

On the nature of withamite from Glen Coe, Scotland.

(With Plate IV.)

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IN 1824 Henry Witham discovered a beautiful red epidote mineral in the lavas of Glen Coe, Argyllshire, which was described by Brewster¹ under the name withamite. An analysis was made by Coverdale² of obviously highly impure material, but later a more complete one was carried out by Heddle³ on carefully hand-picked mineral. Heddle⁴ admits, however, that his analysis shows 'by no means a satisfactory agreement with the composition of epidote', and from his figures it would seem very likely that his analysed material was also impure. In the Glen Coe Geological Survey Memoir⁵ no further data were recorded of this mineral, Heddle's analysis and description merely being quoted.

The writer visited Glen Coe and collected material in a cutting on the new road, approximately $5\frac{1}{2}$ miles west of King's House (Geological Survey, sheet 53), where it is fairly well exposed. It occurs in a fine-grained, rather altered andesitic rock, as narrow veinlets up to 120 mm. in length and 50 mm. in width; also as infillings of vesicles. The veinlets may be straight or highly irregular; in the former case they possibly follow joint-planes, for the rock will often fracture along such a plane, producing one or two surfaces covered with the red epidote mineral. The vesicles vary greatly in size from approximately 0.3 to 70 mm., and in the larger ones calcite is a common associate. Whether in vein or

¹ D. Brewster, Description of withamite, a new mineral species found in Glenco. Edinburgh Journ. Sci., 1825, vol. 2, pp. 218-221.

² T. Thomson, Outlines of mineralogy, geology and mineral analysis. London, 1836, vol. 1, p. 377.

³ M. F. Heddle, Minerals new to Britain. Min. Mag., 1882, vol. 5, pp. 1-25 (withamite, p. 15).

⁴ M. F. Heddle, Chapters on the mineralogy of Scotland. Trans. Roy. Soc. Edinburgh, 1899, vol. 39, p. 355.

⁵ E. B. Bailey and H. B. Maufe, The geology of Ben Nevis and Glen Coe. Mem. Geol. Surv. Scotland, (sheet 53), 1916, p. 179.

vesicle, this epidote mineral always appears to be separated from the surrounding rock by a thin layer of milky-white epidote. Some of the vesicles may also be filled with a deep-green epidote. Rarely it occurs in a fine-grained reddish-brown andesitic rock which appears to be a phase of the main rock type, the colour being due to brownish-red oxides of iron.

In thin section the vesicles average about 1.0 mm. across. The epidote mineral which entirely fills the vesicles may be: (1) a single grain often with subidiomorphic to idiomorphic outline; or (2) much more frequently a mass of radiating fibres diverging from one or more centres. This radiate or spherulitic arrangement is often so well developed (pl. iv, fig. 5) that a perfect black cross may be seen between crossed nicols. In the reddish-brown rock, the vesicles may contain some xenomorphic quartz.

The chemical composition of the epidote mineral varies between wide limits in separate vesicles and even in the same vesicle. The variation is particularly well shown where radiating fibres are developed; in this case the centre or nucleus of the 'spherulite' is usually a dark red, while the outer extremities of the fibres are common, pale yellow, moderately ferruginous epidote. From the centre to the extremities there is a complete and gradual variation in the colour (pl. iv, fig. 5). Rarely in the larger amygdales, instead of a gradual change in colour, there may be a rather sharp zonary banding. In one beautiful example (pl. iv, fig. 3) of radiate arrangement from three centres, besides the usual gradual change in colour, there are three zonary bands, the widest 0.2 mm. in width, in which the epidote mineral appears to be filled with tiny inclusions. Such radiate arrangement with red centres grading off into colourless borders is not an unusual feature in piedmontite, similar occurrences having been noted by Lausen¹ from Pat Hills, Arizona, by Guild² from Tucson Mountains in the same state, and by Yamasaki³ from Shinano, Japan. Chemically, this colour variation is due to the gradual decrease in the Mn_2O_3 content outwards from the centre, the latter giving strong reactions for manganese, while the pale yellow or colourless epidote shows only a trace.

With the object of discovering the exact chemical composition of the

¹ C. Lausen, Piedmontite from the Sulphur Spring valley, Arizona. *Amer. Min.*, 1927, vol. 12, pp. 283-287. [*Min. Abstr.* 3-456.]

² F. N. Guild, Piedmontite in Arizona. *Amer. Min.*, 1935, vol. 20, pp. 679-692. [*M.A.* 6-380.]

³ N. Yamasaki, On the piedmontite-rhyolite from Shinano. *Neues Jahrbuch Min.*, 1898, vol. 2, pp. 253-254.

red epidote, the mineral was separated from a specimen in the museum of the Department of Mineralogy and Petrology, Cambridge. By careful manipulation, finally in Clerici solution, it was possible to free the concentrate from all the colourless epidote. The analysis of this is given under B in table I. Material collected on a visit to the locality made it possible to obtain a greater quantity of concentrate by ordinary separation methods. This concentrate was ground down to pass through a 300-mesh sieve and then centrifuged so that a more dense, i.e. more manganiferous concentrate than that analysed before was obtained (analysis C). It must be pointed out, however, that these two analyses, though of a perfectly pure epidote mineral, represent the concentrate which optically does show slight variation, especially B. Nevertheless they serve to show the nature of the red epidote mineral.

TABLE I. Analyses of withamite from Glen Coe.
(A by M. F. Heddle, 1882; B and C by C. O. Hutton.)

	A.	B.	C.
SiO ₂	43.230	38.75	37.57
Al ₂ O ₃	23.090	24.71	24.70
Fe ₂ O ₃	6.675	10.77	11.31
TiO ₂	—	0.41	0.24
FeO	1.131	n.d.*	n.d.*
MgO	0.884	0.43	0.09
Mn ₂ O ₃	0.138 (MnO)	0.83	0.96
CaO	20.003	21.86	23.32
SrO	—	0.31	0.09
Na ₂ O	0.935	0.26	nil
K ₂ O	0.962	0.11	nil
Li ₂ O	0.253	n.d.	n.d.
H ₂ O + 110° }	2.400	{ 1.93	1.83
H ₂ O - 110° }		{ 0.07	0.21
	99.701	100.44	100.32
Sp. gr.	—	3.38-3.40	3.39-3.40

* Owing to the presence of Mn₂O₃ in the mineral, FeO cannot be determined with any approach to accuracy.

Although the structure of epidote is not yet fully understood, the analyses B and C have been calculated in table II on the basis of 13 oxygen atoms to the unit cell and the results expressed by the structural formula suggested by Machatschki,¹ viz. X₂Y₃Z₃(O,OH,F)₁₃.

Machatschki states that manganese may come in to either the X or the Y groups or be spread between them by reason of the intermediate

¹ F. Machatschki, Die kristallochemischen Beziehungen zwischen Epidot-Zoisit und Orthit-Allanit. Centr. Min., Abt. A, 1930, pp. 89-96. [M.A. 4-357.]

TABLE II. Calculation of chemical formulae.

	B.	Metal atoms.		C.	Metal atoms		
SiO ₂	38.75	3.046	3.04z	37.57	2.979		} 3.00 z
Al ₂ O ₃	24.71	2.284	} 2.99 Y	24.70	2.304	{ 0.021 2.283	
Fe ₂ O ₃	10.77	0.623		11.31	0.675	} 3.00 Y	
TiO ₂	0.41	0.023		0.24	0.014		
MgO	0.43	0.052	0.09	—			
Mn ₂ O ₃	0.83	0.046	} 1.90 X	0.96	0.057	{ 0.028 0.029	} 2.01 X
CaO	21.86	1.842		23.32	1.984		
SrO	0.31	0.014	0.09	—			
Na ₂ O	0.26	—	nil	—			
K ₂ O	0.11	—	nil	—			
H ₂ O + 110° ...	1.93	1.010	1.01	1.83	0.951	0.95	
H ₂ O - 110° ...	0.07	—		0.21	—		
	100.44			100.32			

B gives the formula (OH) (Ca, Sr, Mn)_{1.9} (Al, Fe, Ti, Mg)_{2.9} Si₂ O₁₂.

C " " (OH) (Ca, Sr, Mn)₂ (Al, Fe, Ti, Mn)₃ (Si, Al)₃ O₁₂.

ionic radius of that cation. In B all the manganese is required in the X group, while in C it is divided between groups X and Y in the ratio 0.029:0.028. The aluminium cation does not enter the four-co-ordinated group z in B, but does so in C to the slight extent of 0.021. (OH) in C is very slightly short of the figure required by the above formula.

The determination of water was carried out according to the method of Penfield,¹ but with the use of a silica tube and the oxy-coal gas blow-pipe flame, for the heat of the Meker burner is not sufficient to drive off all the (OH) as Smethurst² found when analysing epidotes from the Malvern Hills. Even his fusion with sodium tungstate at 1000° C. failed to liberate the amount of water demanded by the structural formula. Although the present writer found that the Glen Coe mineral failed to yield its total water on fusion with Na₂WO₄, it readily did so before the blowpipe. Smethurst, however, does not appear to have employed the latter method of attack.

The optical characters of the material (analysis C) for sodium-light are:

α 1.733, β 1.750, γ 1.762,³ all ± 0.002 ; $\gamma - \alpha$ 0.029.

Elongation β , $\alpha:c = +2^\circ \pm 1^\circ$; $2V$ $78^\circ \pm 1^\circ$, negative.

α clear yellow, β pale amethyst, γ deep purplish-red; $\gamma > \alpha > \beta$.

¹ W. F. Hillebrand and G. E. F. Lundell, Applied inorganic analysis. New York, 1929.

² A. F. Smethurst, Anomalies in the analytical determination of water in epidote. Min. Mag., 1935, vol. 24, pp. 173-179.

A few grains gave a γ value as high as 1.767 ± 0.002 .

From the analyses and the optical data it would seem reasonable to consider the red mineral a poorly manganiferous piedmontite. The three refractive indices of the mineral are slightly higher than that of a common epidote having a Fe_2O_3 content of 11–12 %; these would be:

Epidote. ¹	Glen Coe mineral.
α 1.730	α 1.733
β 1.749	β 1.750
γ 1.760	γ 1.762

This increase is most probably due to the incoming of approximately 4–5 % of the $(\text{OH})\text{Ca}_2(\text{Al}, \text{Mn})_3\text{Si}_3\text{O}_{12}$ molecule. If it had been possible to obtain a concentrate of the most deeply coloured mineral, which unfortunately always occurs at the centre of the smaller amygdales, it is probable that the Mn_2O_3 content would have approached a figure in the neighbourhood of 2 %.

The characteristic feature of the pleochroic scheme of the Glen Coe mineral is the pale tint for the β vibration-direction, a feature in which it strongly resembles piedmontite from western Otago, New Zealand,² although the absorption of the latter mineral is much more intense. Lacroix,³ though he does not state the absorption, compares the pleochroism of the Glen Coe mineral with that of piedmontite from Saint Marcel in Piedmont and Jakobsberg in Sweden.

The association of piedmontite with lavas is frequently the case in American localities where the mineral has been observed in rhyolites,⁴ andesites,⁵ and felsites.⁶ For the source of the various components necessary for the formation of this poorly manganiferous piedmontite the writer does not believe that it is necessary to look beyond the lavas themselves, for the break-down of ferromagnesian minerals and feldspars would supply all the necessary oxides including manganese. This supposition does not necessarily assume that the ferromagnesian constituents were rich in manganese, for the piedmontite merely represents a concentration of the manganese which was probably derived from a large

¹ A. N. Winchell, *Elements of optical mineralogy*. New York, 1933, pt. 2, p. 313.

² F. J. Turner, Note on the occurrence of piedmontite in quartz-muscovite-schist from Shotover valley, western Otago, New Zealand. *Min. Mag.*, 1933, vol. 23, pp. 416–418.

³ A. Lacroix, *Propriétés optiques de la withamite*. *Bull. Soc. Franç. Min.*, 1886, vol. 9, pp. 75–77. *Matériaux pour la minéralogie de la France*. IV. *Épidote manganésifère (piédmontite) de l'île de Groix*. *Ibid.*, 1888, vol. 11, pp. 148–149.

⁴ G. H. Williams, *Piedmontite and scheelite from the ancient rhyolites of South Mountain, Pennsylvania*. *Amer. Journ. Sci.*, 1893, ser. 3, vol. 46, pp. 50–57.

⁵ C. Lausen, *loc. cit.*

⁶ F. N. Guild, *loc. cit.*

volume of andesite. In the piedmontite-bearing felsites from Tucson Mountains, Arizona, Guild (loc. cit., p. 691) shows that the manganese content is no more than is frequently found in normal rhyolitic rocks, and hence states that 'a rock, in order to develop piedmontite does not necessarily have to contain more manganese than is found in normal rocks'. A glance at the analyses of the Glen Coe rocks in the Geological Survey Memoir (loc. cit., pp. 182-183) does not show one with any abnormal amount of manganese. Whatever physico-chemical conditions are necessary for the formation of piedmontite rather than normal epidote, it is clear that those conditions did not obtain for the entire period required for the infilling of the cavities and veinlets, but that they gradually changed. Thus on the outer borders of the amygdales we have not piedmontite but a common epidote with an iron content¹ identical or very close to that of the piedmontite in the centre.

There is no evidence what these physico-chemical conditions were, but two possible hypotheses may be suggested:

(1) Temperature of the circulating solutions may have played some part, a higher temperature facilitating the formation of the piedmontite molecule. With a gradual decrease in the value of this factor, conditions favourable for the production of a manganiferous epidote slowly failed, a normal epidote forming instead. (2) There may have been merely a gradual failure in the supply of manganese.

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EXPLANATION OF PLATE IV.

Withamite from Glen Coë, Scotland.

FIG. 1. A polished specimen of a large amygdale (broken in two), showing much withamite, the milky-white outer zone of epidote and plentiful calcite. $\times \frac{1}{2}$.

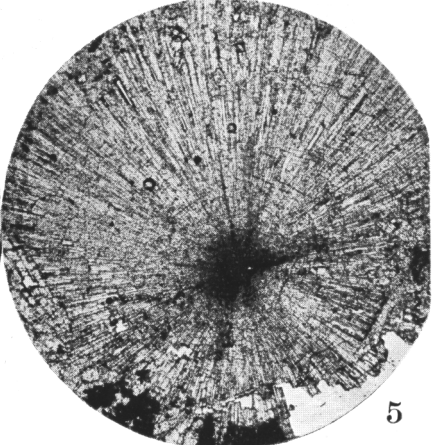
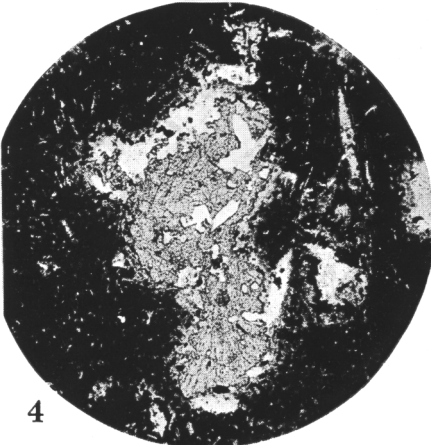
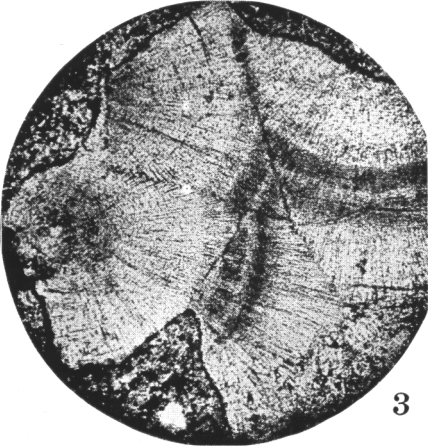
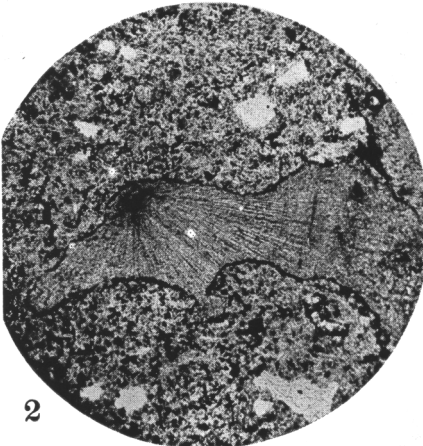
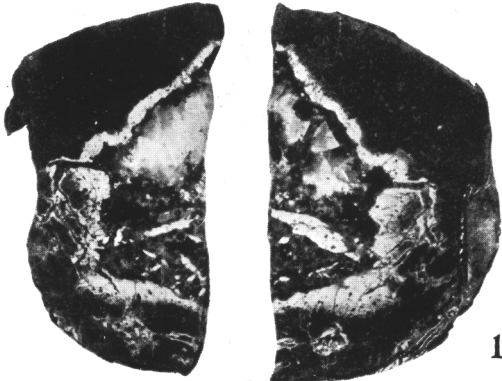
FIG. 2. An irregular amygdale showing radiating structure with dark red centre or nucleus, in fine-grained andesitic rock. $\times 30$.

FIG. 3. A large amygdale with the withamite radiating from three centres and also a zony banding of dark inclusions. $\times 30$.

FIG. 4. Amygdale showing subidiomorphic to idiomorphic outline of withamite with slight radiate arrangement, and fairly plentiful quartz. $\times 30$.

FIG. 5. An amygdale with perfect spherulitic arrangement and deep red, manganese-rich centre. $\times 30$.

¹ Fe_2O_3 content was estimated by means of an approximate determination of the birefringence with a quartz wedge.



C. O. HUTTON : WITHAMITE FROM GLEN COE