

# Studies of the orthoamphiboles

## III. Hydroxyl spectra of gedrites

ANTHONY D. LAW\*

Department of Geology and Mineralogy, University of Oxford

**ABSTRACT.** Infra-red spectra of gedrites have been measured in the hydroxyl region ( $3800\text{--}3500\text{ cm}^{-1}$ ). The spectra can be related to those of clinoamphiboles and of anthophyllites, and show the normal amphibole pattern of peaks whose intensities reflect the proportions of different cations in the adjacent octahedral sites. The absorption is weak especially in spectra of gedrites high in Al. Hyperfine splitting of peaks has been observed in anthophyllite spectra (Law, 1981) but the extent of hyperfine splitting in gedrite spectra is limited. The underlying baseline absorption, upon which the hydroxyl peaks are superimposed, becomes steeper and more awkward to estimate in gedrites. Some higher frequency peaks, probably arising from unit cells with *A* sites occupied by Na, are observed.

**MEASUREMENT** of hydroxyl spectra of amphiboles is a well-established technique (see for example Strens, 1974). In the region of the infra-red spectrum between  $3800$  and  $3500\text{ cm}^{-1}$  a broad absorption appears, upon which are superimposed a group of sharp bands which represent the stretching frequencies of the hydroxyl group at O3 in the amphibole structure.

The O3 hydroxyl is above the approximate centre of a roughly equilateral triangle formed by the three cation positions *M1*, *M1*, and *M3* at the centre of the amphibole double chain. Variation in the cation occupancy of these three 'central' *M* sites causes variation in the O-H stretching frequency. In many amphiboles Mg and  $\text{Fe}^{2+}$  predominate in *M1* and *M3*, and ferromagnesian amphiboles such as cummingtonite-grunerite (Burns and Strens, 1966) or tremolite-actinolite (Burns and Greaves, 1971) give four major peaks which are due to combinations MgMgMg (peak A), MgMg $\text{Fe}^{2+}$  (peak B), Mg $\text{Fe}^{2+}\text{Fe}^{2+}$  (peak C), and  $\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{2+}$  (peak D) in the three central sites. The *M1* and *M3* positions are almost equal in their effect upon O3, but the variation from equality has an important effect upon the spectra which has

been discussed by Burns and Law (1970), Strens (1974), and Law (1976).

Hydroxyl spectra have been determined for many amphiboles, and peak positions do not vary widely. For example, peak A varies from  $3672\text{ cm}^{-1}$  in actinolite (Burns and Greaves, 1971) to  $3659\text{ cm}^{-1}$  in holmquistite (Law and Whittaker, 1981). As each Mg is replaced by  $\text{Fe}^{2+}$  the peak shifts by some  $10\text{--}15\text{ cm}^{-1}$  to lower frequency (this shift is also consistent in different amphibole series). Peak line-widths (full width at half height) are in the range  $3.5\text{--}6\text{ cm}^{-1}$  in the majority of spectra, so that the major peaks are clearly resolved. Their relative intensities reflect the proportions of Mg and  $\text{Fe}^{2+}$  in the sites.

Nomenclature of peaks follows Bancroft and Burns (1969). A typical amphibole spectrum, of a cummingtonite with about 55% Fe component (Mason, 1953), was illustrated by Law (1981).

Apart from the relatively rare holmquistite, anthophyllite, and gedrite are the only amphiboles known to crystallize in the orthorhombic space group *Pnma*. Anthophyllite is unique among amphiboles in containing mainly Mg in all the *M* sites. Stout (1972) suggests that an upper limit for the accommodation of Na and Al in the anthophyllite, as opposed to the gedrite, structure is  $\text{Na}_{0.1}(\text{Mg}_{3.7}\text{Fe}^{2+}_{2.7}\text{Al}_{0.5})\text{Si}_{7.5}\text{Al}_{0.5}\text{O}_{22}(\text{OH})_2$ , at the metamorphic grade represented by the Telemark suite. The distinction between anthophyllite and gedrite, the latter being the subject of this paper, is discussed in detail by Robinson *et al.* (1971) and by Stout (1971, 1972).

A previous paper (Law, 1981) reported qualitative features of the hydroxyl spectra of anthophyllites. This paper reports qualitative results from a similar study of gedrites. In gedrite, as in hornblende among the clinoamphiboles, the chemical composition is complicated by the presence of Al and  $\text{Fe}^{3+}$  in the central sites as well as at *M2*; of Na (and limited K) in the *A* sites; and of some Na and Ca at *M4*. There is replacement of Si by Al (and possibly  $\text{Fe}^{3+}$ ) in tetrahedral positions.

\* Present Address: BP Petroleum Development (Overseas) Ltd., Britannic House, Moor Lane, London EC2Y 9BU.

Papike and Ross (1970) reported detailed X-ray structural investigation of two gedrites, including site occupancies; both these gedrites are included in the present study.

#### Experimental

Spectra were determined using pressed KBr discs, prepared with vacuum-dried reagent grade KBr. Perkin-Elmer 125 and 225 spectrophotometers were used. To give an overall impression of the spectra, each was first recorded at a fast scan speed on a narrow scale; for accurate measurement, a slow scan was recorded on an expanded scale. The baseline underlying the hydroxyl absorption was drawn in by hand and, after correction, peak parameters were estimated using an unconstrained least squares program. Fuller details are as given by Law (1981).

#### Specimens

The chemical compositions and other details of the orthoamphiboles whose spectra are reported here are given in Table I, together with a number of relevant analyses from the literature. The recalculation of the formula unit of amphiboles is not straightforward; the question has been discussed by Borg (1967) and by Stout (1972). Evading the problem, the 24(O,OH,F) recalculation is used here except for microprobe analyses, for which recalculation is to 23(O). In practice, the recalculation used is unlikely to affect the conclusions drawn. Microprobe analyses of some specimens were made by Mrs A. Hall of the British Museum (Natural History) in 1969; elements analysed were Ca, Mg, Fe, Al, and Si.

*Gedrite 001*, from Bamle, Telemark, Norway, is a greenish-grey gedrite occurring in a dark-grey mica schist with biotite, garnet, and feldspar. Gedrites from Bamle are described by Des Cloizeaux (1877), Pisani (1877), and Kunitz (1930); Kunitz's analysis is cited by Rabbitt (1948, no. 19—not in fact no. 18 as given). Kunitz's gedrite must be significantly different from this specimen; his description of it is 'rotlich' (reddish). A microprobe analysis was made.

*Gedrite 003*, from Bancroft, Ontario, Canada, is described by Tilley (1957). It is clove brown in colour and was made available as a pure separate.

*Gedrites 004 and 005* are from Kalvola, Finland. Eskola (1936) describes several specimens from the Kalvola garnet amphibolite; these are specimens from the Helsinki University collection, dating from the early nineteenth century. Gedrite was separated from one specimen and analysed, and is cited by Rabbitt (1948, no. 2). From the description, this may resemble gedrite 004. None of the specimens appear to resemble 005. Gedrite 004 is from a fine-grained dark-grey rock, from which large garnet crystals have been lost. Gedrite 005 is weathered and contains numerous opaque grains.

*Gedrite 006*, from Traskbøle, Finland, may be the same as one of two Traskbøle orthoamphiboles reported by Eskola (1914) and cited by Rabbitt (1948, nos. 13 and 16; no. 13 appears reasonably close to the microprobe analysis of this gedrite).

*Gedrite 008* is from Bullsbrook, Western Australia (Simpson, 1931). In its Fe/Mg ratio it is similar to 003, but is much higher in Al. The analysis is cited by Rabbitt (1948, no. 7).

*Gedrite 009* is an almost 'end-member' ferrogedrite whose composition, ignoring alkalis, approximates  $\text{Fe}_2\text{Al}_2\text{Si}_6\text{Al}_2\text{O}_{22}(\text{OH})_2$  (Seki and Yamasaki, 1957). It is worth noting that the analysis shows  $\text{Al}^{\text{vi}} + \text{Fe}^{3+} + \text{Ti} = 2.2$ , so there are expected to be at least 0.2 of these ions outside M2. If the formula unit is recalculated to 15 cations excluding alkalis (assumed to be in A), a significant reduction of OH is needed to balance the formula: the gedrite may be OH-deficient. The rock from which this gedrite comes is a very fine-grained hornfels in which the amphibole occurs as porphyroblasts and as a constituent of the matrix.

*Gedrite 010* is the 'hydrous' Glen Urquhart gedrite of Francis (1955, 1956); Hey (pers. comm.) states that the high  $\text{H}_2\text{O}$  in the published analysis arises from a thin layer of chlorite on the grains which was overlooked in the original analysis. Francis did not give an analysis for chlorite from the assemblage, so correction of the analysis is not possible. An incomplete microprobe analysis is used here.

*Gedrites 016 and 017* are from the Orange area, Massachusetts, and are described by Robinson and Jaffe (1969, nos. I34I and I34JX respectively). Gedrite 016 is one of the two gedrites for which detailed X-ray structural investigation was carried out by Papike and Ross (1970, no. 002).

*Gedrite 018* is from Mason Mountain, N. Carolina (Henderson, 1931; Heinrich, 1950; Barker, 1961). This is the other gedrite studied by Papike and Ross (1970, no. 001). A wet chemical analysis of the Mason gedrite was given by Henderson (1931), but did not include Na so that Papike and Ross re-analysed it by microprobe. Henderson's analysis shows low  $\text{Fe}^{3+}$  so the microprobe approximation for Fe is assumed by Papike and Ross to be acceptable.

Without detailed investigation it is impossible to classify a single orthoamphibole of intermediate composition unambiguously as anthophyllite or gedrite. In the full study of which this report is part, a threefold grouping proved useful; specimens are referred to as 'anthophyllites' (high in Mg, very low in Al and Na), 'low-aluminium gedrites' (intermediate in Mg, intermediate in Na and Al), and 'high-aluminium gedrites, (high in Na and Al, and often higher in Mg than  $\text{Fe}^{2+}$ ). The grouping is reflected in the infra-red spectra, which for anthophyllites are described by Law (1981), and in the Mössbauer spectra (Law, unpubl.), though there are no very clear divisions and the distinction is made for convenience rather than because of any petrological significance.

TABLE Ia  
Composition of gedrites used in this study

Analysis	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	H <sub>2</sub> O <sub>+</sub>	H <sub>2</sub> O <sub>-</sub>	F	Cl	Sum
001m	44.4	13.1	-	-	18.4*	-	15.1	0.5	-	-	-	-	-	-	91.5
002	56.27	2.07	-	0.40	13.81	0.59	23.99	1.15	-	-	-	1.83	-	-	100.11
003	50.06	7.28	0.20	0.96	18.42	0.57	18.40	0.87	0.76	0.02	2.32	0.08	none	0.06	100.00
004m	42.7	13.5	-	-	26.1*	-	10.5	0.5	-	-	-	-	-	-	93.3
005m	46.8	10.1	-	-	23.2*	-	14.8	0.4	-	-	-	-	-	-	95.3
006m	47.2	7.9	-	-	21.6*	-	15.8	0.2	-	-	-	-	-	-	92.7
008	45.38	14.70	-	0.94	18.14	0.31	15.26	0.62	1.20	0.19	2.77	0.23	-	-	99.74
009	38.41	19.72	0.48	2.21	33.54	2.30	0.03	0.13	0.16	0.04	2.06	-	0.13	-	100.11
010m	46.5	12.9	-	-	11.4*	-	21.1	0.6	-	-	-	-	-	-	92.5
016	40.75	19.81	0.25	1.22	19.29	0.25	13.81	0.27	1.92	0.04	2.68	-	-	-	100.38
017m	44.72	15.46	0.48	2.41	15.87	0.37	16.69	0.47	1.67	0.01	2.11	-	-	-	100.24
018m	45.52	18.33	0.62	2.93*	0.13	22.09	0.22	1.78	-	-	-	-	-	-	98.62
R 2	43.70	10.88	0.55	3.52	26.53	0.24	11.48	0.54	1.24	0.15	1.21	-	-	-	100.04
R 13	48.00	7.73	0.73	1.00	1.11	26.11	0.18	16.66	0.64	1.21	0.24	1.09	-	-	99.87
R 16	50.10	7.35	0.73	none	22.18	0.25	16.64	0.60	0.54	none	1.15	-	-	-	99.63
F	43.03	26.65	0.75	0.66	11.69	0.13	9.59	1.28	0.48	0.21	4.72	none	-	-	99.19
H	44.22	23.79	-	0.20	9.21	0.16	20.69	0.02	-	-	1.42	-	-	-	99.71
K	51.62	10.32	-	1.94	3.72	0.87	26.82	1.29	0.32	0.68	2.23	-	-	-	99.81

"m" indicates microprobe analysis; Fe as FeO (marked \*).  
A dash indicates that no analysis figure is given; "none" indicates that the element was found absent.  
016: Li<sub>2</sub>O 0.03%, Cr<sub>2</sub>O<sub>3</sub> 0.01%, P<sub>2</sub>O<sub>5</sub> 0.04%  
017: Li<sub>2</sub>O 0.04%, P<sub>2</sub>O<sub>5</sub> 0.07%

Formula unit

	K	Na	Ca	Mg	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Mn	Ti	Al <sup>vi</sup>	Si	Al <sup>iv</sup>	O	OH	F	Oct	
001	-	-	0.08	3.44	2.35*	-	-	-	1.15	6.79	1.21	(22)	(2)	-	7.02	
002	-	0.17	5.00	1.61	0.04	0.07	-	0.20	7.86	0.14	22.29	1.71	-	-	7.09	
003	0.00	0.21	0.13	3.94	2.21	0.10	0.07	0.02	0.42	7.19	0.81	21.78	2.22	none	7.10	
004	-	-	0.08	2.44	3.41*	-	-	-	1.15	6.67	1.33	(22)	(2)	-	7.08	
005	-	-	0.06	3.31	2.91*	-	-	-	0.77	7.02	0.98	(22)	(2)	-	7.04	
006	-	-	0.03	3.61	2.77*	-	-	-	0.66	7.23	0.77	(22)	(2)	-	7.07	
008	0.03	0.34	0.09	3.27	2.18	0.10	0.04	-	1.00	6.51	1.49	21.35	2.65	-	7.05	
009	0.01	0.35	0.00	0.41	0.39	0.26	0.30	0.06	1.65	6.01	1.99	21.79	2.15	0.06	7.03	
010	-	-	0.09	4.59	1.39*	-	-	-	1.01	6.79	1.21	(22)	(2)	-	7.08	
016	0.01	0.54	0.04	2.97	2.32	0.13	0.03	0.03	1.23	5.87	1.13	21.42	2.38	0.00	7.00	
017	-	0.41	0.07	3.55	1.89	0.26	0.04	0.05	0.98	6.38	1.82	21.95	2.01	0.04	7.27	
018	-	0.46	0.03	4.52	1.14*	-	-	-	0.02	0.06	1.20	6.24	1.76	(2)	-	7.45
R 2	0.03	0.37	0.09	2.62	3.39	0.41	0.03	0.06	0.68	6.69	1.31	23.87	1.13	-	7.68	
R 13	0.05	0.36	0.10	2.85	3.30	0.13	0.02	0.11	0.62	7.26	0.74	23.90	1.10	-	7.54	
R 16	0.00	0.16	0.09	3.66	2.73	none	0.03	0.08	0.66	7.38	0.62	23.87	1.13	-	7.41	
F	0.04	0.13	0.18	1.94	1.33	0.07	0.01	0.08	2.16	5.84	2.10	17.63	4.27	-	5.94	
H	-	-	0.00	4.25	1.06	0.02	0.02	-	1.95	6.09	1.91	23.69	1.31	-	7.30	
K	-	0.12	0.08	0.19	5.42	0.42	0.20	0.10	0.65	7.00	1.00	21.98	2.02	-	7.18	

† "Oct" = total of octahedral cations (including alkalis)

- 002: Cl 0.00
- 016: Li 0.02, Cr 0.00, P 0.00, Cl 0.00
- 017: Li 0.02, P 0.00, Cl 0.00

- F: Francis (1955) K: Kunitz (1930)
- H: Henderson (1931) R: Rabbitt (1948)

TABLE Ib

Gedrites: locations, donors and analysis

Specimen	Location	Donor	Analysis
001	Baile, Telemark, Norway	via Prof. R.G. Burns	*
002	Kongsberg, Norway	via Prof. R.G. Burns	Iskyl (1925)
003	Bancroft, Ontario, Canada	Prof. R.G. Burns	Tilley (1957)
004	Kuurila, Kalvola, Finland	Heisinki Yliopisto Kivimuseo	*
005	House of Vehmanperaa, Kalvola, Finland	Heisinki Yliopisto Kivimuseo	*
006	Traskåle, Perniö, Finland	Heisinki Yliopisto Kivimuseo	*
008	Bullbrook, Western Australia	BM(NH), BM 1932,1088	Simpson (1931)
009	Kitakami mountainland N.E. Japan	Prof. Y. Seki	Seki & Yamasaki (1957)
010	Glen Urquhart, Inverness, Scotland	BM(NH), BM 1955,319 (same as BM 1955,63)	* [Francis (1955)]
016	Orange area, Massachusetts, USA	Prof. P. Robinson	Robinson & Jaffe (1969), no. 134I
017	Orange area, Massachusetts, USA	Prof. P. Robinson	Robinson & Jaffe (1969), no. 134JX
018	Mason Mountain, North Carolina, USA	USNM, 92684	Henderson (1931); Papke & Ross (1970)

Notes

BM(NH): British Museum (Natural History), courtesy USNM: United States National Museum  
For 010 the original accession number given by Francis (1955) is BM 1955-63; this is the same as the specimen used here (Embrey, pers. comm.)  
Where \* is marked under "Analysis", microprobe analyses were performed by Mrs. A. Hall, British Museum (Natural History)

P.G. Embrey

### Introduction to results

The spectra of gedrites are presented in summary form in fig. 1, and peak parameters are summarized in Table II. Anthophyllite 002, from Law (1981), is included to link these results to those of the previous study.

Gedrite 003 is the '31.6% Fe anthophyllite' whose spectrum was reported at low resolution by Bancroft *et al.* (1966) and was also described briefly by Burns and Law (1970). Anthophyllite 002 is the '23% Fe anthophyllite' of Bancroft *et al.* (1966).

In general, gedrites have more Fe than anthophyllites and the hydroxyl absorption should be stronger for peaks B and C than for A and D. In practice, low-Al gedrites give spectra which follow this pattern, though absorption is weaker than in anthophyllites, in holmquistite (Wilkins *et al.*, 1970; Law and Whittaker, 1981), or in some clin amphiboles (such as the cummingtonite spectrum referred to earlier). High-Al gedrites have extremely weak hydroxyl absorption. Most gedrites are dark in colour (grey, dark green, black); this adds to the difficulty of obtaining spectra in the infra-red region, where they absorb strongly. Most spectra had to be determined with an attenuator in the reference beam. In comparing gedrite spectra with those of other amphiboles, it is important to stress that the same techniques of sample preparation, and similar quantities, were used for gedrites as for both anthophyllite (Law, 1981) and holmquistite (Law and Whittaker, 1981). The low absorption which will be described is a feature

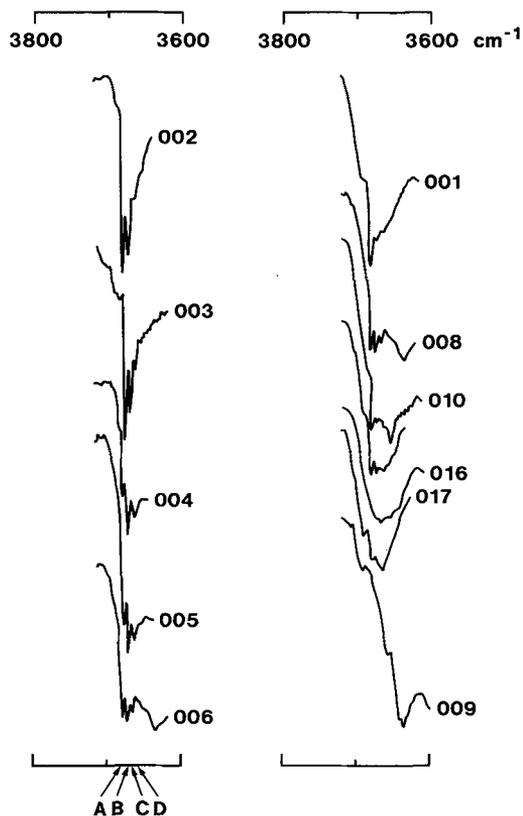


FIG. 1. Hydroxyl spectra of gedrites (drawn from the fast scan spectrometer trace). Vertical scale, transmittance.

TABLE II. Peak positions and half-widths in gedrites

	A	B	C	D	Other	A (mean)
001	3671.0(1.9) 3666.3(4.9)	3656.9(4.6)	3645.5(2.3)	—	E 3650.6(3.0)	3666.8
003	3670.1(1.5) 3666.3(4.9)	3654.4(4.3)	3639.2(5.4)	3626.0(3.8)	E 3647.0(3.6) F 3634.0(3.8)	3666.7
004	3664.6(4.5)	3650.1(5.3)	3634.1(5.8)	3616.3(3.8)	F 3625.1(2.8)	3664.6
005	3668.9(1.8) 3665.1(3.9)	3651.7(6.1)	3635.6(5.8)	3617.2(4.8)	F 3627.6(3.0)	3665.8
006	3669.0(1.9) 3664.9(4.7)	3650.4(6.0)	3635.7(6.1)	3625.3(1.4)	K 3654.4(4.3)	3665.3
008	3669.2(1.2) 3665.7(4.2)	3652.6(6.3)	3636.7(5.8)	—	K 3660.6(2.6) L 3643.7(2.4)	3666.0
009	—	—	—	[3618]	—	—
010	3665 (5)	3654 (5)	—	—	—	—
016	[3660]	[3650]	—	—	—	—
017	3666 (6)	3653 (6)	—	—	—	—
018	3662 (10)	3643 (9)	—	—	—	—

All values in  $\text{cm}^{-1}$ . Half-widths in parentheses after the position.

For peak A, two values in the first column indicate hyperfine components.

Values in brackets [ ] are not computer fitted.

requiring explanation and is not due to experimental limitations.

Where hydroxyl peaks can be resolved and their positions can be estimated, the frequencies obtained are comparable to those of other amphiboles. The separation between the major peaks A, B, C, D is the typical  $10\text{--}15\text{ cm}^{-1}$ , and most line-widths are in the range  $3.5\text{--}6\text{ cm}^{-1}$ . In some spectra, peak A in particular is fitted by a pair of peaks. This is taken to represent a residuum of the hyperfine splitting observed for anthophyllites (Law, 1981). The parameters of such closely overlapping peaks are individually unreliable; they do not behave independently in fitting, and often one peak acquires a narrow line-width or low intensity where the two peaks should be more nearly equal. Parameters of such peaks often show a strong negative correlation; the effect of this is that while the parameters individually are subject to considerable uncertainty their mean or sum may be much better defined, because the correlation coefficient contributes to the combined variance. Thus it is possible to obtain a reliable mean position despite uncertainties in computer fits of this kind.

Some qualitative information about site occupancies can be inferred from the spectra, but quantitative site occupancies calculated from the fitted peak intensities are not presented in this report.

Several determinations were made for each amphibole. I have chosen here to describe a single representative spectrum for each, rather than attempt to give mean results.

### Results

The spectrum of *gedrite 003*, shown in fig. 2 and Table III, is similar in its general features to that of anthophyllite 002 (Law, 1981). This orthoamphibole, however, is higher in Fe and lower in Mg than the anthophyllite. This is reflected in the intensity distribution of the hydroxyl

peaks, peaks C and D being more pronounced than for 002. Some hyperfine splitting of peaks is observed in this specimen. This is reflected in the computer fit. The highest frequency peak is rather small and narrow; this peak, and its dominant neighbour, are assigned as components of peak A. The two overlap closely and are not well resolved from one another by the fitting process, but the mean position obtained for peak A ( $3666.7\text{ cm}^{-1}$ ) should be reliable and is consistent with values for other ortho-amphiboles.

The smaller peaks to low frequency of peaks B and C do not have the abnormally small line-width of the high frequency component of A. They are treated as genuine minor peaks due to either Al or  $\text{Fe}^{3+}$  in the central sites. In this as in most gedrites, the formula unit indicates  $\text{Al} > \text{Fe}^{3+}$ . However, it is well established that Al in amphiboles preferentially enters M2. Papike and Ross (1970) assigned no Al to M1 or to M3 in their refinements. For this reason, the minor peaks are assigned as E ( $\text{MgMgFe}^{3+}$ ), below B, and F ( $\text{MgFe}^{2+}\text{Fe}^{3+}$ ), below C. A small shoulder below D could not be fitted, but indicates the presence of peak H ( $\text{Fe}^{2+}\text{Fe}^{2+}\text{Fe}^{3+}$ ). The alternative assignment involving Al, as L ( $\text{MgFe}^{2+}\text{Al}$ ) and M ( $\text{Fe}^{2+}\text{Fe}^{2+}\text{Al}$ ), would raise the question why peak K ( $\text{MgMgAl}$ ) is not observed when  $\text{Mg} > \text{Fe}^{2+}$  both in the overall composition and, from the relative intensities of the major peaks, in M1 and M3.

The maximum optical density value ( $y$  scale in the figures) for 003 is about 0.35. This is similar to the value for anthophyllite 002, 0.40, but much less than for the high-Mg anthophyllites, which approach 1.0 (Law, 1981).

*Gedrite 004* is typical of high-Al gedrites in that the hydroxyl peaks are of very low intensity. The maximum optical density is about 0.1. The spectrum can be fitted as a simple combination of the four major peaks (in some spectra, peak D could not be fitted), plus a fifth assigned as F. The low absorption means that to attempt more detailed fitting would be to over-interpret the data, and even this fit must be interpreted with caution.

*Gedrite 005* also exhibits residual hyperfine splitting of peak A. Peaks A, B, and C are well resolved. Peak D is present as a discernible shoulder, but in computer fitting its estimation is subject to a large uncertainty due to uncertainty in drawing the baseline and to the limitations of the computer fitting process. There is a small shoulder visible, which can be fitted, to low frequency of peak C: this is assigned as F, preferring an  $\text{Fe}^{3+}$  assignment to one with Al for reasons similar to those given for 003.

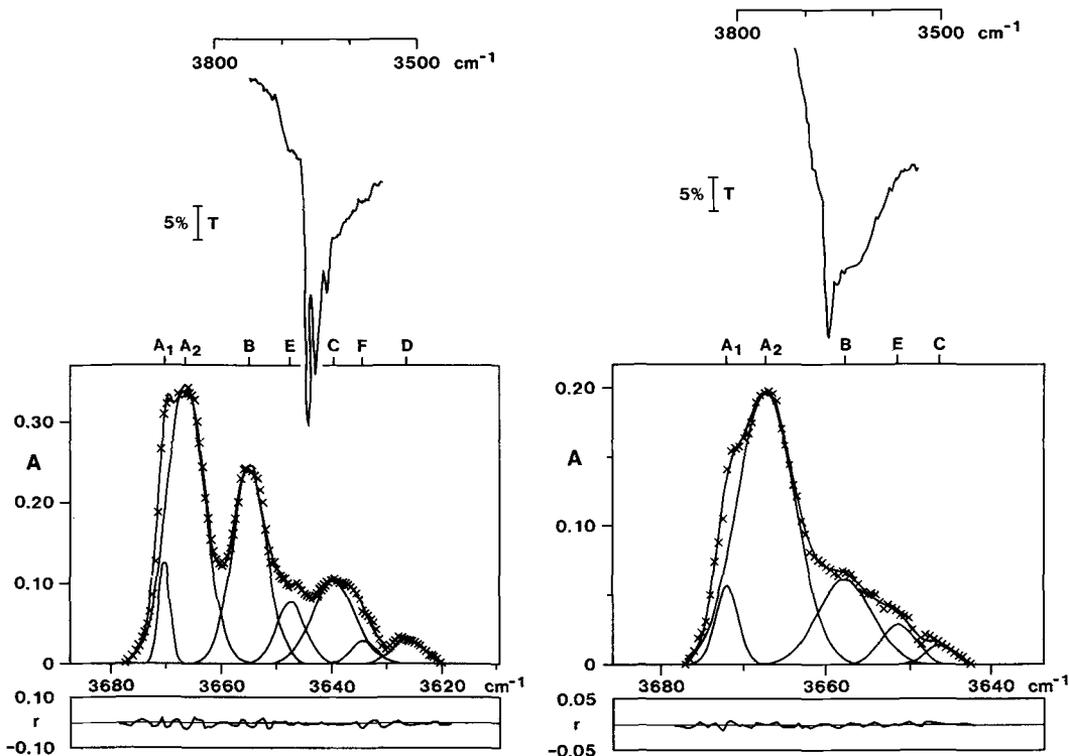
For *gedrite 006* the highest frequency major peak is estimated as a pair of overlapping peaks, but neither of these is narrow as in previous spectra. This specimen has high Al, and the Traskbøle analysis of Eskola (1936) is with zero  $\text{Fe}^{3+}$ , so it seems reasonable to assign the lower frequency peak of this pair as K and the higher as A. Two peaks are also estimated under the second absorption maximum, again a departure from the pattern shown by other gedrites: the second of these peaks can be assigned as L.

The hydroxyl spectrum of *gedrite 001* (fig. 3 and Table IV) is less intense. The maximum optical density value is about 0.2. Here the hydroxyl fine structure is superimposed on a steeper baseline than in any of the previous spectra, and the baseline itself has a more regular line

TABLE III. *Infra-red spectrum of gedrite 003*

Peak	Position	Half-width	Intensity
A <sub>1</sub>	3670.1	1.5	0.047
A <sub>2</sub>	3666.3	4.9	0.427
B	3654.4	4.3	0.264
C	3639.2	5.4	0.137
D	3626.0	3.8	0.030
E	3647.0	3.6	0.070
F	3634.0	3.8	0.025

Notes: 1. Position and half-width in  $\text{cm}^{-1}$ .  
2. Intensities normalized.



FIGS. 2 and 3. FIG. 2 (left). Hydroxyl spectrum of gedrite 003. The upper part of the diagram shows the low resolution (fast scan) spectrometer trace, as in fig. 1. The lower part shows the corrected hydroxyl absorption with computer-fitted peaks. Crosses represent the measured points. Vertical scales: upper diagram, percent transmittance (T); lower diagram, absorbance (A) with residual (r) in absorbance units. FIG. 3 (right). Hydroxyl spectrum of gedrite 001 (as fig. 2).

shape. The hydroxyl peaks are less clearly resolved, peak A being the only distinct one. This specimen marks an intermediate point between low-Al and high-Al gedrite spectra.

A number of different fits were attempted to this spectrum. The only reasonable one, shown here, estimated two components to peak A in the now familiar pattern, and three peaks in the remainder of the absorption. The simplest interpretation assigns these latter as peaks B, E, and C in order of decreasing frequency.

For *gedrite 008* the peaks are a little more intense and a hyperfine component is fitted in peak A; this, of several

TABLE IV. *Infra-red spectrum of gedrite 001*

Peak	Position	Half-width	Intensity
A <sub>1</sub>	3671.0	1.9	0.073
A <sub>2</sub>	3666.3	4.9	0.650
B	3656.9	4.6	0.194
C	3645.5	2.3	0.022
E	3650.6	3.0	0.061

Notes: as for Table III.

determinations, was the only spectrum of this gedrite which could be fitted. The fit requires minor peaks between A and B as well as below B, and for this reason the preferred interpretation involves Al rather than Fe<sup>3+</sup> (though, in view of the low absorption, it is unwise to place too much weight on this result). A small shoulder to low frequency of peak C may represent peak M, but the attempt to fit could not be justified. The spectrum is shown in fig. 4 and Table V. This is the last gedrite to give results which can be interpreted with any certainty.

The Glen Urquhart *gedrite 010* shows weak absorption to which no more than two peaks could be fitted (assigned as A and B). The surficial chlorite may affect the spectrum, contributing extra hydroxyl groups. The baseline is steep and has a sharp minimum.

The spectrum of *gedrite 017* is similar to that of 010, which has somewhat similar composition, but without the steep underlying baseline. A rough fit to two peaks was obtained.

*Gedrite 016* is the first of the two specimens for which X-ray site occupancies determined by Papike and Ross (1970) allow calculation of what the spectrum ought to look like (as outlined for holmquistite by Law and Whittaker, 1981). Assuming all Fe to be Fe<sup>2+</sup>, calculated intensities are: A, 0.274; B, 0.445; C, 0.239; D, 0.042. The

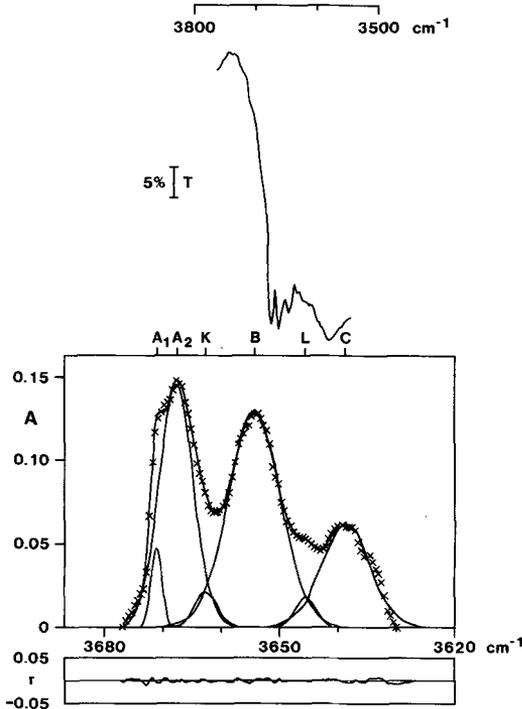


FIG. 4. Hydroxyl spectrum of gedrite 008 (as fig. 2).

probable presence of  $Fe^{3+}$  will modify these values. The actual spectrum, shown in fig. 5, has no clear hydroxyl absorption. Peaks are discernible but extremely weak. The maximum absorption is at about  $3650\text{ cm}^{-1}$ ; this agrees with the calculations above which show that peak B should have the highest intensity. Peak A may be identified with a shoulder at about  $3660\text{ cm}^{-1}$ . The underlying baseline falls to a minimum within the region of normal hydroxyl absorption, but it is quite clear from the spectrum that this is not a hydroxyl absorption in the same sense.

For *gedrite 018*, the X-ray site occupancies of Papike and Ross (1970) give the following predicted intensities: A, 0.697; B, 0.268; C, 0.034; D, 0.001. In the actual spectrum, absorption is again low but some fitting is possible. Two peaks below  $3680\text{ cm}^{-1}$  are estimated, and assigned as A and B which are expected from the X-ray data to be the most intense. Again the minimum of the underlying baseline is within the hydroxyl region. There is also a noticeable broad absorption estimated by the computer at about  $3690\text{ cm}^{-1}$ . Shoulders or peaks at about this frequency can be seen in the spectra of many of the gedrites (see fig. 1). As discussed later, they may originate from unit cells with occupied A sites. For 018, the only one for which any quantitative estimate could be made, the relative intensity of the high frequency peak is somewhat under 0.5. This value compares well with the analysis figure of 0.48 Na per formula unit.

The unusual *gedrite 009* has a spectrum with a steep baseline whose minimum is at about  $3570\text{ cm}^{-1}$ .

TABLE V. Infra-red spectrum of *gedrite 008*

Peak	Position	Half-width	Intensity
A <sub>1</sub>	3669.2	1.9	0.030
A <sub>2</sub>	3665.7	4.9	0.315
B	3652.6	6.3	0.416
C	3636.7	5.8	0.187
K	3660.6	3.0	0.029
L	3643.7	2.4	0.029

Notes: as for Table III.

Hydroxyl absorption is extremely weak, though discernible, and no attempt was made to fit the data. The only major peak to be expected is peak D, and correspondingly the hydroxyl absorption has its minimum at about  $3618\text{ cm}^{-1}$ . As in 018, there is a peak at about  $3690\text{ cm}^{-1}$ ; the formula unit shows Na = 0.36.

Discussion

*Absorption intensities.* A striking feature of the overall study of the orthoamphiboles is the way in which hydroxyl absorption intensities decrease from anthophyllite to high-Al gedrite. There are indications that oxidation ( $Fe^{2+} + OH^-$  to  $Fe^{3+} + O^{2-}$ ) may have reduced the absorption due to Fe in the central sites: estimates of Fe in  $2M1 + M3$  in gedrites from hydroxyl spectra are consistently

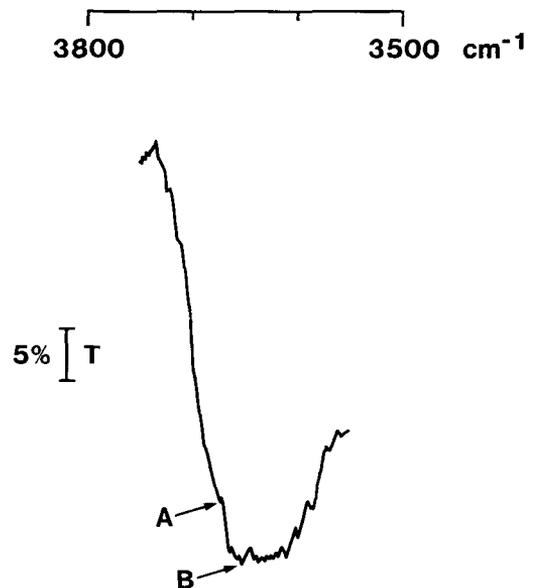


FIG. 5. Hydroxyl spectrum of *gedrite 016* (transmittance diagram only).

below those from Mössbauer spectroscopy (Law, unpubl.). Part of the problem arises from the dark-mineral colours. It is particularly disappointing that the two Orange area gedrites, for which detailed structural information is available, give such low absorption intensities.

*Hydroxyl peak parameters.* Gedrite hydroxyl spectra reveal some traces of the hyperfine splitting of absorptions described for anthophyllites, in the A peak where a small peak is common to the high frequency side of the main fitted Gaussian. Peak positions (using mean values for peak A) across the series are consistent, but the spread of values increases from A to B to C to D. This is because the values for C and D come from the much less reliably resolved gedrite spectra, and there are also fewer values than for A and B.

Fig. 6 shows the (weighted mean) position for peak A in gedrites, and for the anthophyllites of Law (1981), plotted against the total Fe and the total Al contents of the amphiboles. It is clear that

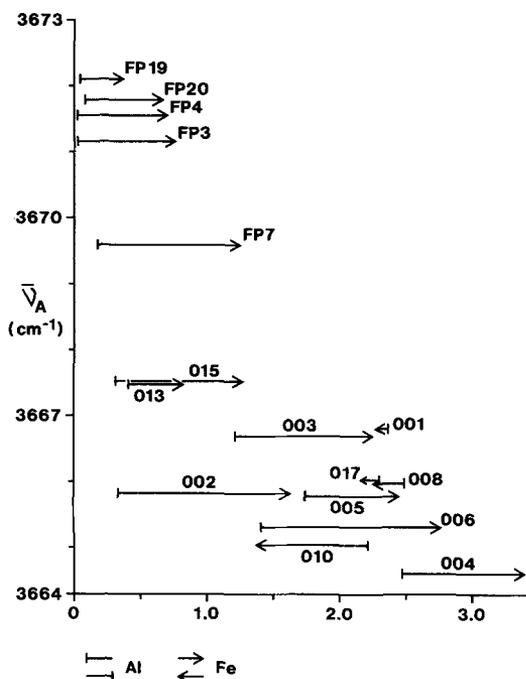


FIG. 6. Plot of the mean position of peak A ( $\bar{\nu}_A$ ) against total Fe and total Al per formula unit. Includes data for anthophyllites from Law (1981); specimens marked 'FP' are described by Fabries and Perseil (1971). Arrows join values for Al (bar end) to values for Fe (arrow end) for same specimen; anthophyllites plot in the upper part of the diagram and gedrites in the lower. Frequency values for O17 and O10 from computer fitting are approximate only.

the frequency of peak A decreases with increasing Fe or Al. There appear also to be two identifiable trends within the series, one corresponding to the gedrites and one to the anthophyllites. This is clearer in the case of Al, which is to be expected since there is major variation in Al between the anthophyllite and gedrite series but less variation in Fe. Uncertainties in the analyses of some specimens obscure the trends but it is clear that in both anthophyllites and gedrites peak frequency falls as Fe and Al increase, and that in gedrites the decrease is less sharp than in anthophyllites. A similar plot for peak B shows much greater scatter although again frequency falls as both Al and Fe increase. For peaks C and D data are fewer and less reliable, and these were not plotted.

Where multiplet structures are fitted, line-widths cannot be estimated. For well-estimated single peaks the line-widths are in the range 3.5 to 6.5 cm<sup>-1</sup> across the orthamphibole series.

*High frequency peaks.* A peak or shoulder around 3690 cm<sup>-1</sup> is observed in most gedrite spectra, and fitted in the spectrum of gedrite O18. Rowbotham and Farmer (1973) have discussed the effect of A-site occupancy on clinoamphibole spectra. Peaks in phlogopite-biotite micas have been shown to be shifted to 3710–20 cm<sup>-1</sup>, compared to 3677 cm<sup>-1</sup> in talc, by the presence of K in interlayer sites (references cited by Rowbotham and Farmer). Synthetic (Na, K) richterites examined by these authors exhibited peaks at 3728 cm<sup>-1</sup> (Na at A) and 3672 cm<sup>-1</sup> (vacant A, typical amphibole frequency), and natural clinoamphiboles showed complex high-frequency bands in the range 3690–710 cm<sup>-1</sup> (compare the spectra shown in fig. 1). It seems likely that similar effects are at work in gedrites. The relative intensity of the high-frequency peak for O18 is consistent with this interpretation. That for O09, although not computer fitted, appears to be of appropriate intensity also.

In any estimation of site occupancies this must be taken into account; however, in practice gedrites which have significant high-frequency absorption also have generally poor spectra and qualitative results would be of limited reliability.

*Baseline.* Another noticeable feature is the change in the underlying baseline from anthophyllite to gedrite. In anthophyllites it is fairly flat, and it is not particularly difficult to estimate its position in order to separate out the hydroxyl absorption. In gedrite spectra the baseline is much steeper, a trend exaggerated by the necessity of using an attenuator in the reference beam of the spectrometer (which has no effect, however, on the numerical calculation of absorption intensity). The baseline may have a definite minimum within the

hydroxyl region. It is difficult to estimate where it meets the spectrum, because this is in the region of the tail of peak D (if present), and uncertainty in baseline affects estimation of peak D more than of other peaks.

#### Conclusion

In this report I have presented qualitative features of the hydroxyl spectra of gedrites, which complement the earlier report of anthophyllite spectra. Data are now available for all the ortho-amphiboles (anthophyllite, gedrite, and holmquistite). I have attempted only limited interpretation at this stage.

Several clear trends can be identified across the anthophyllite-gedrite series. In anthophyllite spectra, hyperfine splitting of the A peak (the dominant one in the spectra) is observed, but as Fe (and Al) increase this is obscured although its effects are still seen in gedrite spectra and must be taken account of in computer fitting. Gedrites low in Al give spectra which are the most directly comparable to those of clinoamphiboles, showing the four major peaks in a pattern whose intensities reflect the composition of the specimen. Gedrites high in Al (and in Na, which may be the more directly important factor since the A site is close to the H of the O-H group) give hydroxyl absorptions of very limited intensity and only limited information can be obtained from these. Such spectra also have a sharper, steeper absorption underlying the hydroxyl fine structure.

In anthophyllites, the frequency of the A absorption (MgMgMg) decreases with increasing Fe content. In gedrites a similar but less sharp trend is observed. Similar behaviour follows increasing Al content.

*Acknowledgements.* I should like to thank the Inorganic Chemistry Laboratory and the Department of Pharmacology, University of Oxford, and the University Chemical Laboratory, University of Kent at Canterbury, for the use of infra-red spectrometers; the donors of specimens who are acknowledged in Table I; the Burdett-Coutts Foundation for a postgraduate studentship; the British Museum (Natural History) for microprobe analyses of nos. 001, 004, 005, 006, 008, and 010, through Dr S. J. B. Reed; Clare Pope, who drew the figures; and numerous people, not least Dr E. J. W. Whittaker, for discussion throughout the work.

#### REFERENCES

- Bancroft, G. M., and Burns, R. G. (1969) *Mineral. Soc. Am. Spec. Paper*, **2**, 137-50.
- Maddock, A. G., Burns, R. G., and Strens, R. G. J. (1966) *Nature*, **212**, 913-15.
- Barker, F. (1961) *U.S. Geol. Surv. Prof. Pap.* **424C**, C336-8 [cited by Papike and Ross, 1970].
- Borg, I. Y. (1967) *Mineral. Mag.* **36**, 583-90.
- Burns, R. G., and Greaves, C. (1971) *Am. Mineral.* **56**, 2010-33.
- and Law, A. D. (1970) *Nature*, **226**, 73-5.
- and Strens, R. G. J. (1966) *Science*, **153**, 770-6.
- Des Cloizeaux, A. L. O. L. (1877) *C.R. Acad. Sci. Paris*, **84**, 1473-5.
- Eskola, P. (1914) *Bull. Comm. géol. Finlande*, **40**, 169-77.
- [with T. Kervinen] (1936) *Ibid.* **115**, 475-87.
- Fabries, J., and Perseil, E. A. (1971) *Bull. Soc. fr. Minéral. Cristallogr.* **94**, 385-95.
- Francis, G. H. (1955) *Mineral. Mag.* **30**, 709-16.
- (1956) *Ibid.* **30**, 173-86.
- Heinrich, E. W. (1950) *Am. Mineral.* **35**, 764-71.
- Henderson, E. P. (1931) *Ibid.* **16**, 563-8.
- Iskyul, V. (1925) [*Experimental investigations in the province of the chemical composition of the silicates*, Petrograd, 1917]. Seen in *M.A.* **2**, 207.
- Kunitz, W. (1930) *Neues Jahrb. Mineral. Abh. A*, **60**, 171-250.
- Law, A. D. (1976) In *The Physics and Chemistry of Minerals and Rocks*, Strens, R. G. J. (ed.), Wiley, 677-86.
- (1981) *Bull. minéral.* **104**, 423-30.
- and Whittaker, E. J. W. (1981) *Ibid.* **104**, 381-6.
- Mason, B. (1953) *Am. Mineral.* **38**, 862-5.
- Papike, J. J., and Ross, M. (1970) *Ibid.* **55**, 1945-72.
- Pisani, F. (1977) *C.R. Acad. Sci. Paris*, **84**, 1509-12.
- Rabbits, J. C. (1948) *Am. Mineral.* **33**, 263-323.
- Robinson, P., and Jaffe, H. W. (1969) *Am. J. Sci.* **267**, 389-421.
- Ross, M., and Jaffe, H. W. (1971) *Am. Mineral.* **56**, 1005-41.
- Rowbotham, G., and Farmer, V. C. (1973) *Contrib. Mineral. Petrol.* **38**, 147-9.
- Seki, Y., and Yamasaki, M. (1957) *Am. Mineral.* **42**, 506-20.
- Simpson, E. S. (1931) *J.R. Soc. West. Austral.* **17**, 137-49.
- Stout, J. H. (1971) *Am. Mineral.* **56**, 212-24.
- (1972) *J. Petrol.* **13**, 99-145.
- Strens, R. G. J. (1974) In *Infrared spectra of minerals*, Farmer, V. C. (ed.), Mineral. Soc. monograph 4, 305-30.
- Tilley, C. E. (1957) *Am. Mineral.* **42**, 412-16.
- Wilkins, R. W. T., Davidson, L. R., and Ross, M. (1970) *Contrib. Mineral. Petrol.* **28**, 280-7.