Stability and relations of the Al-Fe epidotes

By R. G. J. Strens

Department of Geology and Geophysics, University of California,
Berkeley[1]

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Summary. The various (P, T) stability fields of iron-free zoisite have been deduced for systems containing excess silica and water with Ca:Al ratios ranging from 1:2 (anorthite) to 3:2 (grossular). Zoisite is a possible phase in all systems with Ca:Al lower than 3:2, attaining its maximum stability at the zoisite (Ca:Al = 2:3) and prehnite (Ca:Al = 2:2) compositions.

The consequences of varying the Al:Fe ratio are next examined. Zoisite with 4 % pistacite is stable to 525° at 2 kilobars, compared with ∼ 585° for clinozoisite and 620 to 630° for epidote (Ps_{35}) at the same pressure. Increasing iron content also stabilizes epidote minerals relative to their low-temperature and high-pressure decomposition products.

Examples of natural zoisite–clinozoisite, zoisite–epidote, and clinozoisite–epidote assemblages are described. It is concluded that zoisite–epidote mixtures result from the disproportionation of clinozoisite outside its own stability field, but within those of zoisite and epidote. The assemblage zoisite–clinozoisite is probably not stable, but further evidence is needed on this point. The assemblage clinozoisite–epidote is stable below 550° C, at which temperature the solvus in the Al–Fe series closes.

RELATIONSHIPS between epidote, clinozoisite, and zoisite were briefly considered by the writer (Strens, 1963) who presented data on coexisting epidote and clinozoisite from the English Lake District, and discussed published data on zoisite–epidote and zoisite–clinozoisite assemblages. To account for these two-phase assemblages, it is necessary to consider the stability of epidote minerals as a function of P, T, and composition, with particular reference to the effects of varying Fe:Al ratio. With this background, the nature of the assemblages zoisite–epidote, zoisite–clinozoisite, and clinozoisite–epidote is discussed. Throughout the paper the following abbreviations are used: An, anorthite; Cor, corundum; Cz, clinozoisite (Al end-member); Ep, epidote; Gt, grossular; Ky, kyanite; Law, lawsonite; Mt, magnetite; Pm, piemontite (Mn end-member); Pr, prehnite; Ps, pistacite (Fe end-member); Qz, quartz; Wo, wollastonite; Zo, zoisite.

P-T stability of epidote minerals

It will be convenient to start by considering the compositional factors governing the P-T stability of iron-poor epidotes (zoisite and clinozoisite), and then to consider systems containing ferric iron and the effects of changing P_{O_2} and of adding albite, $(Na,K)_2O$, and $(Fe,Mg)O$.

The following discussion is limited to systems with excess quartz and water, in which the $Ca:Al$ ratio is the main compositional variable, and the stability field of zoisite in the P-T plane will be considered for four different compositions having the $Ca:Al$ ratios of anorthite, zoisite, prehnite, and grossular ($1:2$, $2:3$, $1:1$, and $3:2$ respectively). An Al_2SiO_5 polymorph enters systems on the alumina-rich side of the anorthite plane, and wollastonite those on the lime-rich side of the grossular plane. With increasing temperature, the phases prehnite, zoisite, and grossular break down in turn, until at high temperature only wollastonite and anorthite remain.

Grossular P-T plane: If zoisite were stable in systems of grossular composition, it would necessarily be accompanied by an alumina-poor phase (e.g. wollastonite), which would in turn imply that grossular was unstable over some P-T range common to the stability fields of zoisite and wollastonite. Since zoisite breaks down to grossular at high temperatures, the garnet field must exceed that of zoisite under such conditions. At low temperatures, the existence of garnet–prehnite assemblages implies that the garnet and prehnite fields meet or overlap, making the existence of a field of zoisite plus wollastonite even less probable. The reaction relation between clinozoisite and wollastonite has recently been described by De Rudder and Beck (1963) from the Willsboro wollastonite deposit, where a zone of grossular intervenes between a clinozoisite vein and the country rock (wollastonite), presumably formed by the reaction:

$$2Cz + 5Wo \rightleftharpoons 3Gt + 2Qz + H_2O. \tag{1}$$

It is thus improbable that either zoisite, clinozoisite, or epidote has any stability field in the grossular plane.

Prehnite plane. The pairs prehnite-zoisite (clinozoisite, epidote), prehnite–grossular (hydrogrossular), prehnite–plagioclase, prehnite–quartz, zoisite (clinozoisite, epidote)–grossular, zoisite (clinozoisite, epidote)–plagioclase, and zoisite (clinozoisite, epidote)–quartz all appear stable, and prehnite–epidote–plagioclase–quartz has been reported by Burnham and Jahns (in Merrin, 1962). The low-temperature stability
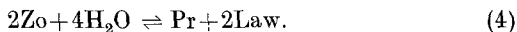
limit of zoisite in the prehnite plane is determined by the reaction:

$$5Pr \rightleftharpoons 2Gt + 2Zo + 3Qz + 4H_2O \qquad (2)$$
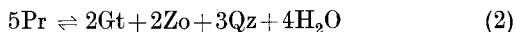
(Strens, unpub.), whilst that in the zoisite plane is determined by:

$$2Zo \rightleftharpoons Pr + 2An \qquad (3)$$

or by:

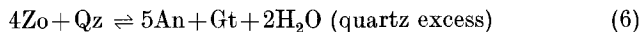$$2Zo + 4H_2O \rightleftharpoons Pr + 2Law. \qquad (4)$$

The assemblage Pr–An occupies at most a small field at low pressures and temperatures, but is enlarged in the presence of albite. Preliminary experimental work (Strens, unpub.) indicates that reactions (2) and (3) both take place below 350° C at 2 kilobars, and possible phase relations are illustrated in fig. 1A. The products of the 'prehnite dissociation reaction':
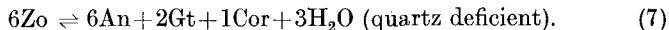
$$Pr \rightleftharpoons An + Wo + H_2O \qquad (5)$$

are metastable relative to $Gt + Zo + Qz$ or $Gt + An + Qz$ within any P-T area common to the stability fields of these phases. At high temperatures the zoisite field in the prehnite plane is limited by the quartz excess or quartz deficient reactions (6) and (7) (below).

Zoisite plane. Many experimental data are available relating to the high temperature breakdown of zoisite (Winkler and Nitsch, 1962; Holdaway, 1963; Fyfe, 1960; Merrin, 1962) and epidote (Fyfe, 1960; Winkler and Nitsch, 1963) with and without quartz. The important reactions are:

$$4Zo + Qz \rightleftharpoons 5An + Gt + 2H_2O \text{ (quartz excess)} \qquad (6)$$

and:

$$6Zo \rightleftharpoons 6An + 2Gt + 1Cor + 3H_2O \text{ (quartz deficient).} \qquad (7)$$

The experimental results are summarized in fig. 1B. Reactions (3) and (4) probably limit the zoisite field at low temperatures, but the anorthite:lawsonite boundary is not yet fixed with sufficient accuracy to define areas of $Law + Pr$ on fig. 1B with any confidence, and only one of many possible schemes is shown. Possible reactions including zeolites have not been considered. At low temperatures and high pressures, zoisite is replaced by lawsonite and garnet:

$$4Zo + Qz + 8H_2O \rightleftharpoons 5Law + Gt. \qquad (8)$$
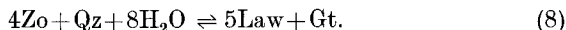
Since the slope of the reaction:

$$An + 2H_2O \rightleftharpoons Law \qquad (9)$$

is approximately 22° per kilobar (Newton and Kennedy, 1963), passing through 405° and 5 kilobars, whilst that of reaction (6) is 35° per kilobar, passing through 690° and 5 kilobars (Holdaway, 1963), the zoisite field is not closed by reaction (8), which is replaced at high temperature and pressure by:
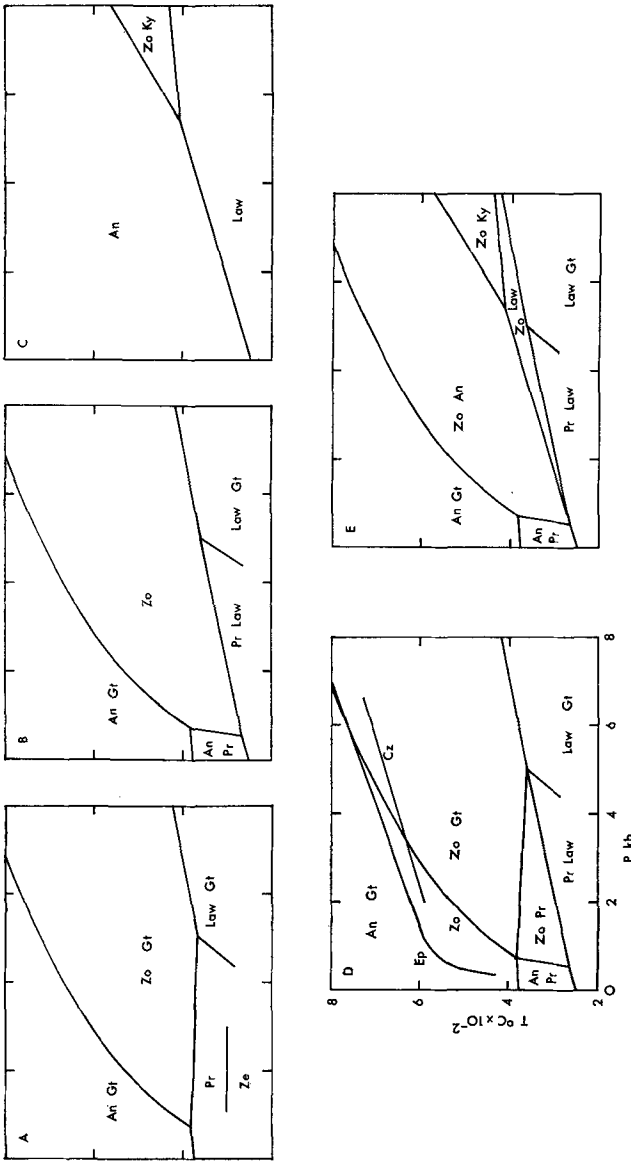
$$6Zo \rightleftharpoons 5Ky + 4Gt + Qz + 3H_2O. \qquad (10)$$
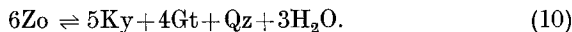
FIG. 1. *P-T* stability of some Ca–Al silicates in the presence of excess silica and water. Possible fields of zeolite have been neglected. The positions of the invariant points at 330°, 0·8 kb and 300°, 5 kb have been estimated by the writer from available experimental, petrographic, and thermodynamic data, and should be regarded only as a first approximation to the truth. Stability fields shown are for prehnite (A), zoisite (B), and anorthite (C) compositions. Grossular is stable over the entire *P-T* area shown at a Ca:Al ratio of 3:2. Wollastonite will normally join assemblages with a higher Ca:Al ratio than grossular, and an Al_2SiO_5 mineral those with a lower Ca:Al ratio than anorthite. Figs. 1 D and E show the assemblages of Ca–Al silicates to be expected between the prehnite and zoisite (D) and zoisite and anorthite (E) compositions: the relative stability of zoisite, clinozoisite, and epidote is also indicated (D).

Anorthite plane. The experimental observations of Newton and Kennedy (1963) are in moderately good agreement with Holdaway's (1963) reinterpretation of Merrin's (1962) data for the reaction:

$$4An + H_2O \rightleftharpoons 2Zo + Sill + Qz, \tag{11}$$
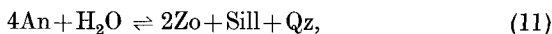
which is replaced at slightly higher pressures by:

$$4An + H_2O \rightleftharpoons 2Zo + Ky + Qz. \tag{12}$$
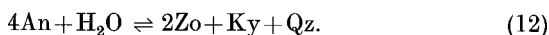
Reactions (6) and (12) intersect at about 20 kilobars, 1100° C, implying reactions (10) and (13); the intersection of (13) with (9) further implies reaction (14).

$$3An \rightleftharpoons 2Ky + Gt + Qz \tag{13}$$

$$3 Law \rightleftharpoons 2Ky + Gt + Qz + 6H_2O \tag{14}$$
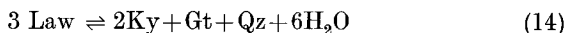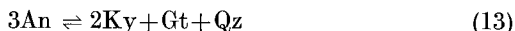
Influence of iron content on stability

Before passing on to the two-phase assemblages, it is necessary to consider the effect of iron content on the stability of epidotes. A considerable amount of evidence has now accumulated to suggest that epidote minerals break down by a reaction of the type:

$$epidote + quartz \rightleftharpoons iron\text{-}rich\ epidote + garnet + anorthite + H_2O \tag{15}$$
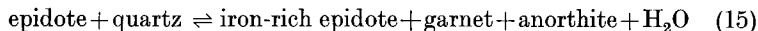
This evidence may be summarized:

The breakdown temperatures of seven epidotes ranging in composition from Ps_5 to Ps_{31} were studied by following the weight-changes of quartz crystals sealed in capsules with mixtures of epidote, anorthite, and grossular. The temperatures of zero loss (i.e. of equilibrium in reaction (15)) varied systematically with Ps content, the univariant curve of reaction (6) being raised by about 3° C for each 1 % Ps added. A run with β-zoisite suggested that it was stable to at least 70° above the temperature found by Winkler and Nitsch (1962) for pure CaAl zoisite.[1]

In a series of runs made using mixtures with 5 to 50 % Ps at 600° and 2 kb, the maximum yield of epidote was obtained from reactants having 30 to 45 % Ps, whilst reactants poor in iron recrystallized to anorthite, garnet, and epidote.

In runs at 2 kb, Fyfe (1960) found that epidote (initial composition Ps_{27}) grew strongly at 630° C and decomposed at 715° to anorthite, garnet, and magnetite, giving a stability limit at this pressure of 670

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[1] β-zoisite formed by the breakdown of natural prehnite in experiments on the system Pr–H_2O was stable to 525° at 2·00 kb, the same temperature as was found in the weight-loss experiments.

$\pm 40°$. The writer has grown epidote in practically 100 % yield from $Cz_{65}Ps_{35}$ and excess quartz, at 630° and 2 kb. Holdaway (1963) re-interpreted Merrin's (1962) data, and made additional hydrothermal runs, showing that clinozoisite of undefined composition was stable to about 585° at 2 kb. Depending on the compositions assumed for the epidote actually produced by Fyfe, and for the clinozoisite, these data indicate a slope of 3 to 5° for 1 % Ps, and are consistent with the view that epidote ($?Ps_{35}$) is stable to at least 630° at 2 kb.

Winkler and Nitsch (1963) studied the reactions of mixtures of bulk composition $Cz_{90}Ps_{10}$ and $Cz_{67}Ps_{33}$ in the presence of excess quartz, and concluded that both compositions were stable to 620° C at 2 kb. The writer considers that the method of interpreting the experimental results adopted by Winkler and Nitsch was such that the same stability field would inevitably be found for different compositions. These workers added 5 % of epidote seeds to their mixture, and regarded epidote of the bulk composition of the mixture (10 and 33 % Ps) as stable when the seeds grew, and unstable when the seeds disappeared. Consider the case in which mixtures of composition Ps_{10} and Ps_{33} are held on the univariant line for the composition Ps_{33}: $Cz_{90}Ps_{10}$ reacts in about 30 % yield to epidote (Ps_{33}), plus 70 % (An, Gt), and the seeds grow; $Cz_{67}Ps_{33}$ recrystallizes in 100 % yield to epidote, and the seeds grow. Only if the temperature exceeds the stability limit of the most iron-rich epidote produced by reaction (15) will the seeds disappear. Winkler and Nitsch (1963) and Merrin (1962) both appear to have obtained larger yields of epidote from iron-rich mixtures; Merrin attributed this to easier nucleation of iron-rich epidote, but this can scarcely have been the case in Winkler and Nitsch's and the writer's seeded runs, and the operation of reaction (15) is more likely. It is concluded that the data of Winkler and Nitsch (1963) apply to a mineral of unknown, but high, iron content, estimated from the writer's observations (see above) as 35 ± 5 % Ps for the point at 620°, 2 kb, and lower for points at lower temperatures and pressures.

The effect of increasing iron content on the quartz-excess and quartz-deficient reactions (6) and (7) may be deduced by making the simplifying assumptions that the anorthite contains no Fe^{3+}, and that Fe^{3+} substitutes into the garnet until this is saturated and thereafter appears as hematite. It is found that reaction (6) holds over the range 0 to 16·7 % Ps, above which hematite joins the products, and the amount of quartz consumed declines steadily, reaching zero at 33·3 % Ps; thereafter quartz appears among the products. The relative amounts of the

various phases for any given bulk composition in excess of 16·7 % Ps are given by:
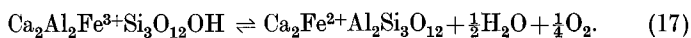
4Ep

$= (5-0.06P)An+(1+0.02P)Gt+(-1+0.06P)Qz+(0.04P)Ht+2H_2O,$
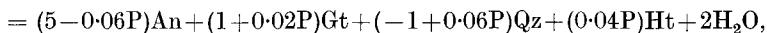
where $P = (\%Ps-16.7).$

In the case of the quartz-deficient reaction (7), hematite should replace corundum among the products, and reactions (6) and (7) thus become identical for epidotes with more than 33·3 % Ps, the divariant PTX surfaces merging as iron content increases. This enables a further estimate to be made of the effect of iron content on stability, since at Ps_0 the two reactions are separated by 90° (Holdaway (1963) gives 690° for (6) and 780° for (7) at 5 kb), whilst at $Ps_{33.3}$ there is zero separation. Hence the average slope over this range is 90/33·3, or 2·7° for 1 % Ps, close to the 3° per 1 % Ps estimated earlier. Increasing Fe:Al ratio should inhibit the low-temperature breakdown of epidote minerals to the iron-poor phases anorthite (usually < 0.5 % Fe_2O_3), prehnite (usually < 1.5 % Fe_2O_3), and lawsonite (usually < 1.0 % Fe_2O_3) since production of a free oxide is energetically unfavourable. Epidote has been synthesized by Winkler and Nitsch (1963) at 315°, 1·5 kb, and has been encountered growing in thermally active areas in New Zealand (Steiner quoted by W. S. Fyfe, personal communication, 1962), Iceland, and California (F. A. F. Berry, personal communication, 1963). The temperatures and pressures range from 150° at low pressure (Iceland) through 200° and 'a few atmospheres' (New Zealand) to about 250° and 500 bars (California). Clinozoisite and zoisite are markedly less common than epidote in low-grade rocks (e.g. Coombs et al., 1959), and probably react to An, Pr, Law, and other hydrous phases at 300–350° C, whereas epidote appears stable to 200° or lower. Increasing iron content thus enlarges the stability field of epidote to both lower and higher temperatures, and possibly also to higher pressures.

Effect of P_{O_2} on epidote stability

The effect of reducing Fe^{3+} to Fe^{2+} is best illustrated by reference to a system with Ca:Al:Fe = 2:2:1 (i.e. $Cz_{67}Ps_{33}$), in which reduction of iron moves the system out of the epidote plane ($2MO \cdot 1\frac{1}{2}M_2O_3$), and into the garnet plane ($3MO \cdot M_2O_3$):

$$Ca_2Al_2Fe^{3+}Si_3O_{12}OH \rightleftharpoons Ca_2Fe^{2+}Al_2Si_3O_{12}+\tfrac{1}{2}H_2O+\tfrac{1}{4}O_2. \qquad (17)$$

Within the stability field of garnet of this composition, the epidote field

is reduced from its maximum extent (epidote plane) to zero (garnet plane). Judging from experimental runs at the P_{O_2} of the Ni:NiO buffer (magnetite field), the garnet composition shown is unstable relative to magnetite, anorthite, and grandite garnet at 700° and 2 kb, so that the epidote field is simply reduced to that of zoisite or clinozoisite. However, the occurrence of large amounts of $CaFe^{2+}$ components in glaucophane-schist garnets (Pabst, 1931; Lee, Coleman, and Erd, 1963) suggests that reaction (17) may be important at high pressures and low temperatures.

Effect of adding albite

Addition of albite to the epidote–quartz system will obviously desta-bilize epidote by an amount equal to the ΔH of mixing of Ab with An produced by the breakdown of epidote, since the reaction:

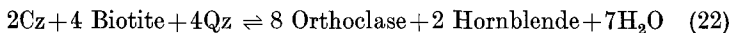$$4Ep + Qz + nAb \rightleftharpoons Gt + (5+n)\ plagioclase + 2H_2O \qquad (6b)$$
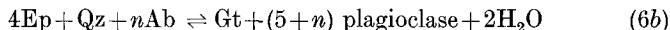
includes the reaction:
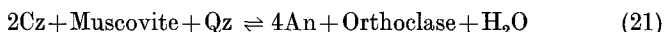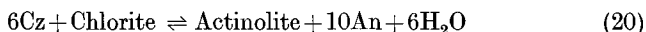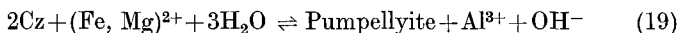
$$Ab + An \rightarrow plagioclase \qquad (18)$$

which is irreversible (i.e. has negative ΔG). This is the 'plagioclase–epidote equilibrium', the effect of which is to create an infinite family of curves, along each of which epidote (of some specified composition) is in equilibrium with plagioclase of varying anorthite content. The equilibrium is complicated by the effect of the peristerite solvus, by the iron content of the epidote, and at low temperatures ($< 550°$ C) by the clinozoisite–epidote solvus.

In the presence of albite, the position of the univariant line is shifted in any reaction in which An takes part, for example (3), (9), (11), (12), (13), and a similar effect will occur in other reactions, e.g. the mixing of garnet produced by destruction of epidote with pyralspite garnet present in the rock.

Effect of adding (Na, K)$_2$O and (Fe, Mg)O

By making possible many other reactions, of which (19) to (22) below are examples, addition of other components further reduces the stability field of epidote:

$$2Cz + (Fe, Mg)^{2+} + 3H_2O \rightleftharpoons Pumpellyite + Al^{3+} + OH^- \qquad (19)$$

$$6Cz + Chlorite \rightleftharpoons Actinolite + 10An + 6H_2O \qquad (20)$$

$$2Cz + Muscovite + Qz \rightleftharpoons 4An + Orthoclase + H_2O \qquad (21)$$

$$2Cz + 4\ Biotite + 4Qz \rightleftharpoons 8\ Orthoclase + 2\ Hornblende + 7H_2O \qquad (22)$$

Zoisite–clinozoisite relations

Assemblages containing zoisite and clinozoisite have formed by metamorphism or metasomatism of basic igneous rocks (Orlov, 1925), by metamorphism of calcareous rocks (Rogers, 1924; Foye, 1926), and in the low-grade regional metamorphism of basic igneous or of calcareous sedimentary rocks. The latter paragenesis is exemplified by a calc-silicate rock from Deep Cove, Doubtful Sound, New Zealand, (54M–4584) in which prismatic crystals of β-zoisite have nucleated epitaxially on clinozoisite. The b- and c-crystallographic axes of the two minerals are coincident, since α, β, γ (zoisite) = γ, β, α (clinozoisite); similar relations were described by Orlov (1925). The clinozoisite has an iron-rich core ($\delta = 0.011$) from which the birefringence decreases outwards, until at the rim it is equal to that of the zoisite ($\delta = 0.005$). In the zoisite–clinozoisite–prehnite rock described by Rogers (1924), the clinozoisite (Fe_2O_3 2.96 % = 6 % Ps) is rimmed by pink zoisite, but the assemblage does not appear to be an equilibrium one. Foye (1926) described a thulite–'epidote' rock from Haddam, Connecticut, but although his description implies that the monoclinic mineral was optically negative (i.e. epidote), the large extinction angle (35°) and the very low index (1.69) appear to preclude this, and the mineral is here regarded as a clinozoisite.

One would certainly not be justified in concluding that the assemblage zoisite–clinozoisite is stable on the basis of the above evidence, but the postulate has not been disproved. Further petrographic data are needed to settle this point.

Zoisite–epidote relations

Present experimental data indicate that both zoisite and epidote are stable to higher temperatures than clinozoisite at pressures in excess of 4 kb, so that clinozoisite disproportions to epidote and zoisite under such conditions:

$$a\text{Cz} \rightleftharpoons b\text{Ep} + (a-b)\text{Zo} \qquad (23)$$

The products of the normal breakdown reactions of clinozoisite are metastable relative to epidote and zoisite within this two-phase region. It seems reasonable to assume that the stability limits of zoisite, clinozoisite, and epidote will all be raised by comparable amounts in quartz-deficient systems, and that the epidote–zoisite field will be preserved. If β-zoisite proves to have higher thermal stability than the pure Al-zoisite used by Winkler and Nitsch (1962), the zoisite and clinozoisite breakdown curves would cross at lower pressures and temperatures, and the two-phase field would be entered sooner.

Reaction (23) is illustrated by an epidote–β-zoisite–almandine–chlorite–bornite–chalcopyrite rock from Longville, Mendocino County, California (M223). This rock is mainly composed of blades of β-zoisite up to 5 cm long, between which occur small amounts of well-crystallized epidote (up to 0.5×0.2 cm), which is often, though not invariably, intergrown with the zoisite. The garnet, chlorite, bornite, and chalcopyrite are present in mafic segregations; quartz has not been recorded. Study of the rock in thin section indicates that the epidote and zoisite formed in equilibrium, and crystal faces of the epidote (which breaks cleanly from the zoisite matrix) show no sign of etching. Microprobe analysis showed both minerals to be homogeneous, with Σ Fe as Fe_2O_3 equal to 1.40 % (zoisite) and 8.66 % (epidote). The epidote thus lies in the centre of the clinozoisite–epidote solvus (17 % Ps), indicating a temperature of formation $\geqslant 550°$, which is in agreement with the experimentally determined stability fields shown in fig. 1.

Clinozoisite–epidote relations

The stable assemblage clinozoisite(Ps_{11})–epidote(Ps_{24}) was reported by Strens (1963, 1964), and taken with the scarcity of minerals having compositions in the range 12 to 22 % Ps, and the rather dense concentration of analyses of clinozoisite and epidote from low-temperature environments around Ps_8 and Ps_{26} seems to provide strong evidence for a gap in the clinozoisite–epidote series, centred on Ps_{17}. The cause of the solvus may be simply explained as follows: the epidote lattice is strained, and hence the free energy of the mixed mineral as a whole is raised, when small Al and large Fe ions occupy adjacent sites, but this strain is removed when separation takes place into two components rich in Al and Fe respectively, in which large and small ions are not occupying adjacent sites. The solvus closes when the enthalpy change on mixing is balanced by the entropy of mixing, i.e. when $\Delta H - T \Delta S = 0$.

There is no experimental evidence on the temperature of closure, but a value of about 550° C is indicated by the petrographic evidence: Firman (1957) recorded compositions of 17 to 30 % Ps from high temperature metasomatic veins near the Shap granite, for which he estimated $T \leqslant 550°$ C; Firman (in Strens, 1964) found a similar composition range in the aureole of the Eskdale granite, for which the maximum temperature is again 500 to 600° C; Strens (1963, 1964) found epidote and clinozoisite, separated by about 13 % Ps, coexisting in vesicles, and in certain lavas and tuffs, for which a temperature of formation of about 400° might reasonably be assumed.

T–X plane for Al–Fe epidotes

A temperature–composition diagram (fig. 2) has been constructed by combining the experimental evidence on epidote stability with the petrographic evidence on the two-phase assemblages.
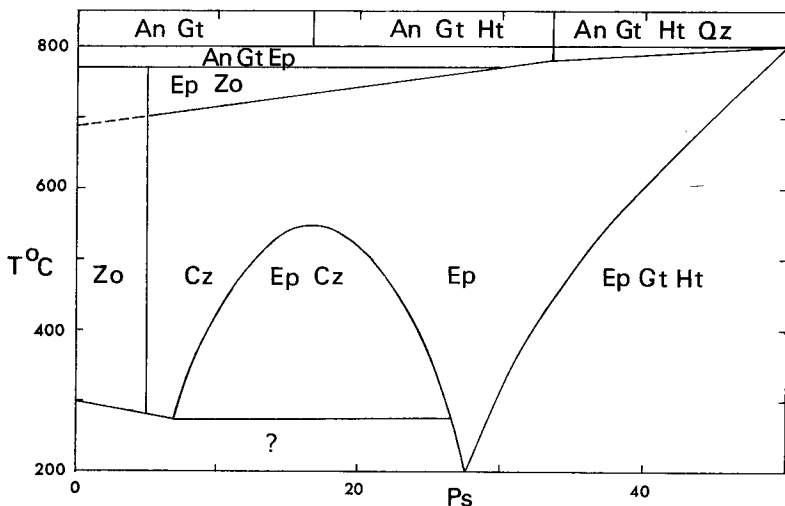

FIG. 2. T–X plane for the Al–Fe epidotes at 5 kb and a P_{O_2} in the hematite field, excess silica and water being assumed present. The zoisite ⇌ clinozoisite transition is placed at 5 % Ps.

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Note added in proof. The curve of reaction (6) has been determined for $Cz_{89}Ps_{11}$ as $528+32\cdot4P-0\cdot4P^2$ (P in kilobars) by M. J. Holdaway (1965, Trans. Amer. Geophys. Union, vol. 46, p. 181). Epidote of unstated composition decomposed at least 45° above this (i.e. $\geqslant$ 635° at 2 kb). R. C. Newton (personal communication, 1965) has determined (6) for zoisite with $1\cdot9$ % Fe_2O_3, and agrees with the writer in placing the reaction above 500° at 2 kb, though Newton's curve lies well below Winkler's at higher pressures. Newton (1965, Journ. Geol., vol. 73, p. 431) has also determined (7), which passes through 574° at 2 kb, with a slope of $+55\cdot3°$/kb.

The effect of these determinations is to displace the field of $Zo+Ep$ to temperatures and pressures higher than those thought to have held during the formation of most zoisite–epidote rocks. If, as seems possible, Zo and Ep are stable to lower temperatures than Cz, a field of $Zo+Ep$ will also exist at low (T, P).

Recent data for reaction (2) indicate that it passes through $375\pm25°$, 2 kb, with a slope of $-7°$/kb.