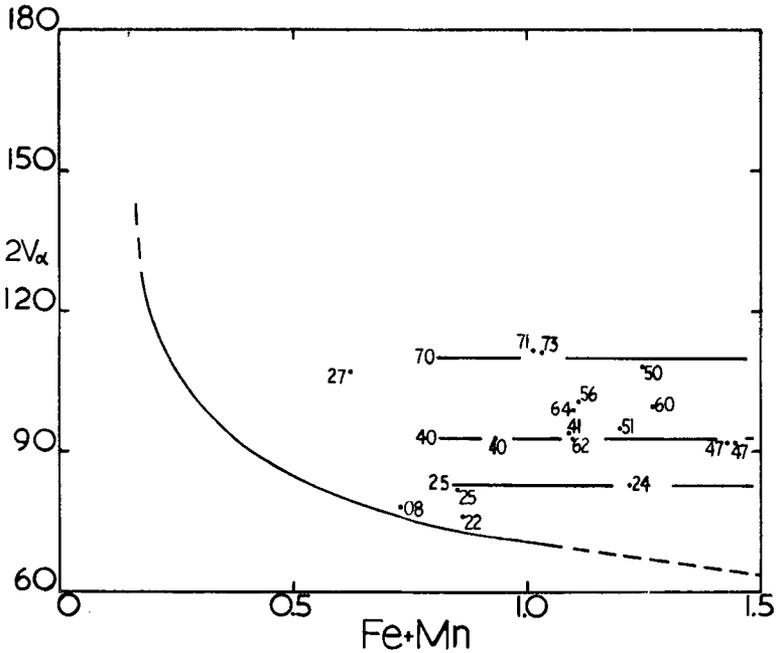


FIG. 7. Dependence of $2V$ on (Fe, Mn) and on the $Mn/(Fe, Mn)$ ratio in the Al-Fe-Mn series. The curve for normal Al-Fe epidotes (fig. 4) is shown. The numbers are $100 Mn/(Fe+Mn)$.

wave-lengths, e.g. at 8300 Å it is $\beta > \gamma > \alpha$, and at 4400 Å $\gamma > \alpha > \beta$ (Malmqvist, 1929; Burns and Strens, *unpub.*).

Dispersion of the optic axes is 4.4° ($2 V_\alpha(\text{C}) 101.4^\circ$, $2 V_\alpha(\text{F}) 97.0^\circ$) for the St. Marcel piemontite of Malmqvist, 1929, and the dispersion of the bisectrices amounts to 3.2° for the same mineral ($\alpha:c$ [001] (F) -10.5° , (C) -7.3°). The presence of strong absorption peaks in and near the visible region may give rise to some anomalous dispersion.

Variation of properties related to site symmetry and occupancy

A regular octahedral site has cubic symmetry, and replacement of Al by Fe in such a site should change all indices equally. If a tetragonal distortion ($c/a > 1$) is applied, the two oxygens lying on the octahedral c -axis, being further from the cation, are less strongly polarized, and the index for light vibrating along c is reduced relative to that for light vibrating along a_1, a_2 . The α -index of a mineral containing octahedra with $c/a > 1$ thus tends to swing parallel to the octahedral c -axis as Fe or Mn replace Al, as, for example, in viridine (c/a 1.12), whilst with $c/a < 1$, γ becomes aligned along the octahedral c -axis. Accepting the site preferences found by Burns and Strens, and making allowance for the symmetry of the mineral as well as that of the sites, we should expect the indicatrix of an Al-Fe epidote to rotate about $\beta = b$ as Fe enters the Al site in epidote (c/a 0.95, $c_{\text{oct.}}:c_{\text{ep.}}$ in (010) plane is $+92^\circ$) with $\alpha:c_{\text{ep.}}$ tending to a value near $+2^\circ$. In fact, $\alpha:c$ [001] decreases from $+90^\circ$ in zoisite to -5° in iron-rich epidote, in very good agreement with prediction. The partial birefringences, $2V$, and $\alpha:c$ [001] change little in epidotes with more than 0.85 Fe, as iron enters the nearly regular AlO site. In Al-Fe-Mn minerals, with significant amounts of Mn entering the AlOH site ($c_{\text{oct.}}:c_{\text{ep.}} + 62^\circ$, c/a 0.95), $\alpha:c$ should tend to -28° , the maximum angle observed being about -13° in the Goldongri mineral with about 0.5 Mn in the AlOH site (Appendix III). Birefringence and $2V$ also continue to change in the Al-Fe-Mn series.

Absorption spectrum and colour

In the form of 60-mesh (400 μ) powder, the colour of Al-Fe epidotes is dependent on iron content, ranging in general from colourless (0.2 Fe), through greenish yellow (0.5 Fe) and yellowish green (0.8 Fe) to dark green (1.1 Fe). Epidotes formed at high temperatures tend to be more strongly coloured than those formed at low temperature. In the Al-Fe-Mn series, a very small amount (0.2 %) of Mn_2O_3 imparts a perceptible pink colour to zoisite, and the Glen Coe withamite (Hutton, 1938) with

0.96 % Mn_2O_3 is strongly pleochroic in thin section. A detailed study of the absorption spectra of Al-Fe and Al-Fe-Mn epidotes will be reported by Burns and Strens.

Infra-red absorption spectra of a number of Al-Fe epidotes have been figured by Strens (1964), who noted a possible shift in position of a number of peaks in the 10μ region with iron content. A more detailed study is now under way.

Thermal and mechanical properties

Thermal conductivity. The major axis of the conductivity ellipsoid makes an angle of -14.5° with the *c*-axis, the axial ratio $\alpha:\beta:\gamma$ being 0.934:1:1.088 (Janettaz in Goldschlag, 1917).

Specific heat. The specific heat of 'epidote' was determined by Oberg (in Goldschlag, 1917) as 0.1861 over the range 16 to 100°C , and by Joly as 0.1876 (av.) over the range 13 to 100° for epidote with $D = 3.430\text{ gm/cm}^3$, corresponding to 0.78 to 0.84 Fe. The value 0.1876 cal/gm or 91.53 cal/mole will be adopted here for the specific heat of epidote with 0.81 Fe at 56°C .

Thermal expansion. Fizeau (in Goldschlag, 1917) determined the thermal expansion of epidote of unknown composition as 0.16 % by volume over the range 0 to 100°C . The writer has estimated the following values for higher temperatures by analogy with diopside and hornblende:

100	200	400	600	800	1000°	° C
0.16	0.42	0.96	1.56	2.20	2.85	% volume increase
0.22	0.53	1.33	2.15	3.04	3.94	cm^3/mole

Compressibility. The average compressibility at room temperature over the range 0 to 12 kb is estimated as 1.1×10^{-6} by analogy with diopside (1.07), augite (1.02), and actinolite (1.30), all of which are chain silicates with densities near that of epidote.

Hardness. The hardness of zoisite, clinozoisite, piemontite, and epidote is generally stated to be 6 to $6\frac{1}{2}$, but in view of the anisotropy of the epidote structure it is likely to vary considerably with orientation.

Cleavage. Orthorhombic minerals show perfect {100} and less perfect {001} cleavage, whilst monoclinic minerals have perfect {001} and occasional poor {100} cleavage. Irregular {010} parting is sometimes seen in clinozoisite and zoisite. Replacement of Ca'' by a trivalent ion, as in allanites, strengthens bonding across the {001} cleavage plane, which runs through the Ca'' positions, and reduces the tendency for {001} cleavage to occur.

Twinning. Zoisite shows no observable twinning. Clinozoisite, epidote, and piemontite show occasional {100} lamellar twinning, and De Rudder and Beck (1963) have noted {10 $\bar{1}$ } twinning in iron-poor clinozoisite. The 'S.A.' mechanism proposed by Wolten and Chase (1964) appears adequate to account for twinning in monoclinic epidotes.

Electrical and magnetic properties

Dielectric constants. Ukai (1954) determined some dielectric properties of epidote at frequencies of 100 to 500 kc/sec, and temperatures up to 700°C ; from the optical properties the composition was near 0.85 Fe. Wappler (1965) has determined the dielectric constants of an epidote of unstated composition as: ϵ_1 7.51, ϵ_{11} 10.79, ϵ_6 14.29 with $\sqrt{\epsilon_{11}:c}$ [001] $\simeq -10^\circ$ at a frequency of 7 mc/sec and room temperature.

Magnetic susceptibility. The magnetic susceptibilities of two epidotes with specific gravities of 3.45 and 3.46 (around 0.90 to 0.96 Fe) were determined by Sigamony (1944) as 22.7 and 23.6×10^{-6} cgsu respectively. If the volume susceptibility of 80.7×10^{-6} cgsu found by Finke (in Goldschlag, 1917) is converted to bulk susceptibility using a density of 3.45 gm/cm^3 , a similar result (23.4×10^{-6} cgsu) is obtained: anisotropy of susceptibility is small ($< 2\%$).

Electrical conductivity. The major axis of the conductivity ellipse is $b[010]$ (Jannettaz in Goldschlag, 1917).

Thermodynamic properties

A plot of S_{298} versus molecular weight for a large number of minerals suggests a value near 80.5 eu for S_{298} of zoisite (data of Kelley, 1960; King and Weller, 1961). Addition of both configurational and non-configurational terms yields values of 82.9 and 85.0 eu for clinozoisite (0.30 Fe) and epidote (0.90 Fe) respectively. Estimates were also made of S_T for zoisite:

T° C	25	200	400	600	800
S	80.5	127	162	195	228

These values compare with $S_{405^\circ\text{C}} = 162$ eu found by Newton and Kennedy (1963) from phase equilibrium studies, and $C_{P,56^\circ\text{C}} = 91.5$ for epidote with 0.81 Fe.

Polymorphism

Zoisite becomes unstable relative to clinozoisite when the iron content exceeds about 0.15 per formula unit: the transition is thought to be second order.

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Appendix I. Determinative methods

Al-Fe series. At the time of writing, satisfactory optical and X-ray methods exist for finding the composition of monoclinic epidotes with < 0.85 Fe, but at higher iron contents these methods are either untested (X-ray) or known to be inaccurate (optical), and chemical analysis is the desirable procedure.

Used in conjunction with fig. 3, determination of $\beta \pm 0.001$ provides a rapid and accurate ($\sigma \approx 0.03$ Fe $\equiv 1\%$ Ps) method of finding the composition of hydrothermal epidotes, which will probably work reasonably well for non-hydrothermal epidotes, other than those from low-temperature high-pressure rocks such as the glaucophane schists. Optical methods are not suitable for zoisites, iron-poor clinozoisites and iron-rich epidotes, but zoisite may usually be distinguished from clinozoisite in oil of $n = 1.710$, since zoisite usually has $\gamma < 1.708$ whilst clinozoisite usually has $\gamma > 1.710$: confirmatory evidence of orthorhombic symmetry should be sought if possible, either by X-ray methods (Seki, 1959), or by searching for inclined extinction in (010) section.

Myer (1965) has described an X-ray method that appears applicable to all epidotes with Fe < 0.85 to 1.0 , including those from the glaucophane schist facies. The method utilizes $\Delta 2\theta$ (020)_{ep.} - (111)_{Si}: % Ps = $(298.5 - 82.7\Delta 2\theta)$; Fe = $(8.955 - 2.481\Delta 2\theta)$. (Note that Myer uses $\text{Fe}_{0.27}^{3+}$ to denote the composition Ps_{27} or 0.81 Fe per formula unit; this is confusing and should be avoided. The equation above is in

terms of Fe per formula unit.) The variation of the (020) spacing with $Fe > 0.85$ is not yet known, but the rate of change of $\Delta 2\theta$ will probably differ significantly from that observed at low iron contents.

A rough idea of the composition of an Al-Fe-Mn epidote may be gained from β or γ and $2V$, using figs. 5 and 7.

Appendix II. Sources of error in the correlation of properties with composition

Major sources of error noted during the present work include (roughly in order of importance) non-determination of FeO in Al-Fe epidotes and of MnO in Al-Fe-Mn epidotes, heterogeneity of sample, errors in orientation and matching the indices of sample and liquid, and failure to use monochromatic light. Sources of scatter (as opposed to bad technique or experimental error) include variation in the Fe:Mn ratio, and differences in the distribution of Fe and Mn between sites.

Small amounts of FeO and MnO have no detectable effect on the indices, whereas 1% (Fe, Mn)₂O₃ raises them by 0.002 to 0.012. Since (Fe, Mn)O contents of epidote minerals range up to 5%, non-determination of FeO and MnO is a very serious source of error.

Microprobe examination of 30 epidotes and 15 piemontites reveals composition ranges up to 0.30 (Fe, Mn), with ranges of 0.05 to 0.10 common. This source of error can be eliminated by working with a narrow density fraction (better than ± 0.005), or by selecting several crystals with the same β index (± 0.002) for optical and X-ray work and microprobe analysis: FeO and MnO contents are then determined on the bulk sample. Ideally, the composition and all properties should be determined on a small single crystal, since zoning is common, and large crystals sometimes show a 'domain' structure, with variations in composition between domains. Variation in Fe:Mn ratio at roughly constant (Fe+Mn) contents is particularly common.

Determination of α and γ is subject to orientation errors, which cause overestimation of α and underestimation of γ and $\gamma-\alpha$; there is no problem with β . Orientation errors have been severe in some published work.

Use of white light gives an effective wavelength in the red for β and γ , and in the yellow for α . The magnitude of the resulting error depends on the dispersion curves of solid and liquid. Indices of piemontites are easily determined in red light, and can then be corrected to *D*-line values if desired.

Appendix III. Notes on some Al-Fe-Mn epidotes: corrections to published data

Ullevis piemontite. Odman (1950) reports a 8.05 Å, c 9.14 Å: these values are actually $a \sin \beta$ and $c \sin \beta$.

Chikla piemontite. Bilgrami (1956) described two piemontites from Chikla, one had 0.42 Fe and 0.93 Mn, with α 1.794, β 1.807, γ 1.819, and $\gamma-\alpha$ 0.025, the other was similar with lower (Fe, Mn) and correspondingly lower indices. By comparison with other piemontites α is very high, and γ and $\gamma-\alpha$ very low. Dr. Bilgrami kindly supplied the writer with a sample of Chikla piemontite (microprobe analysis Fe 0.66, Mn 0.78), the indices of which were determined as α 1.772, β 1.813, γ 1.860, $\gamma-\alpha$ 0.088. The density is 3.543 gm/cm³. The redetermined indices agree well with those reported by Nayak and Neuvonen (1963) for a piemontite of similar composition (Fe 0.68, Mn 0.75) from Goldongri.

Goldongri piemontite. The values of $2V_\alpha$ (68°) and $\alpha:c$ (38°) reported for this mineral by Nayak and Neuvonen (1963) depart widely from those expected for a mineral of this composition ($2V$ about 90, $\alpha:c$ about -10°), and it seems possible that they represent $2V_\gamma$ and $\gamma:a$ respectively. If this view is correct, $2V_\alpha$ is 112° and $\alpha:c$ is -12.6°, compared with $2V$ calculated from the indices of 92°.

Långban piemontite. Two samples of piemontite from Långban (including one

thought by Malmqvist himself to be that described in 1929) were analysed. Both contained 1.13 (Fe, Mn), whereas the analysis by Jakob gives 1.78 (Fe, Mn). Malmqvist's optical data suggest a figure near 1.2 (Fe, Mn). The cause of the anomaly is not known, but it may be attributable either to the unusually high Na₂O, K₂O, and H₂O contents of this mineral, to the presence of Mn in a third site, or to accidental exchange of samples in the course of the analytical or optical work. Whatever the cause, use of the Långban data in optical variation diagrams appears inadvisable.

Strens (1964). Synthesis and properties of piemontite, *Nature*, vol. 201, p. 175. The correctness of the published data for the Långban and Chikla minerals had not fallen under suspicion at the time of writing this paper, and consequently the variation curves from which the figures given in table I were taken were seriously in error. The discussion of properties in the 1964 paper should be ignored in favour of that in the present paper.

TABLE III. Properties of 'high index' epidotes

No.	Reference	Fe ^{''}	α	β	γ	$\gamma-\alpha$	2 V _{α}	$\alpha:c$ [001]	
1	Malmqvist, 1929	0	1.7156	1.7172	1.7208	0.0052	113.8	+12.3	
2	"	"	0.10	1.7176	1.7195	1.7232	0.0056	98.3	+2
3	"	"	0.20	1.7238	1.7291	1.7343	0.0105	90.7	0
4	"	"	0.35	1.7228	1.7342	1.7444	0.0216	86.6	- 1.4
5	Ernst, 1964	0.70	1.731	1.752	1.772	0.041	95	5*	
6	"	"	0.70	1.739	1.760	1.779	0.040	100	4
7	"	"	0.72	1.736	1.757	1.778	0.042	95	2
8	"	"	0.59	1.728	1.746	1.766	0.038	100	2
9	"	"	0.67	1.735	1.754	1.775	0.040	105	3
10	this paper	0.69	1.740	1.762	1.780	0.040	—	—	
11	Ernst, 1964	0.54†	1.753	1.781	1.812	0.059	90	3	

1-4, Malmqvist, 1929, Table 33, Nos. 1, 2, 4, 10; 5-9, Ernst's (1964) Ep 4, 13, 15a, 16, and 17; 10, epidote from Californian glaucophane schist, locality not known; 11, Ernst's (1964) piemontite (Ep 2).

* The sign of $\alpha:c$ is not stated, but it is presumably negative. † plus Mn^{'''} 0.31.

Appendix IV. High index epidotes from the glaucophane-schist facies

Indices of clinzoisites and epidotes from the glaucophane schists of California and Japan and from certain Alpine rocks (table III) plot well above those of most hydrothermal, metasomatic, and metamorphic epidotes of similar Fe₂O₃ content. Since glaucophane schists are high pressure rocks, the possible existence of a low-volume epidote polymorph was indicated, but comparison of the X-ray data of Ernst (1964) for five high-index epidotes with those of Myer (1965) for ten hydrothermal epidotes revealed no significant ($\geq 2 \text{ \AA}^3$) difference in volume, whereas the calculated (Gladstone-Dale) volume decrease to produce the observed change in indices is about 10 \AA^3 . Neither is a change in the distribution of iron between the sites responsible, as the variation curves for high- and low-index epidotes would then converge at 0 Fe, rather than remaining parallel over the whole range of Fe contents. An observable change in unit-cell volume would also be expected.

Two obvious possibilities remain, firstly, a change in structure at constant volume (i.e. second order polymorphism), and secondly, major differences in composition. Careful comparison of powder photographs of a glaucophane-schist epidote (table III, no. 10) and a low-index epidote of similar Fe₂O₃ content (Strens, 1964, table III,

no. 1) revealed no significant differences in intensity or spacing, and no obvious absences or additional lines. Any structural change must therefore be a minor one, making it correspondingly less likely that so large a change in indices would result.

The average composition of five glaucophane schist epidotes (Ernst, 1964) was next compared with that of five normal (low index) epidotes having the same average Fe content (table IV). It is clear from this table, and from the analyses of the minerals recalculated to 26(O, OH) that in the glaucophane schist minerals a significant proportion of the Al and Ca has been replaced by other ions. Calculation

TABLE IV. Comparison of compositions of high- and low-index epidotes

	Epidote II*	Epidote I†	(II-I)	Replacement
SiO ₂	39.31	37.43	+1.88	?
Al ₂ O ₃	20.99	24.84	-3.85	Replaced by Ti, Si, Mg, Fe ⁺
TiO ₂	1.75	0.10	+1.65	Al
Fe ₂ O ₃	11.04	11.32	—	—
FeO	3.05	0.44	+2.61	Al, Ca'
MnO	0.30	0.12	+0.18	Ca'
MgO	1.78	0.47	+1.31	Al, Ca'
CaO	18.27	23.47	-5.20	Replaced by Mn ⁺ , Fe ⁺ , Mg, Na, K
Na ₂ O	0.67	0.26	+0.41	Ca'
K ₂ O	0.30	0.21	+0.09	Ca'
H ₂ O	2.63	1.87	+0.76	—
P ₂ O ₅	0.21	0.20	+0.01	—

* Average of Ernst's Ep 4, 13, 15a, 16, 17. † Average of Nos. 5-9, Deer, Howie, and Zussman (1962), Table 33; Na₂O, K₂O, and P₂O₅ were not determined in these analyses, and values have been taken from Strens (1964) Table IV, Nos. 1-5. Average indices of Ep II α 1.739, β 1.754, γ 1.774, and of Ep I (from fig. 4) α 1.721, β 1.739, γ 1.753: difference (II-I) α 0.013, β 0.015, γ 0.021, γ - α 0.008, mean refr. ind. 0.016.

from the specific refractivities indicates, however, that constant volume replacement of (Ca, Al) by Fe⁺, Mg, Mn⁺, Na, and K would not increase the mean index. Substitution of (Ti, Si) plus (Fe⁺, Mg) for 2Al could produce an effect of the required magnitude, but detailed study of the analyses does not support this scheme, e.g. Ernst's piemontite has both the highest difference in mean refractive index and the lowest Ti content, and no correlation appears to exist between Ti content and difference in mean refractive index.

In conclusion, whilst it appears that real differences in optical properties exist between glaucophane schist and normal epidotes, the cause of these differences is by no means clear.

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