1066

A chondrodite-humite-spinel marble from Sørfinnset, near Glomfjord, northern Norway

By R. BRADSHAW and B. E. LEAKE

Dept. of Geology, The University, Bristol 8

[Read 17 September 1964]

Summary. A chemical and modal analysis of the marble, together with chemical analyses of the coexisting spinel and the chondrodite-humite mixture are given. The spinel, a $8\cdot101\pm0\cdot001$ Å, $n\cdot731\pm0\cdot003$, is much richer in iron (Niggli's mg $0\cdot90$), than the humite mixture (mg $0\cdot99$), which agrees with the only previous analysis of a coexisting spinel and humite mineral. It was not possible to separate the two humite minerals from each other and analyse them, but the analysis of the mixture shows less iron than any previously analysed chondrodite or humite; the composition is very near to that of humite although the mixture contains at least 50 % chondrodite. It is pointed out that there are serious discrepancies between the chemical analyses of some of the humite minerals contain irregular numbers of olivine and Mg(OH,F)₂-TiO₂ layers would fit the available chemical analyses of the humite minerals very well but more structural work is needed as the present scenty X-ray results do not confirm this view. It is suggested that Ti substitution in the humite minerals is primarily controlled by the availability of F in the rock.

THE analysed marble is a member of the Melöy group of metamorphosed Eocambrian and Lower Palaeozoic rocks in the Glomfjord area of northern Norway (fig. 1). The rocks, which are dominantly psammitic in the lower part of the sequence and pelitic with subordinate marbles, calcareous schists, and psammites in the upper part, have undergone amphibolite-facies metamorphism. No detailed petrological account of the Melöy group has yet been published but a number of descriptions can be found in unpublished theses (Ackermann, 1960; Walton, 1959; Nicholson, 1960).

An outline of the structure of the area and of its general geology has been given by Hollingworth *et al.* (1960), by Nicholson and Walton (1963), and by Rutland *et al.* (1960). Near Sørfinnset the Melöy group is in contact with the Bjellåtind granite, which is a small mass associated with the Glomfjord granite further to the south. These granites have contacts, banding, and schistosity concordant with their metasedimentary envelopes and it is believed that the concordancies were produced during early fold movements. It is thought that the granites are essentially of Pre-Cambrian age and that there has been only a little reworking and selective mobilization to give local granite veins and pegmatites. There are no large masses of intrusive granite in the Sørfinnset area and the analysed marble is several hundred feet above the Bjellåtind granite. Under the marble is a thin quartzite and under this is a thick garnet-biotite-muscovite-quartz-plagioclase schist,



FIG. 1. Map of the Sørfinnset area, northern Norway, showing the location of the analysed specimen and its geological setting.

containing large, irregular muscovite, tourmaline+albite pegmatites. A hornblende-clinozoisite-sphene-apatite-microcline-plagioclase-quartz rock occurs above the marble. Humite minerals are often found in this marble along the strike but not in such large amounts as at the locality from which the analysed specimen came.

Petrography and chemistry of the marble. The rock has a granoblastic, reticular fabric in which calcites of mean grain diameter about 1 to 2 mm enclose the chondrodite-humite, spinel, brucite, and pyrrhotine,

all of which have an average grain diameter of about 0.2 mm except the brucite which averages 0.05 mm. The pyrrhotine is formed of perfect hexagonal plates. The calcite generally has twin lamellae, while about half the humite mineral grains show twin lamellae in a thin section if a universal stage is used. The chondrodite and humite are intimately associated and are often interleaved with (001) as a common plane of junction. Neither the spinel nor the pyrrhotine show any association with each other nor with the chondrodite-humite. Brucite replaces both humite minerals but some of the brucite may be primary.

Table I gives the chemical and modal composition of the marble together with the chemical analyses of the spinel and humite mixture from the marble. Except for the F determinations the chemical analyses were carried out by the method of Riley (1958*a*) after drying the powders at 110° C. Comparison of the modal analysis and a molecular norm (table I) shows good agreement of the mode and the chemical analysis but reveals that there is probably a slight deficiency of silica and carbon dioxide in the chemical analysis while it is probable that the modal analysis underestimates the spinel content thus accounting for the excess alumina and some of the excess magnesia in the chemical analysis. It can also be deduced that there is a small amount of soda in the calcite and probably more than 1% of magnesia as well. Both these elements, in these amounts, are common in calcites in marbles.

The original rock was evidently a limestone with a little dolomite and a small amount (about 5 %) of clay material, which provided the silica and alumina, the latter being just sufficient to give a positive al-alk value compared with the usual slight negative value obtained from completely pure limestones and dolomites. The very low potash suggests that the clay was a montmorillonite. It is believed that the fluorine and the sulphur were originally present in the limestone because their amount is similar to that found in unmetamorphosed limestones (Rankama and Sahama, 1950, p. 764; Pugh, 1956). There was sufficient dolomite to react with all the clay material to give chondrodite, humite, and spinel and leave a little magnesia over to enter the calcite.

Mineralogy

The spinel forms pale green rounded grains. The analysis shows an excellent balance between the trivalent and divalent groups with an excess of only $0.11 \% Al_2O_3$ which is probably partly the cause of the high summation of the analysis. An X-ray spectrographic analysis

	I	5	3		4		5	9		5	
SiO_2	2.44	35-82	0.65	$\mathbf{S}_{\mathbf{i}}$	0.016	si.	3.7	Calcite	90.62 ± 0.6	Calcite	87.38
AI_2O_3	1.58	0.22	68.06	Τi	100.0	al	ŀ₄	Chondrodite-	7.98 ± 0.6	Chondrodite-humite	7.98
e ie								humite		Spinel	0.85
TiO ₂	0.06	0.57	0.13	Al	1-932 \ 1.00	, fi	15.2	Spinel	0.85 ± 0.2	Fe ² for pvrrhotine	0.12
Fe_2O_3	0.06	0.34	2.70	Fe^{3+}	0.049 / 1.92	ں م	82.8	Pvrrhotine	0.25 ± 0.1	Brueite	0.98
F_{eO}	0.28	0.50	2.85	Fe^{2+}	0.058	alk	9.0	$\tilde{Brueite}$	0.28 ± 0.1	Excess or deficient atoms	
MgO	6.41	$58 \cdot 20$	25-75	Mn	0.001	ti.	0-05			Si	-0.33
CaO	50.01	0.27	0.00	M_{g}	0-926 0.95	р Д	0.00		89.98	Ē	0.09 + 0.09
Na_2O	0.22	0.12		Zn	(800.0	, ×	0.05			Al	66.0+
K_2O	0.02	0.02				mg	0.97			Fe ³	0.0+
MnO	0.02	0.02	0.04			al-a	lk 0-8			$\rm Fe^2$	+ 0.03
2nO			0.42							Mo	+ 1.76
$P_{2}O_{5}$	0.01	0.02								Ca Ca	10.58
H_0.H	0.34	1.80								Na	10.35
Ŀ.	0.22	3.32								3	
co₂	38.80	00-0									100-00
	100-47	101.22	100.60								
$0\equiv \mathbf{F}$	0.09	$1 \cdot 40$									
	100.38	99-82									
I. Cho	ndrodite	e-humit	e-spinel	marble	e (N418) fr	om 3]	km east o	of Sørfinnset, ne	ar Glomfjore	l, northern Norway. Analy	ysis by
а. 2 2	i. Leak	e except	F which	ı is by	W. H. Her	dsman.	į		, ,		
2. Cho 3. Spir	nel from	e-numr the ma	a mixtui rble (N4	18, n	1 the marble $1 \cdot 731 + 0 \cdot 00$	э (N412 03: а 8	5). UL less	than 0·10 %. A 01 Å. Cr is less	Analyst: B. E than 500 mm	l. Leake. n Anelyst, R F Leebe	
4. Ato	mic rati	ios of th	e spinel	analysi	is to 4 oxyg	en.	, , ,			NUMBER OF STATISTICS	
5. Nigi	gli num	bers of a	analysis	.							
6. Moo	lal anal	ysis of t	the marb	le (N4.	18). 6000 p	oints v	vere coun	ted and for this	number ± 2	times standard deviation v	alue is

TABLE I

- given. This is purely the statistical counting error and does not include errors such as how representative the slides counted
- were of the analysed rock. 7. A molecular norm of analysis 1. Chondrodite-humite and spinel calculated to modal volume and analysed composition. All the $\rm CO_2$ calculated into calcite. Fe^a allocated to modal pyrrhotine of determined composition Fe₄₈S₅₂.

gave less than 500 p.p.m. Cr. The silica (0.65 %) is definitely largely contained in the spinel and is not due to contaminating minerals as the analysed powder was at least 99.9 % pure, being checked both optically and by X-rays, and as an added precaution it was exposed to $HF-HClO_4$ for several hours. The refractive index is 1.731 ± 0.003 and the cell-size $a 8.101 \pm 0.001$ Å. Different values of the refractive index and cell-size for the pure end-members have been reported by different workers (Deer, Howie, and Zussman, 1962, vol. 5, p. 56; Flinter, 1963, p. 195), and our values are practically within the range (n 1.733 to 1.740; a 8.089 to 8.111 Å) calculated for the composition 93.26 % MgAl₂O₄, 3.44 % FeAl₂O₄, 2.49 % Fe₃O₄, 0.81 % ZnAl₂O₄. It is probable that the cell-sizes of spinels depend not only on their composition but also upon their temperature of formation and thermal history (Hafner and Laves, 1961, p. 321; Clark, Ally, and Badger, 1931, p. 545). The physical properties are close to those determined by Bothwell and Hey (1958, p. 886) on a chlorospinel but the Sørfinnset spinel contains less Fe₂O₃ and TiO₂ and correspondingly more Al₂O₃. If all the Zn in the rock is concentrated in the spinel then using the modal analysis it is calculated that the rock must contain 22 p.p.m. Zn. This is less than the average value of 50 p.p.m. Zn quoted by Rankama and Sahama (1950, p. 713) for a typical unmetamorphosed limestone.

The composition of the pyrrhotine has been determined by measuring its 102 spacing, which is 2.0694 ± 0.0005 Å, and using the graph given by Arnold and Reichen (1962, p. 106), the composition is Fe_{47.6}S_{52.4}, which is within the range of composition of most natural pyrrhotines.

An X-ray diffractogram was made of the chondrodite-humite mixture free from any spinel, calcite, pyrrhotine, or brucite. The presence of abundant chondrodite and humite and a trace, not more than 5 %, of clinohumite was established but both olivine and norbergite were absent. A careful search of four thin sections on the universal stage resulted in the definite identification of only a single clinohumite grain. Specific identification of humite in the thin sections was made though this is surprisingly difficult because most of the untwinned grains have no cleavage and so it is optically impossible to prove them orthorhombic or monoclinic. That separate grains of humite exist was also confirmed by extracting an unusually large grain from the rock and carrying out a diffractometer scan, which showed nearly pure humite, but even this had a little admixed chondrodite. Thus of the humite minerals there are practically only chondrodite and humite present in the rock and in the separated mixture of humite minerals. Because of their similar physical properties and their intergrown nature it was not possible to separate these two humite minerals and so the material analysed was a mixture of the two. The proportions are difficult to estimate but from diffractograms of mixtures of pure humite and chondrodite (from other localities) it is certain that there is more than 50 % of chondrodite in the mixture and probably about 60 %. Because humite cannot usually be specifically identified in the thin sections it is not possible to point-count the chondrodite and humite separately. The number of twinned grains in the thin section that can be observed with a universal stage suggests very roughly about 50 % chondrodite but this does not include untwinned chondrodite. It is therefore probable that the mixture is about two-thirds chondrodite and onethird humite.

Twenty-three determinations of the $2V_{\gamma}$ by direct measurement between the optic axes of both humite and chondrodite gave results between 62° and 72° with 19 of the results being $65\pm3^{\circ}$. No consistent difference could be detected between the humite and the chondrodite grains and measurements on intergrown humite and chondrodite grains showed either no difference in 2V or else a difference within the experimental error, which is about $\pm2^{\circ}$. This determination is the lowest ever recorded for natural chondrodite which ranges from 2V 70-80° with some unreliable calculated 2V's extending down to 60°. Humites range in observed 2V from 65 to 81° so that the Sørfinnset humite is within the known variation of 2V but at the lower end of the range. The clinohumite grain gave $2V_{\gamma} = 70^{\circ}$ while 2V's have been recorded from 55° to 76° with one determination 'near 90°' (Larsen, 1928, p. 357).

The refractive indices of the three humite minerals show some variation but the following are the mean results, each with an estimated error of ± 0.003 :

Clinohumite				$\alpha 1.645$	β 1.657	$\gamma 1.676$	$2V_{\gamma} 70^{\circ}$
Humite .				1.637	1.650	1.670	65
Chondrodite	•	•	•	1.617	1.627	1.649	65

Deep yellow patches have a slightly higher refractive index than the paler parts of the same grains. The determined refractive indices are within the known range of all three humite minerals but the humite and chondrodite indices are distinctly high in view of the low Ti and the exceptionally iron-poor nature of the analysed humite mixture. They are only explicable if the Sørfinnset humite minerals are either exceptionally rich in (OH) relative to F or rich in forsterite relative to $Mg(OH,F)_2$ or if both possibilities are true, which is shown to be so by the chemical analysis. This is because brucite has a mean refractive index of about 1.59 whereas sellaite has a value of 1.38 and forsterite about 1.65. Thus any iron- and titanium-poor humite with a mean refractive index of 1.63-1.65 must be relatively rich in both forsterite and brucite and poor in sellaite.

The yellow colour of the humite and chondrodite is irregular, patchy, and often shows a distinct increase near to cracks and near to alteration to brucite. It is possible that the yellow colour may result from late alteration, possibly hydration, and in support of this suggestion is the fact that several slides that we have from Limecrest Quarry, near Sparta, Sussex Co., New Jersey, have chondrodite that has a strong yellow colour at the periphery of the grains but not such a strong colour within the chondrodite grains; this also suggests that the colour is partly the result of a marginal late alteration process.

There are several notable features about the chemistry of the chondrodite-humite mixture. It contains very little iron, the total content of $\text{FeO} + \text{Fe}_2\text{O}_3 + \text{MnO}$ is only 0.86 wt. %, which is less than any previously obtained value on any chondrodite, humite, or clino-humite and only one norbergite analysis is known that shows less iron (0.73 %; Larsen, Bauer, and Berman, 1928, p. 350). The previous lowest-iron-bearing chondrodite has only a little more iron and MnO (0.92 %; Sahama, 1953, p. 10) but no humite analysis has been reported with less than 2.22 % FeO (Penfield and Howe, 1894, p. 199) and this analysis did not report Fe₂O₃ or MnO. Both the Sørfinnset chondrodite and the humite must therefore be closer to the pure Mg end-members than any previously analysed natural chondrodite or humite.

The F content of the mixture, 3.32 %, is also remarkably low, for all the published chondrodite analyses have F between 4.01 and 8.62, and even humite usually has considerably more F, ranging up to 5.43 %, there being only two determinations lower than 3.32, one by Penfield and Howe (1894, p. 199) of 3.08 and another by Sahama (1953, p. 12) of 2.77. As a partial check on the F in the chondroditehumite mixture the F content of the marble was calculated from the modal amount of humite mineral and its F content, assuming that no other mineral is present that contains F. The determined value on the rock of 0.22 % F is within experimental error of the calculated value of 0.26 and does not suggest that the reported F in the chondroditehumite mixture is too low. Since (OH) partly replaces F in humite minerals the accuracy of the H_2O^+ determination is highly relevant, for the H_2O^+ value (1.80 %) is typical of chondrodite and humite and is not high, contrary to what might be expected with such a low F value. The H_2O^+ was determined by the method of Riley (1958b, p. 42) using an electric furnace at 1200° C and a stream of dry nitrogen. The result obtained is believed to be more accurate than results given by Penfield's method (1894, p. 30) though neither method is entirely satisfactory because of the uncertain role of F in forming HF. In addition the H_2O value was partially checked by weighing the loss on ignition and correcting for loss of F. An X-ray spectrographic examination of the mixture showed that there was less than the detection limit of 0.10 % Cl present.¹ Thus the F in the analysed mixture is lower than in any previously analysed chondrodite and in all but two humite analyses while the (H_2O+F) total of 5.12% is also lower than any previously analysed chondrodite and there is only one humite analysis with lower (H_2O+F) (3.68%; Sahama, 1953, p. 12).

The analysed mixture is extremely rich in silica, 35.82 %, the highest published silica value for chondrodite being 34.50 % by Sjögren (1882, p. 113), while only two humite analyses, both by Penfield and Howe (1894, p. 199) contain more silica. The high silica and low F are significantly related, for the most silica poor member of the humite series is norbergite (SiO₂ ca. 28-29 %) while chondrodite, humite, and clinohumite possess progressively more silica as the proportion of F falls so that forsterite, which contains no F, has more silica (about 42 %) than any humite mineral. A plot of silica against F in the humite minerals shows this relationship and also makes clear that the silica and F content of the Sørfinnset chondrodite-humite mixture is very close to a statistically fitted line. It should be appreciated that the silica determination, which was made colorimetrically after fusion with NaOH, is independently determined from the H₂O and F and therefore the position of the mixture on fig. 2 is good evidence of analytical reliability. Moreover, the analysis agrees with the deductions made from the refractive indices. Thus for a humite mineral the analysed mixture is not abnormal but it is abnormal in having a composition near to that of humite when it is largely composed of chondrodite. The significance of this is discussed later.

The titania content of the chondrodite-humite mixture is not unusual for a chondrodite and is close to the average of all analysed chondrodites (fig. 3). The lack of Ti substitution in olivines and the fact that Ti does not readily accept fourfold coordination seems to rule out appreciable entry of Ti into the olivine layers in humites and so it is

¹ Scapolite occurs in some rocks at Sørfinnset.



FIG. 2. Plot of $H_2O + F + Cl$ wt % against SiO₂ wt. % for all analysed humite minerals.



FIG. 3. Plot of TiO₂ wt. % against $H_2O + F + Cl$ wt. % for all analysed humite minerals. There is a well-marked negative correlation between $H_2O + F + Cl$ and TiO₂ in clinohumites.

generally accepted that Ti in sixfold coordination replaces Mg in the $Mg(OH,F)_2$ layers, the charges being balanced by accompanying substitution of F or (OH) by oxygen. This hypothesis raises the question as to why the most titaniferous humite mineral is clinohumite as this has

the smallest number of Mg(OH,F)₂ layers of all the humites and should therefore have the least sites available for Ti to substitute into. Analysed clinohumites contain up to 5.40 % TiO₂ (Borneman-Starynkevich and Myasnikov, 1950, p. 138) (fig. 3) while the most titaniferous humite analysis published has 2.00 % TiO₂ (Sahama 1953, p. 12) and chondrodites do not exceed 1.27 % TiO₂ (Thiele 1940, p. 64), most of the available chondrodite analyses having less than 0.50 %; the only norbergite analysis with TiO₂ reported has 0.01 % (Sahama, 1953, p. 8). The reason why Ti substitution for Mg becomes more common with decreasing numbers of Mg(OH,F), layers is probably related to F deficiency in the rock. The formation of norbergite, chondrodite, humite, and clinohumite is progressively more favoured with diminution of available F. Should there be inadequate F even to form clinohumite, then Ti may replace Mg, allowing 2F- to be replaced by 20²⁻. Thus the eight published clinohumite analyses that have 1.50 TiO_2 wt. % or more (av. 3.42) do not exceed 1.02 % F (av. 0.53) whereas the six published clinohumites with less than 1.50 %TiO₂ (av. 0.77) contain up to 5.04 % F (av. 2.58). Accordingly, Ti not only increases from norbergite to clinohumite but also from F-rich to F-poor clinohumites.

Figs. 2 and 3 do not show sharply demarcated compositions for the humite minerals corresponding to the theoretical formulae: Mg(OH,F)2. Mg₂SiO₄ \mathbf{for} norbergite, $Mg(OH,F)_2.2Mg_2SiO_4$ for chondrodite, Mg(OH,F)₂.3Mg₂SiO₄ for humite, and Mg(OH,F)₂.4Mg₂SiO₄ for clinohumite. Thus if, following Sahama (1953, p. 25), the oxygen combined with Ti in TiO_2 is added into the OH+F, then for the forty-one published post-1900 humite group analyses there is appreciable overlap in the ratio of $4Si:(O_{Ti}+OH+F)$ for clinohumite (4:1.45-2.52) and humite (4:1.99-2.87) while many humites exceed the ratio of 4:2.71 found in the Sørfinnset mixture, which is close to the theoretical value for humite (4:2.66), not chondrodite (4:4). The range of both chondrodite $(4:3\cdot37-4\cdot80)$ and norbergite $(4:5\cdot95-8\cdot79)$ is also considerable. The anomalous position of the Sørfinnset mixture is paralleled by Sahama's (1953, p. 12) analysis of the Hermala humite which is almost identical with the theoretical composition of clinohumite.¹ If TiO_2 is not grouped with the $Mg(OH,F)_2$ layers the discrepancies from the theoretical values, particularly for the Hermala humite, which has 2.00 % TiO₂, become even more marked.

¹ It is interesting that the optical properties of the Hermala humite, $\alpha = 1.641$, $\beta = 1.649$, $\gamma = 1.672$, $2V_{\gamma} = 61^{\circ}$, are very similar to those of the Sørfinnset humite.

Although some of the spread of the results may partly reflect the presence of small amounts of admixed other humite minerals in the analysed specimens, this is unlikely to be a complete explanation because of the size of the discrepancies concerned, as Sahama (1953, p. 16) has pointed out. Thus he showed that the theoretical Si:(OH,F)ratio of 4:4.00 in chondrodite is only changed to 4:3.86 by an impurity of 10% of humite. Moreover, his new analyses (op. cit., pp. 8-14), although of material checked by X-ray analysis and shown to be completely pure, deviated very appreciably from the theoretical ratios of Si: $(O_{ri} + OH + F)$. Nor is it likely that the well-known difficulties of determining water and fluorine accurately are solely responsible for the discrepancies for not only do some of the analyses deviate very greatly from the theoretical compositions but some of the most discrepant analyses are the most recent and are by reliable analysts. It has already been shown that the Sørfinnset analysis has good agreement between the amounts of silica and water+fluorine. Although some substitution of Mg in the Mg(OH,F), layers by Al^{3+} and Fe^{3+} , in addition to Ti⁴⁺, enables some O to replace OH and F, the amounts of Al³⁺ and Fe³⁺ in humites are generally fairly small and so substantial replacement of OH and F by O seems to be ruled out. Moreover, this replacement cannot explain a few of the analyses, including three apparently excellent analyses of pure material (Sahama, 1953, p. 9) that contain too much $O_{r_i} + OH + F$ for the theoretical formulae, not too little. This raises the possibility that the departures from the theoretical formulae of the humite minerals might be more serious than can be ascribed either to contamination, analytical errors, or substitution of O for OH and F. One possibility is that sometimes humite minerals are found that contain irregular numbers of Mg(OH,F)₂-TiO₂ layers for a given number of Mg₂SiO₄ layers.

In order to test this theory chemically and compare the variation within the humite minerals all the available humite analyses were calculated to the common fixed basis of 4Si and the resulting theoretical formulae of the humite minerals on this basis are given with fig. 4. This enables the ratio of the number of $Mg(OH,F)_2$ -TiO₂ layers to the number of $4(Mg,Fe)_2SiO_4$ layers to be obtained. The cations, excepting Si and the eight bound in the $4(Mg,Fe)_2SiO_4$ layers, were plotted against the number of $O_{Ti}+OH+F$ anions, while to show the common spread of olivine analyses the twenty-one olivine analyses quoted by Deer, Howie, and Zussman (1962, vol. 1, p. 10) have also been plotted, after calculation to the same basis, but the trace of water found in olivine

1076

analyses has not been considered, as this is probably largely related to alteration of the olivine.

The plots tend to fall to the right of the theoretical line which may be partly due to a combination of low determinations of water, fluorine, and silica¹ together with the substitution of small amounts of Al, Ti,



FIG. 4. Cations in Mg(OH,F)₂-TiO₂ layers calculated on a constant basis of 4Si, and plotted against the number of $O_{Ti} + OH + F + Cl$ atoms also in these layers. On this basis norbergite, chondrodite, humite, and clinohumite have 8, 4, 2.66, and 2 $(O_{Ti} + OH + F + Cl)$ respectively per 4Si.

and Fe^{3+} for Si in the olivine layers, as small amounts of these elements are found in olivine. Except for this tendency the plots as a whole scatter greatly though generally the variation is parallel to a line joining the theoretical compositions and the mean of the plots of each humite member is close to the theoretical composition. Chemically these results would be admirably explained by stacking variable numbers of Mg(OH,F)₂-TiO₂ layers with variable numbers of olivine layers in

 1 Silica can easily be lost as ${\rm SiF}_4$ if special precautions are not taken (Sahama, 1953, p. 7).

the manner known to give heteropolytypism in the phyllosilicates. For thermodynamic and symmetry reasons it is likely that a marked tendency to approach the theoretical compositions of the humite minerals will exist so that most analyses should approach the theoretical proportions known to be present in many humites. But under suitable conditions perhaps other numbers of $Mg(OH,F)_2$ -TiO₂ layers may be interleaved between the olivine layers and vice versa, and if this is so

d	Ι		d	I		d	I	
*5.02	w	\mathbf{CL}	*3.39	m	С	2.43	w	н
*4·85	m	С	*3.31	w	н	2.42	w	С
4.72	vw		3.24	vw	\mathbf{CL}	2.41	w	$\mathbf{CL} + \mathbf{H}$
4·61	w	н	*3.03	\mathbf{ms}	С	*2.36	w	\mathbf{CL}
4.45	vw	\mathbf{CL}	2.99	vw	н	2.33	\mathbf{m}	С
3.99	w	С	2.88	vw	н	2.29	\mathbf{ms}	С
3.98	w	н	2.85	m	С	2.26	vs	C + H + CL
3.92	\mathbf{m}	н	2.76	\mathbf{s}	H+C+CL	2.19	vw	н
3.88	w	\mathbf{CL}	2.71	w	\mathbf{CL}	2.15	w	C+CL
3.72	m	С	*2·68	\mathbf{ms}	H + C	2.12	mw	$\mathbf{C} + \mathbf{H}$
3.71	m	\mathbf{CL}	2.62	\mathbf{ms}	C + CL	2.03	vw	С
*3·66	m	н	2.58	vw	H + C	1.88	vw	С
3.64	w	н	*2.55	w	\mathbf{CL}	1.74	\mathbf{vs}	C + CL + H
3.58	\mathbf{m}	С	2.52	s	C + CL	1.51	vw	$\mathbf{C} + \mathbf{H}$
*3·56	\mathbf{ms}	С	2.48	vw	С	1.49	\mathbf{ms}	H+CL
3.49	\mathbf{ms}	C + CL	*2.45	\mathbf{ms}	н	1.40	w	C + H

TABLE II. X-ray powder data for the Sørfinnset humite mixture

C-Chondrodite.

CL-Clinohumite.

H—Humite.

* Diagnostic spacings according to Sahama (1953, p. 46).

then significant departures of the cell parameters should occur from those found in the theoretical compositions. Van Valkenburg's (1961, p. 146) unsuccessful attempt to synthesize compositions corresponding to $5Mg_2SiO_4.MgF_2$ and $MgSiO_4.2MgF_2$ does not prove that other compositions might not be synthesized if the right conditions could be obtained.

Unfortunately we have been unable to discover whether significant changes in the cell parameters do occur, for no single crystal or detailed X-ray work has been published on the humite minerals since the original crystal structures were determined by Taylor and West (1928, 1929). Moreover, even the chemical compositions of the samples used by Taylor and West are unknown. Table II lists the d spacings of the Sørfinnset humite mixture down to 1.40 Å, calculated from measurements made on a number of diffractograms. An indication is also given of which humite minerals have a d spacing close to those recorded on the Sørfinnset mixture.

It can be seen that all the lines considered to be diagnostic of three of the humite minerals-chondrodite, humite, and clinohumite-are present. All lines with an I/I_1 value of 20 or greater, as tabulated on ASTM cards 12-527, 12-544, and 12-755 and 12-755a for chondrodite, clinohumite, and humite respectively, are present with the exception of 3.453, 3.430, and 2.744 for humite and 3.44 and 2.60 for clinohumite. Several weak lines listed on the ASTM cards were not recorded on the diffractograms. The line at 4.72 Å cannot be matched with any for the humite minerals and may well represent a trace of brucite, which has a very strong line at 4.77 Å. The four ASTM cards listed above, based on patterns for pure samples of the three humite minerals under discussion, show a total of at least 140 lines down to a spacing of 1.40 Å and several of these lines are given by reflections from two or more planes. There is no doubt therefore that many of the peaks on our diffractograms are composite and the measurements made on them must be used with caution. The d spacings for all three minerals correspond fairly closely with those already published being in almost every case within 0.01 Å. It is not possible therefore to deduce any structural changes from such small variations, which are within experimental error, and generally the results indicate that no major departures from the accepted cell parameters occur but they do not rule out the possibility of some randomly stacked layers being present.

Because of the overlap of the peaks it is also not possible to make sufficiently precise measurements from which to calculate cell sizes.

The resolution of the present unsatisfactory relationship between composition and structure in the humite minerals must be left unanswered, but it is clear that detailed X-ray work is urgently needed.

The Sørfinnset chondrodite-humite mixture has a higher mg, 0.99, (mg = MgO/(MgO+FeO+2Fe₂O₃+MnO)) than the associated spinel (mg 0.90), which agrees with the only other analysed coexisting pair known to us (Eckermann, 1922, p. 758), which is a chondrodite (mg 0.96) associated with spinel (mg 0.78). In both pairs the spinel is richer in iron than associated humite mineral. This agrees with the fact that while complete solid solution between Mg spinel and Fe spinel exists, no iron-rich humite minerals are known, the most iron-rich humite mineral so far described being a clinohumite containing only 14.25 % FeO and having an mg of 0.84 (Sjögren, 1894, p. 44). Any iron in a spinel-humite marble is therefore concentrated in the spinel. R. BRADSHAW AND B. E. LEAKE ON HUMITES ETC.

Acknowledgements. We wish to thank Dr. P. C. Wright for determining the Zn content of the spinel by X-ray fluorescence and Mr. Laker of Bristol Siddeley Engines for confirming the absence of appreciable Cr and Cl in the humite mixture. Professor Sahama kindly sent us some samples of pure, analysed humite minerals.

References

ACKERMAN (K. J.), 1960. Unpublished Ph.D. thesis, University of London.

ARNOLD (R. G.) and REICHEN (L. E.), 1962. Amer. Min., vol. 47, p. 105.

- [Вовмемам-Starynkevich (I. D.) and Муазмікоv (V. S.)], Борнеман-Старынкевич (И. Д.) и Мясников (В. С.), 1950. Доклады Акад. наук СССР, (Compt. Rend. Acad. Sci. URSS), vol. 71, р. 137.
- BOTHWELL (D. I.) and HEY (M. H.), 1958. Min. Mag., vol. 31, p. 886.
- CLARK (G. L.), ALLY (A.), and BADGER (A. E.), 1931. Amer. Journ. Sci., ser. 5, vol. 22, p. 545.
- DEER (W. A.), HOWIE (R. A.), and ZUSSMAN (J.), 1962. Rock-forming minerals. Longmans, London.
- ECKERMANN (H. VON), 1922. Geol. För. Förh., vol. 44, p. 381.
- FLINTER (B. H.), 1963. Amer. Min., vol. 48, p. 195.
- HAFNER (S.) and LAVES (P.), 1961. Zeitschr. Krist., vol. 115, p. 321.
- HOLLINGWORTH (S. E.) et al., 1960. 21st Internat. Geol. Congress, Part 19, p. 33.
- LARSEN (E. S.), 1928. Amer. Min., vol. 13, p. 354.
- ----- BAUER (L. H.), and BERMAN (H.), 1928. Ibid., p. 350.
- NICHOLSON (R.), 1960. Unpublished Ph.D. thesis, University of London.
- ------ and WALTON (B. J.), 1963. Norsk Geol. Tidsk., vol. 43, p. 1.
- PENFIELD (S. L.), 1894. Amer. Journ. Sci., ser. 3, vol. 48, p. 30.
- ----- and Howe (W. T.), 1894. Ibid., vol. 47, p. 188.
- PUCH (W. J.), 1956. Mem. Geol. Surv. U.K.: Mineral resources of Great Britain, vol. 37.
- RANKAMA (K.) and SAHAMA (Th. G), 1950. Geochemistry. Univ. of Chicago Press.
- RILEY (J. P.), 1958a. Anal. Chim. Acta, vol. 19, p. 413.
- RUTLAND (R. W. R.) et al., 1960. 21st Internat. Geol. Congress, Part 19, p. 43.
- SAHAMA (Th. G.), 1953. Annales Acad. Sci. Fennicae, ser. A. III, Geol.-Geogr., no. 31.
- SJÖGREN (Hj.), 1882. Zeitschr. Kryst. Min., vol. 7, p. 113.
- —— 1894. Bull. Geol. Inst. Uppsala, vol. 2, p. 44.
- TAYLOB (W. H.) and WEST (J.), 1928. Proc. Roy. Soc., ser. A, vol. 117, p. 517. —— 1929. Zeitschr. Krist., vol. 70, p. 461.
- THIELE (E.), 1940. Chemie der Erde, vol. 13, p. 64.
- VAN VALKENBURG (A.), 1961. Journ. Research Nat. Bureau Stand. A, vol. 65A, p. 415.
- WALTON (B.), 1959. Unpublished Ph.D. thesis, University of London.