Epidotes of the Borrowdale Volcanic rocks of central Borrowdale

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Summary. Epidote and clinozoisite are widely distributed in the andesitic lavas and tuffs of the Borrowdale Volcanic Series. Four main types of occurrence may be distinguished, namely quartz–epidote vein fillings; 'Shap type' veins, bordered by pink reaction zones rich in SiO_2, Na_2O, and K_2O; autometasomatized lavas and tuffs; and tuffs subjected to alkali metasomatism. Epidote alone formed in the quartz–epidote veins; clinozoisite is found with epidote in the other types of occurrence.

Epidote and clinozoisite formed in vesicles at pressures of 10–280 kg/cm², at temperatures of 300–550° C; epidote associated with pre-Bala mineral veins formed in the range 130–550° C at 1000 kg/cm²; epidote around the Caledonian granites probably formed up to 600° C at about 2000 kg/cm². Clinozoisite crystallized together with epidote in the vesicles, demonstrating a gap in the clinozoisite–epidote solid solution series. Early formed epidote in vesicles is more strongly coloured than late epidote, although the compositions of the earliest and latest fractions are identical.

Analyses and optical determinations gave a range of epidote compositions from 20·8 to 29·6 % pistacite. There is no evidence for any effect of rock composition, or of pressure and temperature of formation on the composition of the epidotes studied. Varying oxygen partial pressure controls the activity of ferric iron, and thus has an effect on composition. Epidotes of small grain size tend to show high FeO contents.

The principal epidote-forming reactions are those involving the conversion of anorthite and orthopyroxene to epidote plus chlorite, the devitrification of volcanic glass, and the breakdown of anorthite during alkali metasomatism. Reactions involving ortho- and clino-amphiboles, clinopyroxene, and garnet were less important. Reaction zones rich in Na_2O plus K_2O probably form at 260–330° C, whilst silicification is the dominant process outside this temperature range.

EPIDOTE is a common, but heretofore neglected mineral in the volcanic rocks of Borrowdale. The presence of epidote has been mentioned by most writers on the petrography of Lake District rocks, but up to 1957, when Firman published his account of the metasomatic epidote veins at Shap, no quantitative work had been done. Oliver (1961) has given some optical data, and a detailed account of the petrography of the epidote nodules found in his area.

The object of this work is to provide more quantitative data on these minerals, and to consider their reactions, stability, and conditions of formation.

Epidote occurrences were divided into four types during the field investigation, viz. quartz–epidote veins, epidote lavas, epidote tuffs, and 'Shap type' veins, distinguished by the presence of reaction zones of the type described by Firman (1957b) from Shap. The quartz–epidote veins showed no apparent geographical control; 'Shap type' veins were confined to the vicinity of the graphite vein; epidote lavas and tuffs were widely distributed, but showed some tendency to be concentrated in certain parts of the stratigraphic column, particularly the Grey Knotts and Longthwaite groups. Firman (1957a), Oliver (1961), and Govinda-Rajulu (1959) were all of the opinion that epidote became more common in the vicinity of major intrusions.

Petrography of the epidote–quartz veins

The assemblage epidote–quartz is characteristic of these veins, and minor minerals are calcite, hematite, chalcopyrite, and malachite after chalcopyrite. The copper minerals are present to a very small extent, but are quite common. Chloritization has often taken place near the veins (e.g. Cat Gill), but chlorite is never found in them, the ferrous iron having been leached out of the veinstones, which are sometimes reddened by hematite.

Epidote in these veins occurs as fine crystals, 0·1 to 25 mm long, and from five to twenty times as long as they are broad: the crystals may be twinned (274207),[1] but only one occurrence of zoned crystals has been recorded (Fleetwith Pike, 207140), and here the zoning is barely distinguishable, and confined to a few crystals. All are optically negative, with 2V high, and absorption $\beta > \gamma > \alpha$ or $\beta > \gamma = \alpha$. The pleochroic scheme is: α neutral, β pistachio green, γ pale green.

The 'Shap type' veins

The term 'Shap type' was adopted as a convenient field description for metasomatic epidote veins accompanied by reaction rims of the type described by Firman (1957b) from Shap: for want of a better term, it is retained. The mineral assemblage of these veins is more complex than that of the epidote–quartz veins; in addition to epidote and quartz, chlorite, 'sericite', albite, and orthoclase are common, hematite, amphibole, calcite, and magnetite are occasional constituents.

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[1] National grid reference.

The normal epidote of these veins is extremely fine in grain $(1-5\,\mu)$, though larger crystals (0·1 to 0·5 mm) are often found in the central parts of a vein. Inclusions are abundant, and suggest a replacement origin. Twinning and zoning are absent, even in the larger crystals; absorption is $\beta > \alpha = \gamma$.

Epidote tuffs

Two types of epidote tuff may be distinguished: the first contains fine grained aggregates of epidote, which lie in a relatively unaltered ground-mass of mica, chlorite, quartz, calcite, and iron oxides; such rocks are thought to have originated through isochemical alteration. The second type shows conspicuous development of alkali feldspar, chlorite and mica being noticeably less abundant than in the 'isochemical' type; presumably the Al_2O_3 and SiO_2 of the rock have formed feldspar rather than mica. Calcite is somewhat more abundant, indicating influx of CO_2; the iron oxide is usually hematite rather than magnetite. This type is inferred to have originated through metasomatic changes brought about by alkaline solutions rich in CO_2. Types intermediate between the 'isochemical' and 'metasomatic' end members exist, in which meta-somatic processes have played a more or less important part.

The 'isochemical' or nodular epidote-tuffs. Epidote aggregates, nodular in form, range from 1 mm to 10 mm in diameter; the epidote crystals comprising these nodules are often radiating in habit, and are then up to 0·5 mm. long, but most of the epidote is in the $10-50\,\mu$ range. The central part of each nodule is occupied by a pure epidote–quartz assemblage, but varying amounts of rock material are incorporated in the outer zone. Epidote is also present as a constituent of the ground-mass, though mica, chlorite, calcite, iron oxides, and quartz form the bulk of this. Alkali feldspars are rare, the alkalis being contained in the mica. Partial replacement of plagioclase crystals by epidote has some-times taken place, but is never very far advanced; replacement by mica, chlorite, and calcite is more common. Twinning and zoning are absent, and pleochroism is never marked. The cleavage is often bent around the nodules, which are thus pre-cleavage. An analysis of such a tuff is given (Table 1, no. 9); it does not differ significantly in composition from other unaltered Borrowdale rocks.

'Metasomatic' or albite–orthoclase–epidote tuffs. Epidote occurs as aggregates of crystals 0·01–0·1 mm long, often scattered through calcite veins, or through the substance of the rock. Clusters of crystals and single crystals up to 0·8 mm in length also occur, usually replacing

plagioclase. Epidote replaces every mineral of the pre-alteration assemblage, plagioclase being most affected, so that 10–80 % of any plagioclase crystal is now epidote. Epidote with minor chlorite replaces clinopyroxene, whilst chlorite with minor epidote replaces orthopyroxene, ortho-amphibole, and clino-amphibole. Albite (An_3–An_7) replaces some plagioclase crystals; others, distinguished by their red coloration, are replaced by orthoclase. Mica is rare.

The formation of tuffs of this type involved alkali metasomatism, accompanied by the introduction of CO_2; oxidizing conditions are suggested, hematite being the typical iron oxide, instead of the magnetite, or magnetite–hematite assemblage of the 'isochemical' tuffs. The chlorite (β 1·605) is poor in iron, presumably due to the greater stability of magnesian chlorite under oxidizing conditions.

Epidote lavas

Epidote lavas are of two types, vesicular and non-vesicular: the non-vesicular variety contains nodular aggregates of minute epidote crystals, reminiscent of the 'nodular' epidote tuffs. Vesicular lavas are those in which cavities existed, which have suffered later infilling by epidote, chlorite, etc.

Vesicular lavas. Fine examples of vesicular lavas that contain epidote are found in the Grey Knotts area and on Eel Crags. The *Grey Knotts* rock is a coarsely porphyritic plagioclase-andesite, in which cavities have been filled by epidote, chlorite, calcite, and low quartz. Epidote and chlorite were formed early, any remaining space in the vesicles being filled by calcite and quartz. The epidote shows a wide range of grain sizes, from 1 to 500 μ, though the average is near 50 μ, with a thickness of about one-quarter of the length. Clinozoisite formed towards the end of the period of epidote deposition, and has about 11 % pistacite (the epidote has about 27 %). Epidote crystals at the rim of a vesicle are more strongly coloured than those formed later, though the birefringence is similar. Twinning and zoning are not seen. The plagioclase phenocrysts have been partly replaced by epidote. Analyses or partial analyses of epidote, chlorite, plagioclase, and rock are given in Table I.

The *Eel Crags* sample contains vesicular patches 1–10 mm in diameter, in a very fine-grained groundmass composed of magnetite, mica, quartz, alkali feldspar, calcite, and chlorite. The vesicle linings show the sequence chlorite(β 1·622)–epidote–quartz–calcite, but deposition of epidote and small amounts of clinozoisite continued to a late stage.

When clinozoisite has crystallized with calcite, it shows preferred orientation parallel to the long diagonal of calcite cleavage rhombs. Epidote is present as short, thick crystals 10–100 μ long, contrasting with the acicular habit of the clinozoisite, which ranges from 100 to 500 μ in length. Early epidote is again characterized by strong colouring and marked pleochroism; late epidote is almost colourless, with no noticeable

TABLE I.

	1	2	3	4	5	6	7	8	9
SiO_2	—	37·71	—	—	—	56·90	—	—	—
TiO_2	0·97	0·16	0·27	0·24	—	1·10	1·27	0·63	—
Al_2O_3	—	23·59	—	—	—	17·95	—	—	—
Fe_2O_3	2·19	13·14	3·19	1·48	1·52	1·60	0·77	3·40	3·26
FeO	4·78	nil	0·89	21·18	—	5·26	1·30	6·97	7·22
MnO	0·20	0·25	—	0·83	—	0·15	—	—	—
MgO	2·09	nil	0·72	12·25	—	3·33	0·49	5·80	3·38
CaO	7·91	22·61	13·13	0·83	0·98	7·48	2·01	8·19	5·86
Na_2O	2·45	0·17	4·81	0·50	4·41	3·25	5·73	1·62	0·21
K_2O	2·12	0·23	2·12	0·58	8·40	1·31	6·75	3·58	3·25
H_2O	—	1·95	—	—	—	1·46	—	—	—
P_2O_5	0·24	0·23	0·03	nil	—	0·28	—	—	—

1. Epidotized plagioclase-andesite, Grey Knotts; 2, epidote from same rock: 3 and 4, plagioclase phenocrysts and chlorite from 1.

5. Feldspar mixture from epidote-tuff (metasomatic type) Grey Knotts.

6. 77006, Oliver, 1961, p. 392.

7 and 8. Reaction zone and mafic segregations from 'Shap-type' vein, Longthwaite Group.

9. 'Nodular' or 'isochemical' type of epidote-tuff, Longthwaite Group.

pleochroism. The birefringence of crystals showing this gradation from light to dark along their length was studied and was found to be constant throughout. Colour and pleochroism in these epidotes is not, therefore, linked with pistacite content, but with the temperature of formation, the pistacite content having remained constant during growth of the epidote crystals. Twinning and zoning are absent. Clinozoisite and epidote have formed together during the later stages of formation of the vesicle fillings, there is no evidence for gradation of properties between the minerals, or of replacement of one by the other. The birefringence of the epidote is 0·039, that of the clinozoisite 0·014.

Slight development of reaction zones has taken place around some vesicles, and this is considered an autometasomatic effect, resulting from a concentration gradient established between the unstable assemblage plagioclase–pyroxene in the groundmass and the stable assemblage epidote–chlorite in the vesicle, which resulted in migration of Fe^{3+}, Fe^{2+}, Mg^{2+}, Ca^{2+}, Al^{3+}, Si^{4+}, into the vesicle.

Non-vesicular epidote lavas. Epidote is normally present as aggregates of crystals of grain size 3–20 μ, associated with large epidote crystals, up to 50 μ long, and very few clinozoisite needles up to 150 μ in length. The groundmass consists of calcite, quartz, alkali feldspar, chlorite, and mica: the epidote is not zoned or twinned, is nearly colourless, and shows no pleochroism. The epidote aggregates appear to have grown by replacement of the groundmass, and contain much foreign matter, except in the central regions of the larger nodules. Plagioclase phenocrysts have often suffered some replacement by epidote, though epidote seldom exceeds 10 % of the volume of such crystals, the remainder being a mica–quartz–calcite–chlorite mixture. These rocks resemble the 'isochemical' or nodular epidote tuffs, and differ only in being lavas.

PRESSURE AND TEMPERATURE CONDITIONS

The *quartz–epidote* veins of Fleetwith Pike and the Longthwaite Group are definitely related to the graphite mineralization, which is considered to be of pre-Bala age. The veins of Fisher Crag and Cat Gill are tentatively correlated with the effects of the Armboth Dyke and the Threlkeld microgranite respectively. These intrusions are also thought to be of pre-Bala age. If of this age the load pressure was approximately 1000 kg/cm², and if a Caledonian age were to be assumed the corresponding load pressure would be about 2000 kg/cm². Alteration of the wall rocks of these veins is of the low temperature type, and calcite, hematite, low-iron chlorite, and quartz are the principal minerals; galena is recorded by Davidson (1948) from the Cat Gill vein. Albitization of plagioclase has not taken place, probably indicating temperatures below 250–260° C (Coombs *et al.*, 1958; Eskola *et al.*, 1935), whilst the temperature of the country rock in Bala times is estimated at 130° C at the level of the veins.[1] The temperature of formation of the quartz–epidote veins is therefore placed in the range 130–260° C, at 1000 kg/cm² load pressure. All 'Shap type' veins are closely associated with the graphite vein, which implies an upper temperature limit of formation[2] of 539–631° C, but since the epidote veins of the present area are somewhat removed from the locus of graphite mineralization, Firman's (1957b) upper limit of 550–600° C for the veins at Shap also seems reasonable in the present case.

The prevalence of albitization again suggests a lower limit of about 250° C. The Shap-type veins probably formed in the range 250–550° C.

[1] R. G. J. Strens, thesis, Nottingham University.
[2] From FeS–ZnS temperature determinations.

at 1000 kg/cm² load pressure; slightly lower or higher temperatures are possible.

Autometasomatic epidotes of the nodular tuffs, and of the vesicular and non-vesicular epidote-lavas are thought to have formed in the volcanic pile at pressures ranging from a few atmospheres upwards. If we assume that reactions would have been completed by the time the rock had been buried to a depth of one kilometre, the upper limit of load pressure would be 280 kg/cm². Temperatures of formation are thought to have been from 250–550° C, from a consideration of the reactions involved.

Metasomatized epidote-tuffs show extensive development of alkali-feldspar, and probably formed most easily at 260–330° C (Eskola *et al.*, 1935). The pressures involved would again be in the range 0–280 kg/cm².

CLINOZOISITE–EPIDOTE RELATIONSHIPS

Clinozoisite and epidote have been found together in Shap-type veins, in epidote lavas, and in a few epidote tuffs. Inspection of contacts between epidote and clinozoisite crystals shows them to be boundaries between chemically and physically distinct crystals, with no evidence whatsoever for replacement or gradation of properties. Clinozoisite has apparently nucleated on epidote, with the b-axes of the two substances parallel. From petrographic evidence, and particularly from study of the vesicular lavas, there would seem to be no doubt that the crystallization periods overlapped, and that the two phases crystallized in equilibrium. If this deduction is correct, a miscibility gap must exist in the region $Cz_{76}Ps_{24}$ to $Cz_{87}Ps_{13}$ (Cz = clinozoisite, Ps = pistacite), under the conditions of epidote formation in the present area (Strens, 1963).

Clinozoisite crystals were three to twenty times the length of the associated epidote crystals and optically positive (epidote optically negative). Other distinguishing features were the absence of pleochroism or visible colouring (epidote slightly to strongly pleochroic, pale to dark yellow-green), low birefringence, and the occasional presence of twinning (epidote in these rocks never twinned). Optical properties determined on coexisting epidote and clinozoisite and the compositions deduced therefrom were:

	B	% Ps	β	% Ps
Clinozoisite	0·012–0·015	11–13	1·717	10·4
Epidote	0·035–0·042	24·4–28·6	1·746	25·8

Epidote alone occurs in the low temperature quartz–epidote veins, and in the metasomatic epidote tuffs. Clinozoisite alone occurs only in

the graphite vein and to some extent in the wall rocks. Clinozoisite is found together with epidote in the Shap-type veins, the epidote-lavas, and the 'isochemical' epidote tuffs. There is thus no obvious correlation with temperature or pressure, except for pure epidote assemblages (low temperature).

The formation of clinozoisite, rather than epidote, in the wall rocks of the graphite vein has been attributed[1] to the low activity of ferric iron under the reducing conditions of graphite deposition. Three following generalizations may be made: Epidote formed alone only in the high P_{O_2} environment of the epidote–quartz veins and in the 'metasomatic' epidote-tuffs, in which hematite is the only iron oxide mineral. Clinozoisite formed alone in the unusually low P_{O_2} environment of the graphite vein, in which magnetite is the iron oxide mineral. Mixtures of epidote and clinozoisite formed in lavas and tuffs not subjected to metasomatic action in which P_{O_2} was such that magnetite or mixtures of magnetite and hematite were stable. The Shap-type veins commonly contain both hematite and magnetite.

Optical properties of epidote group minerals

Refractive indices were determined by conventional immersion methods, in sodium light. When the α and γ indices are of poor accuracy only the easily measured β index is given. Birefringences (B) were determined by means of the Berek compensator on sections containing quartz; the results are thought to be accurate ± 0.003. The density of the Seathwaite alkaline clinozoisite was determined by the method of Straumanis (1953).

Comparison of compositions derived from the optical properties (β and γ indices and B) of analysed epidotes with those derived from the analyses shows good agreement. Reliance may therefore be placed on the optically determined compositions of epidotes not analysed, the β and γ indices and reliable values of B being utilized. 'Reliable' values of B are those determined on sections containing quartz. Optically derived compositions are presented in Tables II and III.

Firman (1957b) and Oliver (1961) give some optical data for other Lake District epidotes, from the Shap and Scafell areas respectively. Firman (personal communication) kindly made available a large number of measurements of birefringence from the aureole of the Eskdale Granite.

Firman (1957b) records epidotes with 16·8 to 28·0 % pistacite from Shap, based on determinations of birefringence (B 0·022–0·041). He also determined the α and γ indices of three epidotes, which have 17·6, 25·6, and 30·0 % pistacite respectively: the range of epidote compositions found at Shap is thus greater than that found in the whole of the present area.

[1] R. G. J. Strens, thesis, Nottingham University.

TABLE II. Optically derived compositions.

Type	No.	B	Pistacite %
Shap	2	0·040	27·6
Vesicular lava	6	0·038–0·042	26·2–28·6
Non-vesicular	4	0·036–0·040	25·0–27·6
Nodular tuff	4	0·038–0·040	26·2–27·6
Metasomatic tuff	6	0·035–0·041	24·4–28·0
Quartz–epidote	1	0·040	27·6

TABLE III. Optical properties of epidotes and clinozoisites.

No.	Nat. Grid Ref.	% Ps	α	β	γ	B	Length (μ)
			Analysed epidotes				
1	206142	27·0	1·724	1·747	1·765	0·041	10000
2	279208	26·8	1·724	1·748	1·763	0·039	1000
3	299164	26·3	1·723	1·746	1·764	0·041	20–40
4	236143	29·3	1·729	1·753	1·772	0·043	3–25
5	211123	27·0	1·725	1·748	1·766	0·041	50–200
6	251164	27·2	—	1·749	—	—	12
7	269136	27·7	1·727	1·751	1·768	0·041	15
8	229132	26·4	—	1·746	—	0·041	6
9	229141	22·0	—	1·740	—	0·031	120–400
10	229133	21·6	—	1·740	—	0·028	12
11	243143	25·9	—	1·747	—	0·038	25
			Epidotes not analysed†				
12	234162	25·8	—	1·746	—	—	10–100
13	219127	25·8	1·723	1·746	1·761	0·038	50
14	279208	27·0	—	1·748	—	—	100–1000
15	220127	26·5	—	1·747	—	—	20
16	247145	28·4	—	1·751	—	—	250
17	‡	17·6	1·716	—	1·740	0·024	—
18	‡	25·6	1·724	—	1·761	0·037	—
19	‡	30·0	1·732	—	1·773	0·041	—
			Clinozoisites not analysed†				
20	269136	—	1·695	—	—	—	200
21	229141	—	1·704	—	—	—	200
22	229133	10·0§	1·705	—	—	0·010	150
23	229132	10·0	1·706	—	1·716	0·010	1000
24	234162	11·5‖	—	1·711	—	0·013	50–150
25	219127	11·8	—	1·715	—	0·014	400
26	219127	10·4	—	1·717	—	0·015	300
			Analysed clinozoisites*				
27	¶	10·3*	—	1·690	—	0·009	2
28	¶	11·1	1·705	1·712	1·717	0·012	5000
29	**	1·8	—	1·694	—	—	—

Clinozoisite samples 20–26 are from the same rocks as epidote samples 7, 9, 10, 8, 12, 13, 13 respectively. * Nos. as in Table IV; composition (% Ps) from analysis; † Composition a weighted mean of values from the optical data; ‡ Firman's (1957b) data for Shap epidotes; § from B; ‖ from β; ¶ samples taken underground; ** Japanese alkaline clinozoisite.

Oliver (1961) gives the birefringence of epidotes in the Scafell area as 0·020–0·028, i.e. 15·6 to 20·3 % pistacite. This is outside the range found in the present work, although the two areas overlap on Grey Knotts.

Firman (personal communication) has recorded birefringences of 0·023 to 0·042 from Eskdale rocks, with a few higher and lower values of doubtful accuracy. This implies the existence of epidotes with 17·4 to 28·6 % pistacite in Eskdale, a range almost identical with that found at Shap.

Infra-red absorption spectra

Seven epidotes and one clinozoisite were examined using the KBr disk technique (0·35 mg epidote to 140 mg KBr), over the wavelength range 4000 to 650 cm^{-1} (2·5 to 15 μ). Peaks were found at 3340, 1102, 1068, 1025, 947, and 885 cm^{-1}, and those in the range 1102–885 cm^{-1} appeared to show a slight shift with iron content. The magnitude of this shift could not be determined at the resolution of $1\,\mu = 2$ cm employed. The spectra obtained are shown in fig. 1, and it will be seen that they are identical in all but the finest detail. The presence of quartz as an impurity in some samples is readily detected by means of the quartz doublet.

Analyses of epidote minerals

Partial analyses (Table IV) were made of twelve epidotes and of two clinozoisites by the methods of Brannock and Shapiro (1956) except for FeO, which was determined by Wilson's (1955) metavanadate method.

Inspection of published analyses that included determinations of SiO_2, Al_2O_3, and H_2O showed that the ideal epidote formula $M^{2+}{}_2M^{3+}{}_3Si_3O_{13}H$ was very closely approached in most cases, and that the error introduced by assuming this formula was within the error of determination of these constituents. In recalculating the partial analyses, the assumption was made that $(Ca+Mg+Fe''+Mn''+Na+K) = 2·000$; $(Fe'''+Al) = 3·000$; $(Si+Ti+P) = 3·000$; $O = 13·000$, $H = 1·000$.

The range of epidote compositions is small, from 21·6 to 29·3 % pistacite; this is in agreement with the results of the optical studies reported above. The well-crystallized (0·1–25 mm) epidotes of the epidote–quartz veins have rather uniform and generally low contents of FeO, MnO, TiO_2, P_2O_5, Na_2O, and K_2O; the amounts of MnO, TiO_2, P_2O_5, and K_2O show little variation from group to group, but FeO and Na_2O are unexpectedly high in some fine grained epidotes from lavas, tuffs, and Shap-type veins.

No evidence has been obtained for differences in Fe^{3+}–Al^{3+} substitu-

tion in epidotes of different grain size. The highest Na_2O content is in an epidote of small grain size, but the Na_2O contents of other epidotes bear no obvious relation to grain size.

A negative correlation was found to exist between FeO content and
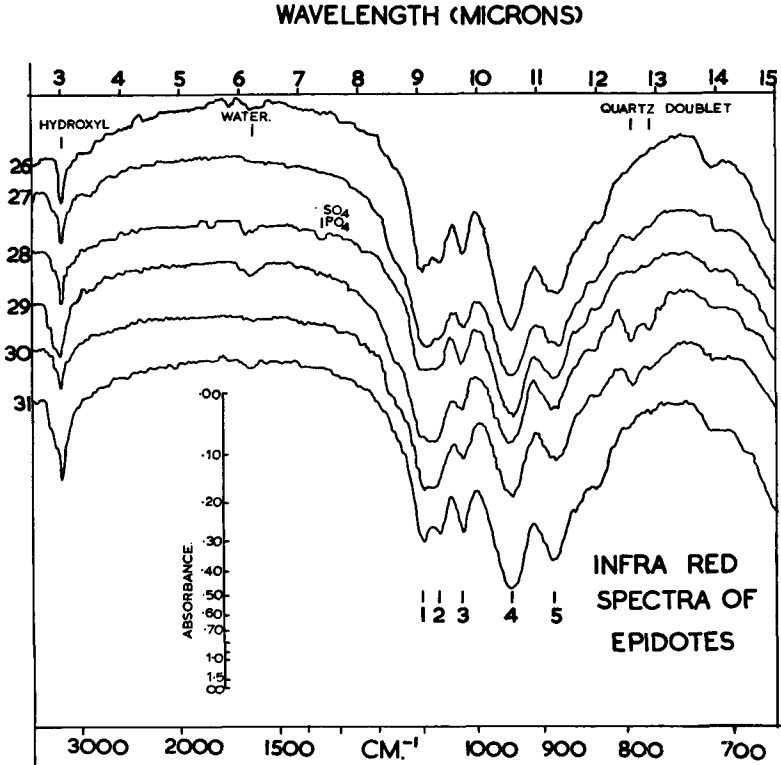
WAVELENGTH (MICRONS)

FIG. 1. Infra-red absorption spectra of epidotes, with characteristic peaks indicated. The numbers 1–5 correspond to the 1102, 1068, 1025, 947, and 885 cm^{-1} peaks. To use the absorbance scale, take the absorbance at 4000 cm^{-1} as 0·10. The numbers 26–31 correspond to analyses 2, 5, 7, 9, 13, and 11 in Table 4.

grain size, FeO ranging up to 2·97 % in one sample. The graph of log (average length of crystal) against log % FeO was a straight line (fig. 2).

Analyses of clinozoisite

Fine grained flaky clinozoisite from the Seathwaite graphite vein contained 2·75 % K_2O and 1·33 % Na_2O, and the low β index suggests that the mineral may be hydrated. Infra-red absorption spectra were obtained for the well-crystallized material (Na_2O 0·12 %, K_2O 1·28 %),

TABLE IV. Partial chemical analyses (by R. G. J. Strens) of epidotes and clinozoisites. The SiO_2, Al_2O_3, and H_2O figures are calculated values from the formula $M_2^{2+} M_3^{3+} Si_3 O_{13} OH$. For optical data see Table III.

	1.	2.	3.	4.	5.	6.	6a.	7.	8.	9.	10.	11.	12.	13.
[SiO$_2$]	37·42	37·23	37·56	37·43	37·71	37·20	37·73	37·43	37·60	36·79	37·67	37·79]	—	—
TiO$_2$	0·22	0·24	0·36	0·20	0·16	0·26	n.d.	0·32	0·48	0·30	0·13	0·35	0·18	0·22
[Al$_2$O$_3$]	23·41	23·32	23·61	22·63	23·59	23·12	23·76	23·10	23·84	25·85	25·18	23·68]	—	—
Fe$_2$O$_3$	13·53	13·60	13·20	14·71	13·14	13·57	12·95	13·88	13·28	11·13	10·84	12·96	5·34	5·81
FeO	0·06	0·13	0·27	0·18	nil	2·44	3·97	nil	1·05	1·92	2·58	1·01	0·36	0·33
MnO	0·20	0·22	0·27	0·20	0·25	0·12	0·33	0·08	0·18	nil	0·25	—	0·25	0·21
MgO	nil	n.d.	0·12	nil	nil	nil	0·82	nil	nil	nil	nil	nil	nil	nil
CaO	22·56	23·22	22·09	21·70	22·61	20·82	17·85	22·97	19·60	21·78	20·99	21·33	18·53	21·97
Na$_2$O	0·30	0·10	0·30	0·45	0·17	0·14	0·52	nil	1·58	nil	nil	0·64	1·33	0·12
K$_2$O	0·20	nil	0·32	0·29	0·23	0·27	0·16	0·39	0·30	0·37	0·20	0·21	2·75	1·28
[H$_2$O]	1·88	1·87	1·88	1·88	1·95	1·81	1·89	1·88	1·90	1·92	1·94	1·88	1·96	1·97]
P$_2$O$_5$	0·22	0·47	0·02	0·08	0·23	n.d.	n.d.	n.d.	n.d.	n.d.	0·22	0·15	0·24	0·24
% Pist.	27·0	26·8	26·3	29·3	27·0	27·2	25·6	27·7	26·4	22·0	21·6	25·9	10·6	11·6

1. Epidote; quartz–epidote vein, Fleetwith Pike.
2. Epidote; quartz–epidote vein, Cat Gill.
3. Epidote; quartz–epidote vein, Fisher Crag.
4. Epidote; quartz–epidote vein, with subsidiary calcite and malachite, Seatoller Fell.
5. Epidote; porphyritic plagioclase–ortho-pyroxene andesite, Grey Knotts. Now altered to epidote–chlorite assemblage. Analysis corrected for 3% chlorite.
6. Epidote; fissure in basic andesite, Low Hows Wood.
6a. Epidote; fissure in basic andesite, Dale Head. Analysis corrected for 4·23 % quartz. β 1·74 ± 0·005; average crystal length 5 μ.
7. Epidote; aggregates in plagioclase-andesite, near Stonethwaite.

8. Epidote; 'metasomatic' type of epidote–albite–orthoclase–chlorite tuff, Hause Gill.
9. Epidote; nodular 'isochemical' type of epidote–chlorite tuff, Seatoller Fell. Rock analysis no. 9, Table 1.
10. Epidote; 'Shap type' vein, Steel Fell.
11. Epidote; 'Shap type' vein, Seatoller Fell.
12. Alkaline clinozoisite; very fine grained flaky variety, associated with calcite, Seathwaite graphite vein.
13. Alkaline clinozoisite; well-crystallized variety, associated with calcite.

and gave a normal epidote pattern (fig. 1), and as the X-ray powder photograph is that of a clinozoisite there is no doubt as to the identity of the mineral.
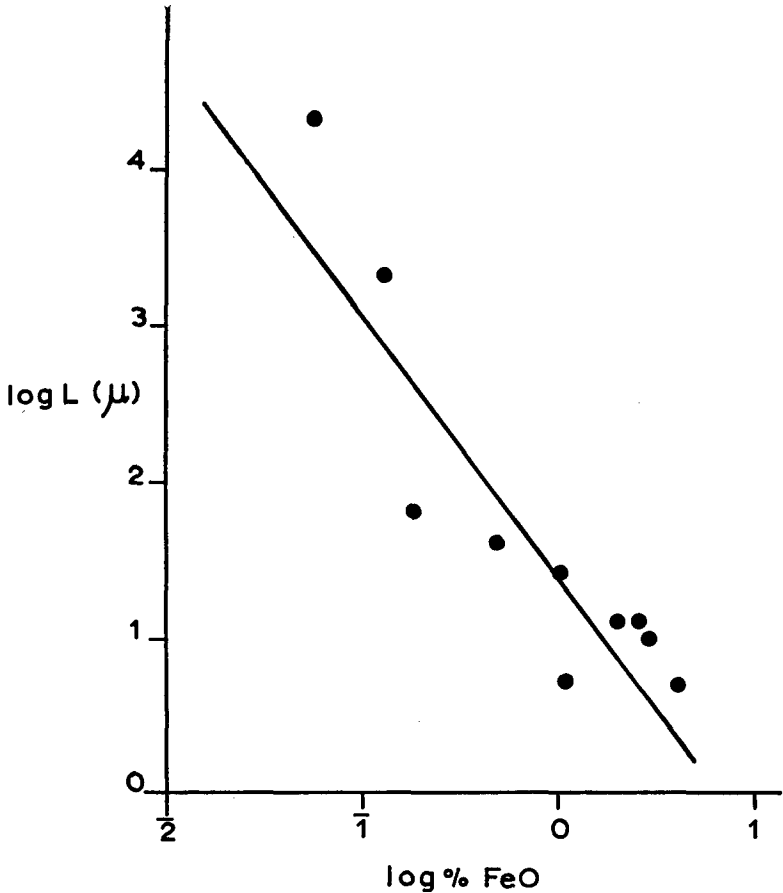

FIG. 2. Plot of $\log_{10}$ average length of crystal (L) against $\log_{10}$ % FeO: the line shown is that fitted by least squares, but the true line is probably slightly concave towards high values of L and FeO, since very large epidote crystals would still contain 0.10–0.50 % FeO.

These data indicate that a considerable amount of $(K,Na)^+$ for Ca^{2+} substitution can take place in clinozoisites. The atomic radii are: Na^+ 0.98 Å, K^+ 1.33 Å, Ca^{2+} 1.06 Å (Goldschmidt, 1954). Half the Ca atoms in epidote minerals lie in the a–b plane parallel with the cleavage;

examination of Ito's (1954) structure suggests that the cleavage will run through his Al_2 positions and that replacement of the Ca_2 and Ca_2' atoms would be relatively easy. Some expansion of the c-axis would be expected with increasing substitution of K^+ for Ca^{2+}, though this tendency might be counteracted by the compensating Si for Al substitution.

Sakurai and Nagashima (1956) give an analysis of a clinozoisite from Arai, Saitama Prefecture, that contains Na_2O 1·14 %, K_2O 1·19 %, and MgO 1·71 %, and the authors thought it necessary to recalculate the K_2O, Na_2O, and MgO to mica, albite, and hornblende respectively. So far as can be ascertained, these minerals are not actually observed to be present in the analysed samples in amounts sufficient to warrant this procedure. The original analysis has therefore been recalculated on the anhydrous basis of $O^{2-} = 25\cdot000$ to give: $(Ca,Mg,Mn,Na,K)_{4\cdot03}$ $(Al,Fe)_{5\cdot47}(Si,Ti)_{6\cdot52}O_{25}$. There is a deficiency of 0·53 atoms in the (Al,Fe) group, and an excess of 0·52 (Si,Ti) atoms. There is a deficiency of $0\cdot55^+$ charges in the (Ca,Mg,Mn,Na,K) group attributable to $(Na,K)^+$ for Ca^{2+} substitution, which would be balanced, within the analytical error, by the transfer of 0·52 $(Si,Ti)^{4+}$ atoms to the $(Al,Fe)^{3+}$ sites. The formula then becomes: $(Ca,Mg,Mn,K)_{4\cdot03}(Al,Fe,Si)_{5\cdot99}(Si,Ti)_{6\cdot00}O_{25}$, in good agreement with the ideal epidote formula $Ca_4(Al,Fe)_6Si_6O_{25}.H_2O$, and a reasonable balance of charges is achieved.

The analysis, and general considerations of crystal chemistry, indicate that paired $(Na,K)^+$ for Ca^{2+} and Si^{4+} for Al^{3+} substitutions probably take place in the alkaline clinozoisites, and this relationship has been assumed to hold in recalculation of analyses of the Seathwaite minerals.

The formation of clinozoisite, rather than epidote, in the Seathwaite vein has been attributed to low Fe^{3+} activity, due to the reducing conditions of graphite deposition.

The density of clear crystals of the clinozoisite was $3\cdot2109\pm0\cdot001$ g/cm³.

FORMATION AND REACTIONS OF EPIDOTE

Two processes account for the majority of epidote-containing rocks in the area: one is the autometasomatic alteration of lavas and tuffs, the other is alkali metasomatism. Numerous reactions of minor importance also occurred, through which epidote partially replaced orthopyroxene, clinopyroxene, ortho-amphibole, clino-amphibole, and plagioclase phenocrysts.
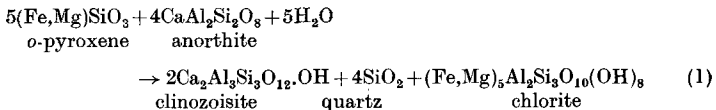
Autometasomatism

Autometasomatic alteration of a lava is well shown by the coarsely porphyritic plagioclase-andesites of Grey Knotts, which have been

converted into epidote–chlorite–magnetite–quartz–mica–calcite–albite
assemblages; the mode of one such rock, derived from a count of 2726
points on three slides, is: Plagioclase phenocrysts 37·8 % by volume,
fine-grained groundmass 47·2, epidote 7·84, and chlorite 6·86.

Some of the epidote is present as inclusions in the altered phenocrysts,
but most is in vesicular patches or scattered through the groundmass.
Chlorite occurs both in vesicular patches and throughout the ground-
mass. The norm, calculated from a partial analysis of the rock (Table I,
no. 1) combined with the modal analysis above, and taking the sp. gr. of
the rock as 2·85, is: chlorite with β 1·621 and D 2·92, 7·07 % by weight;
epidote ($Cz_{73}Ps_{27}$, D 3·43) 9·20; anorthite 37·90 and albite 20·70, together
making a plagioclase of composition $Ab_{63}An_{37}$; orthoclase 12·60; mag-
netite 3·77; calcite 0·51; others (mainly quartz) 8·25. In fact, much
of the normative orthoclase represents modal mica, which cannot easily
be estimated. Some of the normative anorthite is present as small
epidote crystals included in the plagioclase phenocrysts, and the plagio-
clase that remains unaltered is not identifiable in thin section. Com-
parison with less altered rocks suggests that it is probably nearer An_{55}
than the figure of An_{63} given above, due to the epidote inclusions
already mentioned.

If some such reaction as:

$$5(Fe,Mg)SiO_3 + 4CaAl_2Si_2O_8 + 5H_2O$$
$$\text{o-pyroxene} \qquad \text{anorthite}$$

$$\rightarrow 2Ca_2Al_3Si_3O_{12}.OH + 4SiO_2 + (Fe,Mg)_5Al_2Si_3O_{10}(OH)_8 \qquad (1)$$
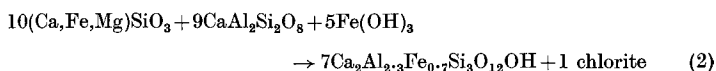$$\text{clinozoisite} \qquad \text{quartz} \qquad \text{chlorite}$$

is considered, then the relative volumes and weights of epidote, chlorite,
and quartz must obviously conform to the requirements of this equation.
Since quartz cannot be estimated, the only guide is that chlorite forms
46·6 % by volume and epidote 53·4 % of the total of chlorite plus
epidote, whilst this reaction yields the theoretical proportions chlorite
44 %, epidote 56 %. The difference is within the error of the modal
analysis, and of the assumptions made as to composition of the various
solid phases.

With the possible exception of some calcium from the plagioclase
phenocrysts, most of the components of the chlorite and epidote must
have come from the groundmass, which formed over 60 % of the volume
of the unaltered rock. It seems reasonable to suppose that this ground-
mass originally contained orthopyroxene, clinopyroxene, plagioclase
laths, and some magnetite; these are the phases that crystallized from

other Borrowdale lavas of the same bulk composition. The presence of about 8 % of orthopyroxene in the groundmass (or 5·3 % in the rock as a whole) would suffice for the production of the amounts of chlorite and epidote actually observed.

A possible epidote-producing reaction involving clinopyroxene is:

$$10(Ca,Fe,Mg)SiO_3 + 9CaAl_2Si_2O_8 + 5Fe(OH)_3$$
$$\rightarrow 7Ca_2Al_{2\cdot3}Fe_{0\cdot7}Si_3O_{12}OH + 1 \text{ chlorite} \qquad (2)$$

The epidote:chlorite ratio produced by such a reaction would be 5:1 by volume. The Ca:Fe:Mg ratio of the pyroxene was taken as 5:2:3, and the Fe:Mg ratio of the chlorite as 2:3; these ratios are close to those actually observed in the Borrowdale rocks.

The first reaction, involving ortho-pyroxene and the anorthite component of the groundmass plagioclase is thought to have been the principal epidote-producing reaction in lavas such as those described above; the second reaction was probably a subsidiary source of epidote and chlorite.
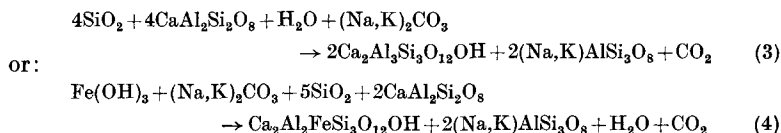
Reactions of volcanic glass, or of fine-grained rocks, such as many of the tuffs, and some of the aphanitic lavas, cannot easily be dealt with in terms of mineral reactions. Accordingly, the result of the bulk alteration of a rock, possibly involving a large number of interlinked reactions, has been studied. The composition chosen was based on the observation by Oliver (1961) that volcanic glass ($n_D = 1·53$) existed in rocks of the Airy's Bridge group. The approximate composition of this glass was obtained from the work of George (1924), and the inter-element ratios were revised to fit those of the Borrowdale rocks, using Oliver's variation diagrams. The final composition, SiO_2 58·10 wt. %, TiO_2 0·97, Al_2O_3 19·15, Fe_2O_3 4·65, FeO 3·10, MgO 2·42, CaO 4·84, Na_2O 1·94, K_2O 3·39, H_2O 1·45, with D 2·55, could recrystallize to: epidote 23·81 vol. %, chlorite 12·56, albite 17·50, orthoclase 21·97, quartz 24·16, with D 2·83.

In fact, mica occurs in most epidote-tuffs, and some modification of the orthoclase figure would be required. Apart from this reservation, the percentages calculated above would fit rocks such as the Longthwaite nodular epidote tuffs.

Alkali metasomatism

The observed effects of the alkali metasomatism are the breakdown of the original mineral assemblage of the rock, and the formation of
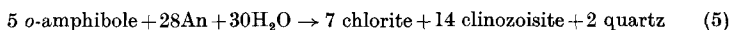
epidote, chlorite, hematite, calcite, and alkali feldspars. The most important reaction from the point of view of the formation of epidote is:

$$4SiO_2 + 4CaAl_2Si_2O_8 + H_2O + (Na,K)_2CO_3$$
$$\rightarrow 2Ca_2Al_3Si_3O_{12}OH + 2(Na,K)AlSi_3O_8 + CO_2 \qquad (3)$$

or:

$$Fe(OH)_3 + (Na,K)_2CO_3 + 5SiO_2 + 2CaAl_2Si_2O_8$$
$$\rightarrow Ca_2Al_2FeSi_3O_{12}OH + 2(Na,K)AlSi_3O_8 + H_2O + CO_2 \qquad (4)$$

Considerable amounts of SiO_2 and alkalis must have been introduced, and FeO, MgO, and CaO were removed. Chlorite and calcite formed through subsidiary reactions involving the pyroxene and plagioclase of the rocks.

Special reactions

Partial replacement of ortho- and clino-pyroxenes by epidote is common; reactions similar to (1) and (2) above were responsible. The replacement of ortho- and clino-amphiboles by epidote presumably took place through reactions such as:

$$5 \text{ o-amphibole} + 28An + 30H_2O \rightarrow 7 \text{ chlorite} + 14 \text{ clinozoisite} + 2 \text{ quartz} \qquad (5)$$

$$1 \text{ hornblende} + 6An + 5H_2O \rightleftharpoons 1 \text{ chlorite} + 4 \text{ clinozoisite} + \text{quartz} \qquad (6)$$

In this and other cases, where reactions have been written to include clinozoisite rather than epidote, it is to be understood that epidote can develop through the oxidation of some of the ferrous iron of the reactants, by reaction with magnetite, or through the introduction of ferric iron. The subsidiary reactions involved are likely to be relatively unimportant, and it would add greatly to the complexity of this work to attempt to account for the presence of iron in the epidotes. Where solutions are known to have been present, ferric iron has been assumed to be available as $Fe(OH)_3$.

Reaction of plagioclase to form epidote may be effected by addition of calcium, ferric iron, and water. Reactions (1) to (6) all involve the anorthite component of plagioclase, and could cause partial replacement of phenocrysts by epidote.

Epidote formed through calcium-iron metasomatism of plagioclase crystals in some of the 'metasomatized' epidote tuffs, though much of the calcium originated through the albitization of plagioclase:

$$2CaAl_2Si_2O_8 + 2Na_2SiO_3 + 6SiO_2 + 2H_2O \rightleftharpoons 2Ca(OH)_2 + 4NaAlSi_3O_8$$
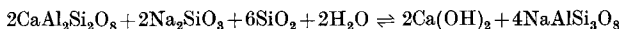
Composition and formation of reaction zones

Firman (1957b) found that the formation of the 'reaction zones' at Shap involved the addition of silica, and the loss of all other constituents

including alkalis. An analysis (Table I, no. 7) of a reaction zone from the present area, with which is associated epidote, chlorite, and amphibole, shows a high alkali content. The 'standard cells' of unaltered rock and reaction zones from Shap and from the present area are given in Table V: it will be seen that silica and alkalis were added to the reaction zone, and all other constituents were lost. No analysis

TABLE V. Chemical changes in the formation of reaction zones, exhibited as 'standard cells' (atomic ratios to 160 (O,OH)) for two pairs of rocks.

	K	Na	Ca	Mg	Fe²⁺	Fe³⁺	Al	Ti	Si	P	O	OH
R.F. 153	5·0	6·1	3·8	2·9	6·0		23·7	0·9	48·4	1·2	152·6	7·4
R.F. 66	1·9	4·0	2·0	0·5	1·8		8·3	0·6	67·8	0·9	155·7	4·3
gained	—	—	—	—	—	—	—	—	15·4	—	3·1	—
lost	3·1	2·1	1·8	2·4	4·2		15·4	0·3	—	0·3	—	3·1
77006	1·5	5·7	7·3	4·6	4·1	1·1	19·4	0·8	51·6	—	160	
L.G. 1	7·8	9·6	1·9	0·7	1·0	0·5	17·5	0·8	58·4	—	160	
gained	6·3	3·9	—	—	—	—	—	—	6·8	—	—	—
lost	—	—	5·4	3·9	3·1	0·6	1·9	—	—	—	—	—

R.F. 173 is unaltered andesite from Shap, and R.F. 66 a reaction zone from the same locality (Firman, 1957b). 77006 is a porphyritic hornblende andesite, from Oliver (1961, table III, p. 392). L.G. 1 is calculated from analysis 7, table I (this paper).

was available of the unaltered rock, so that a similar rock (Oliver's no. 77006 in his 1961 paper) was used in the calculations; the silica, alumina, and water contents of the reaction zone were calculated from the partial analysis, and a knowledge of the minerals present. The changes in composition are so great that such methods are justified.

So far as can be seen, the reaction zones are composed of quartz, albite, and orthoclase; small amounts of hematite give the rock its pink colour.

The temperature range of formation of the 'Shap type' veins, and of the associated reaction zones, was considered earlier in this paper, and it was concluded that most of these veins formed in the range 250–550° C. As all these veins, including the analysed example quoted above, are associated with the graphite mineralization, the load pressure is placed at about 1000 kg/cm².

Eskola's experiments (1935) suggest that albitization of plagioclase feldspars takes place most easily between 260 and 330° C; pure silification, as at Shap, may develop at temperatures outside this range, whilst extreme enrichment in alkalis, as in the present case, takes place near 300° C.

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