

Gedrite from Glen Urquhart, Inverness-shire.

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THIS note describes a hydrous gedrite from Glen Urquhart for which the presence of an appreciable excess of oxygen atoms over the normal 96 per unit cell has been established. This is associated with an approximately equal deficiency of cations. The type of isomorphous replacement here discussed is hitherto unrecorded in the amphibole group.

FIELD OCCURRENCE.

The hydrous gedrite occurs as an almost monomineralic rock, gedritite, which was found at only one place in Glen Urquhart. This is a road cutting at the junction of the Milton-Kiltarlity road with a side road to the Gartally farms, a quarter of a mile from Milton. This must be the locality described by Heddle¹ as 'near the Free Church of Millton', where he obtained hydrous anthophyllite and other minerals.

The gedritite carries a grey or iron-stained crust on which radiating fans of the amphibole with prisms up to 6 cm. in length appear. On fresh surfaces the prisms have the typical clove-brown colour from which anthophyllite gets its name. Occasionally the rock holds giant hornblendes; one such crystal measures 11 × 7 × 4 cm. Accessory hydrobiotite, talc, rutile, and serpentine are present in the rock.

The occurrence is in a zoned hydrothermal body in a large serpentinite mass. The gedritite zone lies between a kyanite-hydrobiotite-rock and the serpentinite. It probably owes its high alumina content to the former and its high water content to the latter rock. A full discussion of the serpentinite mass and the zoned body will be given in later papers.

PHYSICAL AND CHEMICAL DATA.

Careful separation by means of heavy liquids and an isodynamic separator removed the small amounts of hydrobiotite, talc, rutile, and

¹ M. F. Heddle, *Min. Scotland*, 1901, vol. 2, p. 40.

serpentine present in the rock. The resulting powder, of typical clove-brown colour, was found to contain no more than a trace of impurity, judged to be less than 1 %. Optical constants of the gedrite are:

Refractive indices.	Birefringence.	Optic axial angle.
α 1.611	$\gamma - \alpha$ 0.021	$2V\gamma$ (measured) 85°
β 1.620		
γ 1.632		
± 0.002		$2V\gamma$ (calculated) 82

X-ray single-crystal and powder photographs were made on the gedrite. Pictures taken with oscillation about c provided a good measurement for that axis which agrees with the powder photographs results. Photographs of crystals oscillated normal to c showed that the needles separated for study are to some extent fibred parallel to c , and were thus unsuitable for measuring the a and b cell-sides. From powder pattern spacings (Fe- $K\alpha$ radiation) on a 19-cm. camera the following cell dimensions were obtained: a 18.52 ± 0.04 , b 17.79 ± 0.04 , c 5.31 ± 0.01 Å. When compared with the figures given by J. C. Rabbitt¹ these are found to lie within the limits of variation of the anthophyllite group and are not extreme. X-ray powder spacings for Fe- $K\alpha$ radiation appear in table I.

TABLE I. X-ray powder spacings of gedrite from Glen Urquhart, Inverness-shire. Taken on a 19-cm.-radius camera with Fe- $K\alpha$ radiation.

$\sin^2\theta$.	$d(\text{Å.})$.	Int.	Indices.	$\sin^2\theta$.	$d(\text{Å.})$.	Int.	Indices.
0.0116	8.99	m	—	0.2036	2.14	w	(502)
0.0138	8.28	s3	(210)	0.2085	2.12	w	(561)
0.0182	7.19	m	—	0.2211	2.06	vw	(840)
0.0475	4.45	w	(040)	0.2391	1.98	vw	(751)
0.0555	4.11	w	(420)	0.2767	1.84	vw	(860)
0.0628	3.87	vw	(131)	0.3145	1.73	vw	—
0.0713	3.63	m	(321)	0.3613	1.61	vw	—
0.0740	3.56	w	—	0.3936	1.54	vw	(12.0.0)
0.0846	3.32	w	(331)	0.4137	1.51	m	(0.12.0)
0.0909	3.21	s2	(440)	0.4654	1.42	vw	(11.6.1)
0.1014	3.04	s1	(610)	0.4712	1.41	w	—
0.1142	2.87	m	—	0.5330	1.33	vw	—
0.1189	2.81	m	—	0.7145	1.15	vw	—
0.1250	2.74	m	(630)	0.8702	1.04	vw	—
0.0325	2.66	m	—	0.8859	1.03	vw	(16.8.0)
0.1434	2.56	m	(202)	0.8947	1.02	vw	—
0.1462	2.53	m	—	0.9268	1.01	vw	—
0.1514	2.49	m	(451)	0.9437	1.00	vw	—
0.1756	2.31	w	(551)				

The indices have been assigned by comparison of $\sin^2\theta$ values with those of K. Johansson (Zeits. Krist., 1930, vol. 73, p. 31). [M.A. 4-356.]

¹ J. C. Rabbitt, Amer. Min., 1948, vol. 33, p. 263. [M.A. 10-416.]

The density was measured on coarse fragments immersed in methylene iodide diluted with benzene. Since no inclusions of iron ore or other heavy impurity are present, the liquid taken as correct is that in which one crystal floated in mid-liquid after centrifuging, the rest having floated to the surface. Since the expected inclusions, especially air in cleavages and cracks, will lower density, the purest crystal is the one with the highest density. This proved to be 3.122 ± 0.010 at 20°C ., referred to water at 4°C .; when corrected for 0.42% of water lost at 110°C ., assumed to be adsorbed water, this becomes 3.150 ± 0.010 .

TABLE II. Chemical analyses and empirical unit-cell contents of gedrite from Glen Urquhart, Inverness-shire.

	1.	2.		1a.	1b.
SiO ₂ ...	43.03	47.72	Si ...	23.97 ± 0.25	26.28
Al ₂ O ₃ ...	26.65	3.84	Al ...	17.50 ± 0.22	19.18
TiO ₂ ...	0.75	0.18	Ti ...	0.30 ± 0.02	0.34
Fe ₂ O ₃ ...	0.66	—	Fe''' ...	0.28 ± 0.06	0.30
FeO ...	11.69	5.74	Fe'' ...	5.44 ± 0.06	5.98
MnO ...	0.13	0.16	Mn ...	0.06 ± 0.003	0.07
MgO ...	9.59	28.75	Mg ...	7.96 ± 0.14	8.72
CaO ...	1.28	5.64	Ca ...	0.76 ± 0.04	0.84
Na ₂ O ...	0.48	0.26	Na ...	0.52 ± 0.10	0.57
K ₂ O ...	0.21	0.19	K ...	0.15 ± 0.04	0.16
H ₂ O + 110° C.	4.72	7.65	O ...	83.57	94.42
H ₂ O - 110° C.	0.42		OH ...	12.43	± 0.76
	99.61	100.13	H ₂ O ...	2.55	
D _{obs.} ...	3.122	2.81	total (O, OH, H ₂ O)	98.55 ± 0.81	102.42
			total (cations)	56.95 ± 0.54	62.44

- Gedrite, Glen Urquhart (B.M. 1955,63). Part of the same specimen is in the Harker Collection, Department of Mineralogy and Petrology, Cambridge, (no. 76,306). G. H. Francis, analyst.
- 'Hydrous anthophyllite', Glen Urquhart. M. F. Heddle, 1901, *loc. cit.*, p. 41.
 - Empirical unit-cell contents, from analysis 1, assuming all the H₂O + is essential.
 - Empirical unit-cell contents, from analysis 1, assuming the unit cell contains 8(OH) and all other water is adsorbed impurity.

A chemical analysis gave the results included in table II, and was supplemented by a spectrographic determination of the trace elements by Dr. S. R. Nockolds, which gave the following values (parts per million): Rb trace,¹ Cs nil, Tl nil, Sr trace, Ba 12, Ga 15, In nil, Sc 15, Yt 12, La trace, Zr 18, Sn trace, Pb trace, V 125, Cr 100, Mo trace, Co 17, Ni 22, F nil.

¹ Trace implies that the element is present, but below the limit of quantitative determination.

An analysis of 'hydrous-anthophyllite' originally given by M. F. Heddle¹ as from 'the Bay of Scourie' (Sutherland), has been quoted by A. Lacroix,² on the authority of a Dr. Wilson, as being from Glen Urquhart, together with a statement that it was the mineral analysed in Heddle's paper. Lacroix then showed from its optics that it was actinolite—disproving to his own satisfaction and Dana's³ that Heddle's 'hydrous-anthophyllite' existed. It may be said that this examination of the wrong mineral from the wrong locality proves nothing. Heddle does record a hydrous anthophyllite from Milton, Glen Urquhart,⁴ for which he records a composition quite distinct from the Scourie analysis; unfortunately this does not approach the composition now found for the gedrite. Much of the gedrite is now represented by pseudomorphs in talc and serpentine after gedrite. In one case a fine specimen with large radiating 'crystals' was found to be composed of pseudomorphous talc and serpentine only after the cutting of a thin section. It thus appears that Heddle analysed a pseudomorph after anthophyllite; this is supported by his analysis (table II, 2) which could be explained as a talc-serpentine mixture.

THE TRUE CONTENTS OF THE UNIT CELL.

Assuming that all the water retained at 110° C. is an essential part of the mineral, the empirical unit-cell contents were calculated, together with approximate probable errors calculated by the method proposed by M. H. Hey;⁵ the results, included in table II, col. 1*a*, are remarkable for the very high content of 98.5 (O,OH,H₂O), a figure quite outside the probable error of the observations.

Apart from a few specialized groups, such as the zeolites, scapolites, and ultramarines, previous work on silicates has always supported an integral sum of (O + OH + F + Cl), invariable within any one isomorphous group of silicates, and it seemed essential to exclude any other possibility before accepting the view that the Glen Urquhart gedrite does in fact contain nearly 99 oxygen atoms per unit cell instead of the 96 normal in the ortho-amphiboles.

¹ M. F. Heddle, *Min. Mag.*, 1882, vol. 4, p. 213.

² A. Lacroix, *Bull. Soc. Min. France*, 1888, vol. 9, p. 7.

³ E. S. Dana, *Syst. Min.*, 6th edn., 1892, p. 384.

⁴ M. F. Heddle, *Min. Scotland*, 1901, vol. 2, p. 40.

⁵ M. H. Hey, *Min. Mag.*, 1954, vol. 30, p. 481, assuming the following possible errors in the chemical analysis: SiO₂ 0.3 %; Al₂O₃ and H₂O 0.2 %; MgO 0.15 %; total iron as Fe₂O₃, FeO, and Na₂O 0.10 %; TiO₂, CaO, and K₂O 0.05 %; MnO 0.01 %.

There are two other possibilities: the mineral might contain substantial amounts of impurities with a more close-packed structure and higher density, so that the observed density is too high through the presence of impurities; or part of the water lost above 110° C. might be adsorbed and not essential water. The first possibility may be ruled out by the thorough purification of the gedrite, which shows less than 1% of impurities under the microscope; the second possibility has been investigated and shown to lead to an even higher empirical unit-cell content of oxygen.¹ If we assume that the gedrite has in fact the commonly accepted content of eight hydroxyl groups per unit cell, we can calculate that 2.76% of the H₂O+ must be adsorbed impurity; correction of the density for this gives a value of 3.357, leading to 102.4 (O,OH) per unit cell (table II, col. 1b). Clearly this interpretation must be rejected.

It is quite clear that in the Glen Urquhart gedrite we have a very unusual amphibole; as the empirical unit-cell contents in table II, column 1a, show, the total cations per unit cell are notably low, and the total oxygen (O + OH + H₂O) is high by approximately the same amount. These appear to be established facts, but their interpretation must be a matter of speculation, pending a detailed structural study of the mineral. It can be interpreted as a replacement of 8(Si,Mg) by 16Al, the remaining 1.5 Al replacing Mg, and the tetrahedral positions in the (Si,Al)₄O₁₁ chains being completely filled; in this case there must be a deficit of nearly 3 cations in the octahedral positions, balanced by a replacement of O by OH to the extent of over four atoms per unit cell (12.4 OH instead of the normal 8). The excess of 2.5 oxygen atoms per unit cell could be water molecules accommodated either in the vacant octahedral positions left by the missing 3 cations, or in adjacent 'A' positions—the lattice positions normally vacant in anthophyllite, but occupied by Na and Ca in many hornblendes. Alternatively, it could be assumed that there are vacancies in the tetrahedral lattice positions of the Si₄O₁₁ chains (the SiO₄ ⇌ (OH)₄ replacement noted in the hydrogarnets and advocated by D. McConnell² in several other silicates); but

¹ In fact, to regard H₂O+ as an impurity, rather than essential, will almost invariably increase the apparent oxygen atoms per unit cell in any mineral. More specifically, it will do so whenever the percentage of oxygen in the mineral is greater than $88/(D+1)$, where D is the density of the mineral. Or, if molecular ratios are calculated in the usual way by division of the percentages of the several oxides by their molecular weights, and an oxygen ratio R_o is derived from the molecular ratios, interpretation of H₂O+ as an impurity will increase the apparent oxygen atoms per unit cell if $R_o > 5.51/(D+1)$.

² D. McConnell, *Amer. Min.*, 1950, vol. 35, p. 166 [M.A. 11-220]; *Clay Minerals Bull.*, 1951, vol. 1, p. 179.

in that case it would not be so easy to understand why the excess of oxygen atoms per unit cell should be approximately equal to the deficit of cations. When more examples of this oxygen excess come to light, regularities may become apparent, but at present any further speculation seems pointless.

PROGRESSIVE HEATING EXPERIMENTS.

In the hope of obtaining additional evidence in confirmation of the view that approximately 1.6% of the water in the Glen Urquhart gedrite is accommodated in interstitial lattice positions, normally unoccupied in anthophyllite, the loss of weight of powdered samples was determined at a series of temperatures up to 1200° C. At temperatures of 500°, 700°, 800°, 900°, and 1000° C. parts of the samples were abstracted, their percentage weight of FeO determined, and their structure tested by means of powder photographs. These samples all possess the powder pattern of the unheated material, but this gets progressively weaker with increasing temperature. A powder photograph of material heated to 1100° C. shows inversion to pyroxene with some amorphous material. The powder photograph after heating to 1200° C. shows a sharper pyroxene pattern with scant remaining amorphous material.

Table III contains the calculated results of the progressive heating.

TABLE III. Compositional changes on progressive heating of gedrite from Glen Urquhart.

Temp. ° C.	(O,OH, H ₂ O).					A.	B.	C.	D.	E.
	Fe ^{III} .	OH.	O.	H ₂ O.	H ₂ O).					
100	0.28*	12.43	83.57	2.55	98.55	0.00	0.00	0.00	0.00	0.00
200	0.28	12.43	83.57	2.55	98.55	0.00	0.00	0.00	0.00	0.00
300	0.88	11.83	84.17	2.42	98.42	0.86	0.26	0.60	0.00	0.26
400	1.78	10.93	85.07	2.20	98.20	2.20	0.70	1.50	0.00	0.70
500	2.46*	9.55	86.13	2.10	97.78	3.72	1.54	2.18	0.64	0.90
550	2.48	9.03	86.40	1.80	97.20	4.80	2.60	2.20	1.20	1.40
600	2.53	8.43	86.69	1.25	96.37	6.60	4.36	2.25	1.76	2.60
650	2.63	7.83	87.04	0.28	95.15	9.16	6.80	2.35	2.26	4.54
680	2.77	7.59	87.25	—	94.84	9.44	7.46	2.49	2.35	5.10
700	2.93*	7.43	87.41	—	94.84	10.10	7.46	2.65	2.35	5.10
750	3.90	6.37	88.40	—	94.77	11.18	7.56	3.62	2.46	—
800	4.84*	3.49	90.32	—	93.81	14.04	9.48	4.56	4.38	—
850	5.23	0.99	91.76	—	92.75	16.54	11.60	4.95	6.50	—
860	5.30	0.41	92.09	—	92.50	17.12	12.10	5.02	7.00	—
900	5.50*	0.19	92.30	—	92.49	17.34	12.12	5.22	7.02	—
950	5.68	0.09	92.40	—	92.49	17.44	12.00	5.40	7.02	—
1000	5.72*	0.00	92.50	—	92.50	17.54	12.12	5.44	7.02	—

1100 inverted to pyroxene.

* Direct values, all others depend on interpolation in the Fe^{III} curve.

The temperature intervals at which weighings were made appear in the first column. In the second are figures for Fe^{III} per unit cell taken by difference from total iron; the intermediate values are interpolated in the Fe^{III} curve. The next four columns show OH, O, H_2O (in excess of 96) per unit cell and the sum of these. Clearly in this heating three processes are at work, each involving loss of H. They are:

Reaction 1, oxidation, $\text{Fe}^{II}(\text{OH}) \rightarrow \text{Fe}^{III}\text{O} + \text{H}$.

„ 2, loss of hydroxyl water, $2(\text{OH}) \rightarrow \text{O} + \text{H}_2\text{O}$.

„ 3, dehydration (loss of interstitial water).

The losses of H atoms per unit cell for these reactions in combination

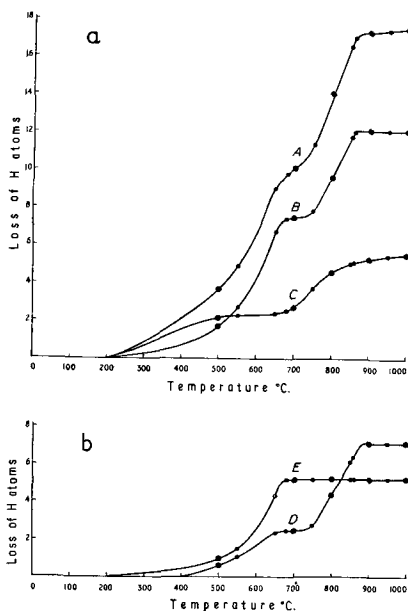


FIG. 1. Progressive heating curves: (a) determined, (b) assuming reaction 3 to have gone to completion just above 650° C. Curves A (reactions 1, 2, and 3), B (reactions 2 and 3), C (reaction 1), D (reaction 2), E (reaction 3) are taken from figures in the corresponding columns of table III. Larger dots correspond to direct determination of Fe^{III} , small dots are interpolated in the Fe^{III} curve.

and separately are given in table III columns A–E and in the curves A–E of fig. 1, to which they correspond. Curve A represents the combined loss of H atoms by reactions 1, 2, and 3. It can loosely be referred to as ‘water lost’. B is the loss of H atoms by reactions 2 and 3, that is by dehydration. C is the loss of H atoms by oxidation of ferrous to ferric iron (reaction 1). These three curves are directly determinable.

D and E represent reactions 2 and 3 respectively; in the absence of any direct evidence by which the division of the values of curve B into reactions 2 and 3 could be assessed, we may assume reaction 3 to have gone to completion just above 650° C. (see H₂O column, table III), and reaction 2 to have started before that.

It appears from this work that reaction 1 begins at quite a low temperature. It is quite marked by 500° C., but then the rate of oxidation appears to slow, though this may be only an apparent check. It may be that the more readily accessible outer parts of the grains have undergone oxidation by 500° C. and that further oxidation is checked until dehydration produces cracking of the grains. Several other possibilities could also be suggested.

Reaction 2 almost certainly starts before the loss of interstitial water is complete, probably about 400° C. There appears to be a check in this dehydration about 650°–700° C., followed by a rapid loss of the remaining water over the range 750°–870° C.

Reaction 3 is the loss of the interstitial water thought to be in the vacant octahedral positions left by the 3 missing cations, or in the adjacent 'A' positions. It starts at about 200° C. and goes on at an increasing rate; it is probably complete just above 650° C. (see above), the greater part of the loss taking place above 500° C.

This work supports the theoretical conclusion that loosely held water molecules exist in this structure additional to the expected 8(OH) per unit cell. It also demonstrates that complete dehydration of two types, $X_7Z_8O_{22}(OH)_2 \rightarrow X_7Z_8O_{24}$ (with oxidation of ferrous to ferric iron) and $X_7Z_8O_{22}(OH)_2 \rightarrow X_7Z_8O_{23}$ can be induced in this amphibole by heating, before its inversion to pyroxene. An examination of the physical properties of anthophyllites in relation to their varying chemical compositions will be presented in a later paper.

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