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*Pennantite, a new manganese-rich chlorite from Benallt mine,  
Rhiw, Carnarvonshire.*

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THE manganese ores of the Benallt mine are pervaded by an orange-coloured mineral which occurs very poorly crystallized as patches and small specks in the matrix. Less commonly it occurs as minute flakes in the ore and sometimes as a constituent of very thin veins which traverse the ore. In some specimens the mineral is better developed. It then shows a good cleavage and resembles in appearance in thin section a weakly pleochroic mica or chlorite. Patches of this mineral in the matrix frequently enclose very small rounded garnets which are believed to be spessartine.

In 1932 Dr. A. F. Hallimond examined some sections of ore from the old Benallt mine for Dr. C. A. Matley and suggested that one of the constituent minerals might be a manganiferous chlorite.<sup>1</sup> Dr. A. W. Woodland<sup>2</sup> identified as a yellow chlorite an important secondary mineral in the manganese ores of the Nant mines, Nant-y-Gadwen, a mile SW. of the Benallt mine. This he regarded as a manganiferous variety of chlorite. He observed its alteration in the weathered ore and noted that the final product of its weathering was a black earthy oxide (loc. cit., p. 209) which he considered was pyrolusite (loc. cit., p. 212).

As part of the study of the manganese ores of the Benallt mine, undertaken in collaboration with Dr. A. W. Groves, it became important to identify with certainty the ubiquitous orange-coloured mineral and to endeavour to determine its manganese content.

An opportunity to do this presented itself when it was found that the walls of thin white and pale pink veins traversing massive ore from the Ty Canol incline were lined in places with small (0.5 mm.) flakes of an orange-brown, micaceous mineral which seem undoubtedly to be the same as the orange-coloured mineral pervading the ore itself.

One of these veins, 5 mm. thick, runs for about a foot through a block of the

<sup>1</sup> C. A. Matley, Quart. Journ. Geol. Soc. London, 1932, vol. 88, p. 263.

<sup>2</sup> A. W. Woodland, Proc. Geol. Assoc. London, 1939, vol. 50, p. 209. [M.A. 8-250.]

massive ore. Portions of this vein were chipped out and separated from adhering fragments of ore. The vein minerals were determined by examination of thin sections, refractive index, density, simple microchemical tests, and, for three of the constituents, by X-ray photographs. The main constituent is an aggregate of minute flakes of a colourless mica and analcime. X-ray photographs of a grain of the aggregate show powder lines and spots which are attributable respectively to fine-grained paragonite and to analcime crystals. Banalsite is present, particularly in some thinner veins. Some of the banalsite crystals are invaded by the fine-grained aggregates of colourless mica, and it is possible that the analcime-paragonite aggregates result from the replacement of banalsite ( $\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ ) with elimination of barium. Some compact, pinkish-buff grains with fibrous texture are identified by X-ray photographs with ganophyllite.<sup>1</sup> Some calcite is present, and there are a few small, colourless, highly birefringent crystals which are probably tephroite. Small orange-red crystals, yellow in thin section, with high refractive index ( $n > 1.84$ ), uniaxial, optically negative, are pyrophanite.<sup>2</sup>

The orange-brown chlorite occurs in the body of the vein as well as on its edges. In thin section it shows a good cleavage and is pleochroic with  $\gamma'$  (parallel to the cleavage) xanthine-orange,  $\alpha'$  orange-buff.<sup>3</sup> Absorption  $\alpha < \beta = \gamma$ . Flakes show a uniaxial, negative optic picture. Refractive indices, measured in sodium-light by the Becke line method, are  $\alpha 1.646 \pm 0.001$ ,  $\beta = \gamma 1.661 \pm 0.001$ .

A few flakes of the chlorite were selected for X-ray examination. X-ray photographs of single crystals and powdered flakes identify the mineral as a member of the chlorite family; moreover, the powder photographs are identical in pattern with those of thuringite from Schmiedefeld, Thuringia,<sup>4</sup> though the new mineral has larger cell dimensions, namely  $a 5.43$ ,  $b 9.4$ ,  $c' 28.5 \text{ \AA}$ .

The value obtained for the corrected density, determined on part of the purest sample used for the chemical analysis, is  $D_4^{16} = 3.06 \pm 0.01$ .

The preparation of a sample for chemical analysis was made in the first place by selecting from the veins chippings which contained visible chlorite. These were broken down in a steel mortar and subjected to density and magnetic separations, the chlorite being readily attracted by the electro-magnet. From the concentrate so obtained about 30 mg. of pure material was separated by careful hand-picking under the microscope. A less pure sample of 40 mg., known to contain appreciable amounts of banalsite and opaque ore-minerals, was used for a preliminary analysis, and for the determination of the water and of the state of oxidation. The results obtained in the preliminary analysis served as a guide in planning the analysis of the purer sample. Alkalis were not determined.

The mineral was opened up by a perchloric acid attack, the silica dehydrated with perchloric acid, and the barium then determined as sulphate. The aluminium and iron were precipitated with hexamethylene tetramine (to avoid contamination by Mn), reprecipitated once, then the iron was determined colorimetrically with sulphosalicylic acid in ammoniacal solution, and aluminium and iron pre-

<sup>1</sup> Ganophyllite was found in the neighbouring Nant mine by Sir Arthur Russell in 1911 (this vol., p. 234).

<sup>2</sup> Identification confirmed by X-ray photograph and manganese test. Pyrophanite has not previously been recorded from the British Isles.

<sup>3</sup> R. Ridgway, Color standards and color nomenclature. 1912.

<sup>4</sup> W. von Engelhardt, Zeits. Krist., 1942, vol. 104, p. 145.  $a 5.37$ ,  $b 9.30$ ,  $c 14.10 \text{ \AA}$ ,  $\beta 97^\circ 20'$ . [M.A. 3-291.]

cipitated together from this solution and weighed as the 8-hydroxyquinoline salts. For some unknown reason, a clean crystalline precipitate of  $\text{NH}_4(\text{Mn},\text{Mg})\text{PO}_4 \cdot 6\text{H}_2\text{O}$  could not be obtained for the determination of manganese and magnesium, so the unsatisfactory precipitate was dissolved and the manganese oxidized to permanganate and so determined. For the magnesium, it was necessary to rely on a value obtained from the less pure sample, by precipitating the manganese in the filtrate from the aluminium and iron with ammonium sulphide, and determining the magnesium as 8-hydroxyquinoline derivative after oxidation of the sulphide. Calcium was sought for in the filtrate from the magnesium but was not found. Titanium was tested for in the aluminium-iron precipitate and shown to be absent. Water was determined by the Penfield method on a 5 mg. portion of the less pure sample.

The state of oxidation being of considerable interest, 10 mg. of the less pure sample was reserved for its determination. This determination raised some difficulties; on the one hand, the mineral might contain all its manganese as  $\text{MnO}$  and part of the iron as  $\text{FeO}$ , or, on the other, part of the manganese might be present as  $\text{Mn}_2\text{O}_3$ , and only a single portion could be spared for the determination. After some preliminary experiments, the following method was found satisfactory: the mineral was attacked in the cold with a mixture of 5 ml. concentrated  $\text{HCl}$ , 5 ml.  $\text{M}/200$   $\text{ICl}$  in concentrated  $\text{HCl}$ , and 1 ml.  $\text{M}/200$   $\text{KI}$ , in a stoppered flask; after four days no unattacked mineral remained, and the solution was titrated (against a blank) with  $\text{M}/400$   $\text{KIO}_3$ , using  $\text{CCl}_4$  as indicator. With this arrangement, any  $\text{Fe}^{II}$  present would reduce part of the  $\text{ICl}$  to iodine, while any  $\text{Mn}^{III}$  would oxidize part of the free iodine (produced by the  $\text{KI}$  addition) to  $\text{ICl}$ ; special tests proved that the solutions of iodine and  $\text{ICl}$  in concentrated  $\text{HCl}$  are satisfactorily stable. The result showed that, within the probable experimental error of about 0.2%,  $\text{FeO}$  and  $\text{Mn}_2\text{O}_3$  are both absent.

The analyses of the two samples are given in table I, together with the empirical unit-cell contents (column C) derived from the analysis of the purer sample (column A), the X-ray measurements, and the density. The probable error figures there given only take account of the probable error of the physical measurements

TABLE I. Chemical analyses and empirical unit-cell contents of pennantite. A, purer sample; B, impure sample; C, empirical unit-cell contents of the purer sample.

	A.	B.		C.	
$\text{SiO}_2$	... 22.64	23.43	$\text{Si}$	... 10.5	} 38.8 } $\pm 0.8$ ( $\Sigma \text{R}$ )
$\text{Al}_2\text{O}_3$	... 18.60	18.76	$\text{Al}$	... 10.2	
$\text{Fe}_2\text{O}_3$	... 4.43	6.80	$\text{Fe}^{III}$	... 1.5	
$\text{MnO}$	... 38.93	32.46	$\text{Mn}^{II}$	... 15.3	
$\text{MgO}$	... [1.48]	1.48	$\text{Mg}$	... 1.0	
$\text{BaO}$	... 1.33	7.40	$\text{Ba}$	... 0.3	
$\text{H}_2\text{O}$	... [9.40]	9.40	$\text{OH}$	... 29.2	} 69.7 } $\pm 1.4$ ( $\Sigma \text{O},\text{OH}$ )
	-----	-----	$\text{O}$	... 40.5	
	96.81	99.73			

(density and cell-dimensions). It is difficult to assess the effects of impurities or analytical errors on the empirical unit-cell contents quantitatively, but some calculations have been made, and show that: if part of the  $\text{MnO}$  and  $\text{Fe}_2\text{O}_3$  are present as ore, the oxygen plus hydroxyl figure ( $\Sigma \text{O},\text{OH}$ ) is raised, improving the agreement with the ideal formula, while the sum of the cations ( $\Sigma \text{R}$ ) is only

slightly affected; if the barium is taken to be present as banalsite (6%), the effect on  $\Sigma(\text{O},\text{OH})$  and  $\Sigma\text{R}$  is similar; if the whole or part of the deficiency in the summation is due to under-estimation of the water,  $\Sigma(\text{O},\text{OH})$  and the hydroxyl figure are increased, but  $\Sigma\text{R}$  is decreased. None of these effects is very great, and it is quite clear that no probable error in the analysis and no probable impurity in the sample can seriously affect the empirical unit-cell contents given, but that when the probable analytical and physical errors are taken into account the most probable value for the oxygen plus hydroxyl figure ( $\Sigma\text{O},\text{OH}$ ) is 72, and for the sum of the cations ( $\Sigma\text{R}$ ) 40. Hence the repeat may be given as  $(\text{Mn},\text{Al})_{24}(\text{Si},\text{Al})_{16}\text{O}_{40}(\text{OH})_{32}$ , with  $\text{Si} : \text{Al}_{\text{IV}}$  near 1.9, and minor amounts of  $\text{Fe}'''$  and  $\text{Mg}$ .

The low  $\text{MgO}$ , low  $\text{SiO}_2$ , high  $\text{Al}_2\text{O}_3$ , and very high  $\text{MnO}$  contents shown by the chemical analysis distinguish this chlorite very clearly from all hitherto described manganese-bearing minerals of the chlorite family and from manganophyllite. On the other hand, the empirical unit-cell contents calculated from the analysis show a very close analogy with the thuringite formula  $(\text{Mg},\text{Al},\text{Fe})_{12}(\text{Si},\text{Al})_8\text{O}_{20}(\text{OH})_{16}$  given by W. von Engelhardt for thuringite from Schmiedefeld, Thuringia (loc. cit., p. 146), and the analogy accords with the evidence of the X-ray photographs. It would appear, therefore, that this chlorite from the Benallt mine is a new mineral analogous to thuringite, but containing  $\text{MnO}$  in place of the  $\text{FeO}$ .

The names manganchlorite (Hamberg)<sup>1</sup> and manganese-chlorite (Eckermann)<sup>2</sup> have been applied to chlorites containing only a low percentage (1.02–2.28)  $\text{MnO}$ , so it is desirable to avoid the use of either of these names for a chlorite so rich in manganese as the mineral here described, and we therefore propose for it a new name, *pennantite*, after Thomas Pennant (1726–1798), the Welsh traveller, zoologist, and mineralogist.<sup>3</sup>

<sup>1</sup> A. Hamberg, Geol. För. Förh. Stockholm, 1890, vol. 12, p. 580.

<sup>2</sup> H. von Eckermann, Geol. För. Förh. Stockholm, 1927, vol. 49, pp. 450–454, and 1944, vol. 66, pp. 721–724. [M.A. 3–474, 9–256.]

<sup>3</sup> W. Campbell Smith, The mineral collection of Thomas Pennant (1726–1798). Min. Mag., 1913, vol. 16, pp. 331–342.