

A contribution to the mineralogy of chloritoid.

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Summary Chloritoids from the Saxa Vord schists in the Shetland Isles and the Dalradian schists north of Stonehaven have been studied optically and chemically. In both cases monoclinic and triclinic crystals occur with $a = b$ in the monoclinic varieties. Twinning is common with twin axes [110] and [230]. The formula of chloritoid is considered in relation to the structure recently suggested by Brindley and Harrison (1952).

CHLORITOID has been recorded from several localities within the United Kingdom. It is well developed in the Shetland Isles, and in Scotland along a narrow belt of ground nearly 22 miles long extending from the coast north of Stonehaven to the valley of the North Esk. In England it has been recorded from the Tintagel area.

The present study is concerned with chloritoid occurring in the Saxa Vord Schists of Unst in the Shetland Isles (Read, 1934), and in the Dalradian Schists north of Stonehaven (Barrow, 1898; Harker, 1939; Williamson, 1953).

Occurrence and petrology. The geology of Unst has been described by Read (1934). He has shown that the island consists of several blocks separated by steep thrusts, the Saxa Vord schists forming part of the Saxa Vord block in the north of the island. The metamorphic history of these schists is as follows (Read, 1934): an early metamorphic phase resulted in the formation of andalusite-staurolite schists; this was followed by a retrogressive metamorphism, which gave rise to the now dominant chloritoid-kyanite schists. Later, thrusting resulted in the development of chlorite-muscovite schists around the margin of the block. Relict grains of staurolite are common in the chloritoid schists whilst andalusite has been pseudomorphed by sericite and kyanite; garnet, which is poorly developed, was considered by Read to have been coeval with andalusite and staurolite. The present study has shown that garnet formed after chloritoid, indicating that the chloritoid-producing retrogressive metamorphic phase was followed by a progressive phase (Snelling, 1954). The chloritoid occurs as rectangular

porphyroblasts about 1 mm. in length with random orientation. Although flakes of this mineral commonly grow on staurolite grains the direct replacement of staurolite by chloritoid has not been observed. Inclusions are remarkably few, consisting mainly of magnetite and occasionally quartz. The analysed chloritoid was separated with some difficulty, and a complete separation from the fine-grained muscovite that forms the groundmass of these schists proved impossible. However, an attempt has been made to correct the analysis for this impurity.

In the coast section between Stonehaven and Aberdeen, chloritoid first occurs about half a mile north of the Highland Border Fault. Anderson (1942) considers that the Dalradian in this section consists essentially of a psammitic group composed of quartzites and schistose grits, and an older pelitic group of mica schists with biotite, chloritoid, or staurolite, depending on the degree of metamorphism. He suggested that the psammites occur in synclines and tentatively correlated them with the Ben Ledi grits, whilst the pelites were correlated with the Pitlochry schists.¹ The chloritoid schists from this area are much coarser in grain size than the Saxa Vord schists. Chloritoid occurs as prominent porphyroblasts often 5 mm. in length. In this section they are extremely ragged and riddled with quartz inclusions. Alteration is common, both chloritoid and chlorite being replaced by a mixture of kaolinite, chalybite, and limonite. The characteristic mineral assemblage is chloritoid, chlorite, and muscovite. Biotite is absent and garnet only occasionally found, though the rocks lie well within the garnet zone of Barrow (1912). Because of the numerous quartz inclusions the separation of a pure sample of chloritoid was impossible, but an attempt has been made to correct the analysis for the excess of silica and is discussed below.

Analyses of the schists from which the two chloritoids were separated are given in table I. The most noticeable difference between the two rocks is the higher Niggli *mg* value of the Stonehaven schist, probably reflecting the high chlorite content of these rocks.

Optical properties. Both analysed chloritoids show the usual pleochroic scheme, with α = green, β = slate blue, and γ = pale yellow; other optical properties are (α , β , and $\gamma \pm 0.003$; $2V \pm 2^\circ$):

Stonehaven	α 1.721	β 1.725	γ 1.728	$\gamma - \alpha$ 0.007	$2V_\gamma$ 55°
Unst	1.716	1.719	1.724	0.008	56°

¹ Several other chloritoid localities were mapped by Barrow (1898) between this section and Glen Esk, all occurring in the Dalradian within a mile or so of the

Most of the grains are twinned, and in view of the recent study by Hietanen (1951) the optic orientations of the chloritoids from both localities have been studied in some detail. Repeated twinning is rare, binary and ternary twins being most common; in all cases the composition plane of the twin lamellae is parallel to the basal cleavage. In the determination of the twin laws the cell dimensions determined by Milne (1949) and confirmed by Brindley and Harrison (1952) were used.

TABLE I. Analyses of chloritoid-chlorite-muscovite schists.

	1.	2.	<i>Niggli values.</i>	1.	2.
SiO ₂	46.46	59.10	<i>si</i>	140.8	239.6
TiO ₂	1.30	0.93	<i>al</i>	53.7	54.0
Al ₂ O ₃	29.48	22.58	<i>fm</i>	29.9	28.7
Fe ₂ O ₃	6.65	0.97	<i>c</i>	1.5	3.4
FeO	3.93	4.40	<i>alk</i>	14.9	13.9
MnO	0.05	0.09	<i>k</i>	0.55	0.68
MgO	1.00	1.82	<i>mg</i>	0.16	0.38
CaO	0.44	0.81	<i>al-(alk+c)</i>	37.3	36.7
Na ₂ O	2.24	1.12			
K ₂ O	4.07	3.74			
H ₂ O+	4.24	3.63			
H ₂ O-	0.09	0.16			
P ₂ O ₅	0.09	0.17			
CO ₂	n.d.	0.65			
	100.04	100.17			

1. Ritten Hamar, Unst, Shetland Islands. Analyst, N. J. Snelling.
2. Red Man, Perthumie Bay, near Stonehaven, Kincardineshire. Analysts, Avery and Anderson, Melbourne.

In most of the Stonehaven chloritoids the twin axis is [110]; this appears to be the most common twin law and has been recorded by Balk and Barth (1934) and Hietanen (1951). In one case the twin axis was [230]; this twin law has not been recorded before. Only one triclinic lamella was measured; this was intergrown with a monoclinic lamella parallel to the basal cleavage. In all cases showing monoclinic optics α was parallel to the basal cleavage, thus $\alpha = b$.

Most of the lamellae measured from the Saxa Vord chloritoids had triclinic optics, but occasional monoclinic lamellae occurred intergrown with twinned triclinic lamellae parallel to the basal cleavage. A similar intergrowth has been figured by Hietanen (1951, fig. 5). As with the Stonehaven chloritoids, $\alpha = b$ in all the monoclinic lamellae.

These determinations confirm Hietanen's observation that both Highland Border Fault. Most of this area is now covered by forest and none of the localities could be found.

optically monoclinic and triclinic forms of chloritoid occur; but only one monoclinic form was observed, with $\alpha = b$. Previous studies have recorded monoclinic forms with $\alpha = b$ and $\beta = b$.

TABLE II. Analyses of chloritoids from Stonehaven and Unst.

	1.	2.	3.	4.	5.
SiO ₂	24.36	n.d.	23.48	28.96	23.85
TiO ₂	2.47	0.05	2.55	0.53	0.56
Al ₂ O ₃	38.43	1.78	39.71	33.56	35.83
Fe ₂ O ₃	4.13	1.09	3.79	8.43	9.00
FeO	20.14	n.d.	20.73	19.05	20.33
MnO	0.63	n.d.	0.66	0.93	0.99
MgO	1.90	n.d.	2.00	1.82	1.94
CaO	0.29	n.d.	0.31	0.32	0.34
Na ₂ O	n.d.	n.d.	—	n.d.	—
K ₂ O	n.d.	n.d.	—	n.d.	—
H ₂ O + 110° C.	6.63	n.d.	6.77	6.70	7.16
H ₂ O - 110° C.	0.03	n.d.	—	0.08	—
	<u>99.01</u>		<u>100.00</u>	<u>100.38</u>	<u>100.00</u>

Atomic proportions calculated on the basis of 14 (O + OH) to the unit cell.

Si	2.032	1.945	2.390	2.000
Al	3.000	3.000	3.000	3.000
Fe ^{'''}	Y	0.782	0.871	0.540
		0.218	0.129	0.460
Fe ^{''}	X	0.041	0.107	0.110
		1.405	1.435	1.314
Mg	0.236	0.247	0.224	0.242
Mn	0.045	0.046	0.065	0.070
Ti	0.155	0.159	0.033	0.035
Ca	0.026	0.028	0.028	0.031
OH	3.692	3.739	3.687	4.002
X	1.908	2.022	1.664	1.913
Y	1.000	1.000	0.786	1.000

1. Chloritoid, Saxa Vord schists, Ritten Hamar, Unst, Shetland Isles. Analyst, N. J. Snelling.

2. Partial analysis of residue after solution of Saxa Vord chloritoid in conc. H₂SO₄. Analyst, N. J. Snelling.

3. Saxa Vord chloritoid recalculated on assumption that all the alumina of col. 2 was present in muscovite and the iron in magnetite.

4. Chloritoid, Red Man, near Stonehaven, Kincardineshire. Analyst, N. J. Snelling.

5. Analysis 4 recalculated so that Si = 2; this requires the assumption that the quartz impurity amounts to 6.61%.

Chemical composition. Analyses of the two chloritoids are given in table II. Particular care was taken in the water determinations, a modified Penfield method being adopted. A silica tube was used in

place of the normal soft glass tube, and was heated with an oxy-coal-gas blowpipe. The temperature reached was sufficient to cause fusion of the samples.

An attempt has been made to correct the analysis of the Saxa Vord chloritoid for inclusions and groundmass impurities by the method used by Simpson (1931) and by Balk and Barth (1934). The mineral was dissolved in sulphuric acid, leaving a residue which consisted of inclusions, impurities, and silica resulting from the decomposition of chloritoid. It has already been mentioned that quartz inclusions are rare in the Saxa Vord chloritoid and no attempt was made to differentiate between quartz occurring as inclusions and silica resulting from the decomposition of the chloritoid. Microscopic examination of the residue revealed a high content of finely divided muscovite and iron ores; it was dissolved in sulphuric and hydrofluoric acids, and total iron, titania, and alumina determined in the usual way (table II, col. 2). Potash, silica, and water were then calculated on the assumption that all the alumina in the residue was present in muscovite; total iron was recalculated to give the proportions of ferrous and ferric iron required by magnetite, and the original analysis was corrected and recalculated to 100 % (table II, col. 3). The low summation of the original analysis is probably due to failure to determine alkalis which would occur in the muscovite impurities and possibly in the chloritoid itself.

The recent work of Brindley and Harrison (1952) has indicated that the structural formula of chloritoid may be written $(\text{Fe}^{2+}, \text{Mg})_2\text{Al}(\text{OH})_4\text{Al}_3\text{O}_2(\text{SiO}_4)_2$. They have shown that the structure consists of layers of aluminium ions sandwiched between silicate layers in a manner similar to the occurrence of potassium ions between the silicate layers of the micas. The silicate layers of chloritoid consist of two sheets of unpolymerized SiO_4 tetrahedra the vertices of which point inwards. The divalent and hydroxyl ions, together with one-quarter of the aluminium ions, are situated within the silicate layers. The packing of the aluminium ions occurring between the silicate layers and the oxygens which form the bases of the SiO_4 tetrahedra of the layers is similar to the aluminium-oxygen packing of corundum. Since there is little replacement of Al^{3+} by other ions in corundum the present writer suggests that the small amounts of Fe^{3+} , Mn^{2+} , Ca^{2+} , and Ti^{4+} usually recorded in the analyses of chloritoid are accommodated within the silicate layers and that the general formula of chloritoid may be written: $X_2Y(\text{OH})_4\text{Al}_3\text{O}_2(\text{SiO}_4)_2$ where X includes Fe^{2+} , Mg^{2+} , Mn^{2+} , Ti^{4+} , Ca^{2+} , and Fe^{3+} and Y includes Al^{3+} and Fe^{3+} . In view of the slight degree

of replacement of Si by Al in unpolymerized SiO_4 tetrahedra the Si values should not depart significantly from 2.

The Saxa Vord chloritoid is in good agreement with this formula even if no correction is made for inclusions. The Stonehaven chloritoid departs considerably from the suggested formula, showing a high Si content, low (OH), and low summations of the X and Y groups. However, it was impossible to separate the chloritoid from the numerous quartz inclusions and there can be no doubt that this is the cause of the high Si and other discrepancies. In table II, col. 5, the analysis has been recalculated to give 2 Si to the unit cell, the resultant formula being very close to the ideal with $(X+Y)$ very nearly 3 and (OH) a little over 4. The calculation shows that the silica of the analysis (table II, col. 4) was high by 6.61 %. These analyses are in agreement with earlier chemical studies (Milne, 1949), which showed that chloritoid was an iron-rich mineral with limited replacement of iron by magnesia.

Milne (1949) has suggested that chloritoid be grouped with the sheet silicates in which the characteristic structural element is the Si_4O_{10} sheet, and that the ideal cell content is $4(\text{Fe}^{2+}, \text{Mg})_2(\text{Al}, \text{Fe}^{3+})_2(\text{Al}_2\text{Si}_2)\text{O}_{10}(\text{OH})_4$. As with margarite (Bragg, 1937), half the silicons in the Si_4O_{10} sheets are replaced by aluminium. The twenty analyses discussed by Milne show good agreement with this formula. Some Si values are higher than 2 but this he attributes to variations in the degree of replacement by Al. The structure proposed by Brindley and Harrison requires that Si values over 2 must be explained by the presence of quartz impurity in the analysed sample. Recalculation of the formula of the Stonehaven chloritoid in accordance with this assumption gives a result in much closer agreement with the ideal unit-cell content accepted both by Milne and by Brindley and Harrison, and provides support for the structure determined by Brindley and Harrison.

Comparison with earlier analyses and refractive index determinations shows a tendency for the refractive indices to decrease with increasing amounts of Mg replacing Fe^{2+} . There is some indication that chloritoids with high ferric iron have higher refractive indices than chloritoids with comparable FeO:MgO ratios but lower ferric iron contents.

Conclusions. Chloritoids from Unst and Stonehaven may be either monoclinic or triclinic, with $a = b$ in the monoclinic varieties. Twinning is common with zone axes [110] and [230] as the twin axes; the composition face is always (001). Intergrowths of monoclinic and triclinic lamellae also occur. Refractive indices increase with increase in the FeO:MgO ratio and the Fe_2O_3 content. The formula of the Saxa Vord

chloritoid agrees well with that suggested by Brindley and Harrison. The Stonehaven chloritoid, however, has a high Si content; this is attributed to quartz inclusions, and satisfactory agreement with the suggested formula is obtained if the analysis is recalculated so that $Si = 2$.

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