# Astrophyllite from Kangerdlugssuaq, East Greenland

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ABSTRACT. Astrophyllite has been found in alkalic pegmatite dykes on the two sides of Kangerdlugssuaq fjord. At the eastern locality, Kraemers Island, the dyke is silica oversaturated and the astrophyllite occurs in a broad tabular crystal habit. The dyke at the western locality, Bagnaesset, is silica undersaturated and the astrophyllite occurs in elongated prisms of acicular habit. Electron probe analyses of the crystals of the two habits have shown systematic chemical differences which not only relate to Mn and Ti compositional variations, but also reveal departures from ideal stoichiometry in varying degrees. Based on this latter feature a model involving polysomatism has been constructed which may explain the differences in crystal habit.

Two Tertiary alkalic pegmatite astrophyllitebearing dykes in the Kangerdlugssuaq region of East Greenland were identified in the 1977 field season. A small number of samples were collected at this time, but a much more comprehensive collection was made when the localities were revisited in 1979. At the second visit, dynamite was used to assist in obtaining adequate amounts of fresh material. The dykes are located at Bagnaesset and Kraemers Island, on the west and east sides, respectively of Kangerdlugssuag Fjord. Fig. 1 contains maps indicating the precise locations of these dykes which are separated by a distance of about 10 km. The Kraemers Island dyke cuts a quartz-bearing syenite and is believed to be genetically related to this body. The dyke on Bagnaesset cuts both gneisses and a quartz-bearing syenite and its genetic relationships are unclear.

In the silica-saturated Kraemers Island dyke astrophyllite has a broad tabular crystal habit with a reddish coppery lustre, whereas in the undersaturated Bagnaesset dyke it shows an elongated prismatic to acicular habit and a darker and more brassy colour. The variations in the crystal habit have been considered in relation to the mineral paragenesis and astrophyllite crystal chemistry, as presented below.

# Petrography of the dykes

In both of the dykes, four distinct zones have been recognized. At Kraemers Island these are referred to as zones 1 to 4, while at Bagnaesset they are designated zones A to D.

The minerals common to all four zones at Kraemers Island are quartz, perthite, astrophyllite, arfvedsonite, aegirine, and zircon. Zone 1 has a coarse-grained texture with grain sizes around 1 cm. Tabular astrophyllite crystals may be 3 cm or greater. Zone 2 is a finer grained version of zone 1, with average grain size around 5 mm. Zone 3 is characterized by an abundance of zircon which comprise over 50% of the rock. Zone 4 is unusually rich in fluorite which in places may account for up to 90% of the rock.

At Bagnaesset zones A, B, and C have similar mineralogy, with the principal minerals being nepheline, perthite, astrophyllite, aegirine, and biotite. The grain size in zone A is coarse, 0.5 to 2 cm, while zones B and C are progressively finer. Zone D is a discordant schistose region at the centre of the pegmatite. Eudialyte is a major component in zone B, and is the main Zr-bearing mineral, though very minor zircon may be found, particularly as inclusions in the astrophyllite. Astrophyllite occurs most commonly in zones B and C, where its crystal habit is typical of this locality, namely prismatic acicular crystals which may be up to several cm in length. It is often closely intergrown with aegirine which occurs in stellate clusters of radiating needles.

The difference in the astrophyllite crystal habit is quite striking between the two localities, and no exceptions have been noted. However, the optical properties of the astrophyllite do not vary much with change in habit, and the pleochroism is the normal orange-gold-yellow. Aegirine at Bagnaesset is more deeply coloured than at Kraemers Island.

### Chemical analyses

Analyses were made of the astrophyllite and associated minerals in polished thin sections, using the ARL-EMX electron microprobe at the University of Toronto. This instrument is equipped with a Si(Li) energy-dispersive X-ray detector, which was used to perform the quantitative analyses. The operating conditions were 20 kV with an incident beam current of 10 nA. Standardization was with respect to kaersutite (for Na, Mg, Al, Si, K, Ca, Ti, Fe), rhodonite (for Mn) and metallic Zr, Nb, and Sn. The raw X-ray spectral data were reduced to oxide concentrations by an 'on line' modification of the computer program, PESTRIPS, of Statham (1975).



FIG. 1. (A) Map of the Kangerdlugssuaq area of East Greenland showing the locations of the detail maps B and C. After Abbott and Deer (1972). (B) Map of Kraemers Island dyke swarm, after Nielsen (1978). The astrophyllite-bearing dyke is indicated by the arrow. (C) Map of the Bagnaesset region after Deer and Kempe (1976). The astrophyllite-bearing dyke is indicated by the arrow.

Each analysis presented represents the mean of at least five replicates. Astrophyllite was analysed using a relatively broad beam (5  $\mu$ m) and long counting times (250–300 s) to ensure accurate analyses.

Analyses of astrophyllite, arfvedsonite and biotite are presented with the amount of H<sub>2</sub>O calculated from ideal stoichiometry. This recalculation produces results which depart somewhat more from 100% than is normally acceptable. The greater part of this divergence is believed to be due to the lack of data on OH and F in these minerals. Fluorine-bearing minerals will show totals that are artificially low whereas minerals in which O substitutes to some extent for OH will yield totals which are too high. A reiterative calculation could be applied to estimate the values of O, OH, F required to produce a total of 100.00%. This calculation, however, would produce no change in the ratios of the metal atomic proportions, which are the key factors used in the following discussions.

A good measure of the accuracy of the values determined for wt. % oxides (other than  $H_2O$ ) is provided by the analyses presented for aegirine. These specimens were analysed alongside the other silicates and, when Fe is reassigned to FeO and Fe<sub>2</sub>O<sub>3</sub> on the basis of ideal stoichiometry, yield totals with a standard deviation of 0.2% from 100.00%.

Astrophyllite may be assumed to conform to the formula  $(K,Na,Ca)_3(Mg,Fe,Mn)_7(Ti,Zr,Nb)_2Si_8(O, OH)_{31}$ , based on the structure determined by Woodrow (1967). Chemical variation and isomorphism is most conveniently discussed in terms of the generalized formula  $W_3X_7Y_2Z_8O_{31}$ .

Analyses of astrophyllite from the four zones from each of the two localities are presented in Table I. Triangular plots of the components of the W, X, and Y groups are shown in fig. 2.

Group W. The highest substitution of Ca for K and Na is in zone D, at 9.5% of the total occupied sites in this group (hereafter described as 'available sites'). The atomic proportions of Ca are generally higher and those of Na lower in the undersaturated pegmatite, with the exception of zone B for which the values are comparable to the astrophyllites of Kraemers Island. These analyses also reflect the tendency of astrophyllites from undersaturated parageneses to have a higher K/Na ratio as shown by Macdonald and Saunders (1973).

Group X. Semenov (1956) has described a complete solid solution between astrophyllite and kupletskite, the Fe-rich and Mn-rich end members respectively. There is quite a wide range of Fe-Mn solid solution for the Kangerdlugssuaq astrophyllites, with those from the undersaturated dyke tending to be more Mn-rich than those from the oversaturated one. The Fe and Mn contents of the Kraemers Island astrophyllites are fairly monotonous, with an Fe: Mn ratio of about 6.5. In the Bagnaesset pegmatite astrophyllite the Fe: Mn ratio is more variable but averages about 2.

Mg substitutes to a small degree for Fe and Mn. In the Kraemers Island specimens it is minor or absent, filling a maximum of 1% of the available sites in the zone 1 samples. In the Bagnaesset astrophyllites Mg shows a steady decrease from zone A to zone D (4 to 2% of available sites). Mg (as  $Mg^{2+}$ ), having a smaller electronegativity and a smaller ionic radius than either  $Fe^{2+}$  or  $Mn^{2+}$ is concentrated in earlier-formed crystals in a given geological environment. Field evidence (inwardly decreasing grain size and zone width) suggests that zones A to D of the Bagnaesset pegmatite may represent zones of decreasing age. Although there are confusing cross-cutting relationships between zones 1 and 4 of the Kraemers Island pegmatite a similar interpretation, with zones 1 to 4 being of generally decreasing age (with some overlap), might be made on the basis of decreasing grain size and dyke width (as well as volatile enrichment in the fluorite-rich zone 4 dykes). Thus, the steady decrease in Mg content shown from zones 1 to 4 and from A to D in the two pegmatites may well be related to successive emplacement of several generations of pegmatite from a single magmatic source in each case.

Manning (1969), from a spectral study of astrophyllite, has suggested that  $Fe^{3+}$  is not located in the octahedral layer, but substitutes for Ti associated with the tetrahedral layer. However, Macdonald and Saunders (1973) published eight wet chemical analyses of astrophyllites from various localities, of which only one showed a value of  $Fe^{3+}$  greater than 0.3 atoms. It seems reasonable to think, therefore, that  $Fe^{3+}$  is relatively minor in the astrophyllite structure and, for this reason, we have expressed all Fe as FeO and assumed it to be present entirely in the octahedral layer.

Group Y. Both Zr and Nb may be appreciable substituents for Ti in this group. Nb is relatively minor in astrophyllites from both the Kraemers Island and Bagnaesset pegmatites. In the Kraemers Island zones the Nb content is fairly monotonous, at about 4% of the available sites. In the Bagnaesset pegmatite it ranges from 2% of the available sites (in zone A) to 5% (zones B and C). Zr is a major substituent for Ti in the Bagnaesset samples, comprising up to 24% of the available sites in zone A. Zone B has a low Zr content compared with the other three zones (only 6% of available sites). Zr is a comparatively minor element in the Kraemers Island astrophyllites, occupying 2-4% of available sites. This is doubtless related to the existence of



FIG. 2. Triangular plots of atomic proportions of elements in the three groups W, X, and Y for astrophyllites from Kangerdlugssuaq.

zircon as a stable phase, occurring as poikiloblasts in the astrophyllite.

The Ti content of the Kraemers Island astrophyllites is quite high, averaging 93% of available sites. With the substitution of Zr for Ti, the average Ti content of the Bagnaesset samples is lowered to 74%. An exception is zone B where the Ti-Zr content is more similar to the Kraemers Island samples.

Group Z. Al substitution for Si in tetrahedral sites is extremely minor in the Kraemers Island astrophyllites  $(0-0.13\% \text{ Al}_2\text{O}_3)$ . Al values are slightly higher in the Bagnaesset specimens,  $0.8-1\% \text{ Al}_2\text{O}_3$  in zones A, C, and D, but Al is, interestingly, absent from zone B. In both cases

 $Al^{3+}$  occupies less than 0.03% of available sites. No systematic variation of Al in the astrophyllite of zones A to D of the Bagnaesset pegmatite was detected.

Group O. Macdonald and Saunders (1973) reported values of F up to 1.1 atoms, with Cl always less than 0.01 %, in their list of eight astrophyllite analyses. In most published analyses (OH,F) tends to be less than 6 atoms and generally ranges from 3.5 to 6 atoms, indicating appreciable substitution of O for (OH,F). This phenomenon makes the calculation of H<sub>2</sub>O and F values from stoichiometry difficult.

Arfvedsonite. Analyses of arfvedsonite from zones 1, 2, and 3 of the Kraemers Island pegmatite

are presented in Table II. The  $Fe_2O_3$  and  $H_2O$  values have been recalculated assuming ideal amphibole stoichiometry.

Several elements seem to show a continuous change in proportion from zones 1 to 3. The contents of Ti, Mn, Na, and K increase from zones 1 to 3 while the values of Al and Mg show a steady decrease. The decrease in Mg content is most notable since it parallels the decrease in Mg in astrophyllite from these zones.

*Biotite.* Two analyses of biotite from zone A of the Bagnaesset pegmatite are given in Table II. The total of weight per cent oxides for the second analysis is too high, due to O replacing (O,OH).

Kempe and Deer (1970) have presented analyses of biotite from a pulaskite in the Kangerdlugssuaq intrusion. They comment that these biotites are less rich in Al and Ti and much higher in Mn and K than most other biotites of igneous paragenesis. It may be seen by comparison (in Table II) that the Bagnaesset biotites analysed are even more depleted in Al and enriched in Mn and K than these Kangerdlugssuaq biotites of Kempe and Deer

Table I. Electron-microprobe analyses of astrophyllite from Kangerdlugssuaq.

	Kraemers Is		Island	Island		Bagnaesset			
Zone	1	2	3	4	A	B	c	D	
S10,	37.62	36.92	36.64	35.85	35.58	37.17	33.74	35.38	
Al 201		0.13	-	_	0.86	_	0.97	0.81	
Tiố,	10.83	10.73	10.76	10,64	8.49	10.53	8.00	8.65	
Zr02	0.52	0.34	0.66	0.67	4.15	1.14	4.10	3.60	
ΥΝο <sub>2</sub> Ος	0.70	0.71	0.77	0.70	0.30	1.05	1.00	0.91	
Feð	32.56	32.70	31.50	31.61	24.50	20.20	24.08	26.42	
MgO	0.20	0.15	-	-	0.93	0.89	0.67	0.50	
Mn0	4.64	4.75	5.68	4.73	11.91	15.80	11.66	10.68	
Ca0	0.99	0.66	0.98	0.87	1.09	0.81	1.18	1.12	
Na <sub>2</sub> 0	2.66	2.39	2.52	3.09	2.35	2.98	2.16	1.87	
<b>К</b> 2Ô	5.56	5.01	5.13	5.58	6.60	5.99	6.58	6.16	
н5о	(5.02)	(4.93)	(4.92)	(4.85)	(4.94)	(5.03)	(4.77)	(4.91)	
รนัก	(101.30)	(99.42)	(99.56)	(98.59)	(101.70)	(101.59)	( <u>98.91</u> )	(101.01)	
Atomic Proportions on the Basis of 31(0,0H)									
Si	7.869	7.861	7.817	7.758	7.558	7.764	7.427	7.567	
A1	_	0.033	-	_	0.215	_	0.252	0.204	
Z	7.869	7.894	7.817	7.758	7.773	7.764	7.679	7.771	
Ti	1.704	1.718	1.727	1.732	1.356	1.654	1.324	1.391	
Zr	0.053	0.035	0.069	0.071	0.430	0.116	0 440	0 376	
NЪ	0.066	0.068	0.074	0.068	0.029	0.099	0.100	0.088	
Y	1.823	1.821	1.870	1.871	1.815	1.869	1.864	1.855	
Fe	5.696	5.823	5.620	5 721	6 353	3 520	4 433	6 726	
Mn	0 822	0.857	1 027	0.867	2 163	2 796	2 176	1 025	
Ma	0.062	0.048	1.027	0.007	0.205	0 277	0.220	1.933	
	6.580	6.728	6 667	6 588	6 791	6 602	6 827	6 930	
	01000	01720	0.041	0+500	0.731	01002	0.027	0.020	
ĸ	1.484	1.361	1.396	1.541	1.789	1.596	1.848	1.681	
Na	1.079	0.987	1.042	1.297	0.968	1.207	0.922	0.776	
Ca	0.222	0.151	0.224	0,202	0.248	0.181	0.278	0.257	
W	2.785	2.499	2.662	3.040	3.005	2.984	3.048	2.714	
он	7.000	7.000	7.000	7.000	7.000	7.000	7.000	7.000	
W+X+Y+Z	19.057	18.942	18.996	19.257	19.384	19.219	19.418	19.160	
Z/Y	4.32	4.33	4.18	4.15	4.28	4.15	4.12	4.19	
N	.19	.20	.10	.08	.16	.08	.06	.10	
Habit	Tabular			Prismatic					

Note: N = (Z/Y - 4)/(6 - Z/Y) - see text for explanation.

(1970). This may reflect an overall differentiation trend in the Kangerdlugssuaq intrusion as a whole, since the pegmatite may well be related to the syenites of the Kangerdlugssuaq intrusion, some of which are undersaturated.

Aegirine. Analyses of aegirines from both pegmatites are given in Table III. Contents of most elements analysed seem to be comparable for both the Kraemers Island and Bagnaesset samples. Ti however, is generally higher in the samples from Kraemers Island.

The aegirine from zone B parallels the high Ti and Mn contents of the Zone B astrophyllite. Aegirine from Zone A has an appreciably higher content of Al and a significantly higher content of Ca than any of the other aegirines analysed. Aegirine from this zone also shows the lowest Na value of all the analyses.

#### Discussion

The chemical analyses of the astrophyllites from Kangerdlugssuaq show that there are small but

Table ∏. Analyses of arfvedsonite and biotite from

Zone SiO <sub>2</sub> Al <sub>2</sub> O <sub>3</sub> TiO <sub>2</sub> Fe <sub>2</sub> O <sub>3</sub>	Ar 1 51.94 0.54 1.26 2.78	fedsonit 2 51.34 0.45	e 3 50.29	A	-Biotite A	*
Zone Si0 <sub>2</sub> Al <sub>2</sub> 0 <sub>3</sub> Ti0 <sub>2</sub> Fe <sub>2</sub> 0 <sub>3</sub>	1 51.94 0.54 1.26 2.78	2 51.34 0.45	3	A	A	*
Si0 <sub>2</sub> Al <sub>2</sub> 0 <sub>3</sub> Ti0 <sub>2</sub> Fe <sub>2</sub> 0 <sub>3</sub>	51.94 0.54 1.26 2.78	51.34 0.45	50.29			
Al 2 <sup>0</sup> 3 Ti02 Fe 2 <sup>0</sup> 3	0.54 1.26 2.78	0.45		36.97	36.40	39.38
TiÕ2 Fe2 <sup>0</sup> 3	1.26 2.78		0.18	9.73	10.08	11.94
Fe203	2.78	1.34	2.08	2.54	3.42	2.26
		3.70	2.87	-	-	3.68
Fe0	27.27	26.74	26.13	26.90	31.44	17.69
MgO	2.19	1.77	0.51	4.91	3.46	10.37
Mn0	1.72	1.78	2.25	5.25	3.90	1.54
CaO	0.87	1.02	0.34	-	0.06	0.15
Na <sub>2</sub> 0	8.64	8.68	8.98	-	0.25	0.68
к <sub>2</sub> õ	1.55	1.60	1.84	10.09	10.02	9.07
н <u>5</u> 0	(1.91)	(1.89)	(1.84)	(3.70)	(3.74)	2.98
Z702	-		-	-	_	0.01
Ba0	-	-	-		num.	0.17
Rb <sub>2</sub> 0	—	-		-	-	0.07
L120	-	_				0.02
Sum	100.67	100.31	97.31	100.09	102.77	100.01
	1	Atomic Pr	oportion	s on the Basis	of 24(0,0	CH(
Si	8.09	8.05	8.15	5.995	5.836	6.073
A1	_	-	-	1.860	1.905	1.927
	8.09	8.05	8.15	7.855	7.741	8.000
Al	0.10	0.08	0.03		_	0.244
Ti .	0.15	0.16	0.25	0.310	0.412	0.262
Fe	0.33	0.44	0.35		_	0.427
Mg	0.51	0.41	0.12	1.187	0.827	2.384
Fe <sup>2+</sup>	3.55	3.51	3.54	3.648	4,216	2.282
Mn	0.23	0.24	0.31	0.721	0.530	0.201
	4.87	4.84	4.60	5.866	5.985	5.800
Na	2.60	2.64	2.82	_	0.078	0.025
Ca	0.15	0.17	0.06	-	0.010	0.025
К	0.31	0.32	0.38	2.088	2.050	1.785
Ba	-	-	_	-		0.010
RЪ		-	-	_		0.007
	3.06	3.13	3.26	2.088	2.138	2.032
он	1.98	1.98	1.99	4.000	4.000	3.066
Sum	18.00	18.00	18.00	19.809	19.864	18-898

\* Biotite, transitional pulaskite, Sondre Syenitgletscher, Kangerdlugssuaq. Wet chemical analysis by Kempe and Deer (1970). All other analyses by electron probe. For arfedsonite  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  have been calculated from Fe on the basis of ideal stoichiometry. OH has been similarly assigned to arfvedsonite and biotite.

Table III. Electron-microprobe analyses of aegirine from Kangerdlugssuaq.

	1	2	3	4	5	6	7	
Si0,	52.23	51.60	53.63	53.00	51.76	51.99	51.23	
Zr0 <sup>2</sup>	0.61	0.61	0.16	0.47	0.48	0.19	0.46	
A1203	-	_	0.97	1.05	0.09	0.50	0.76	
Tið,	2.98	2.01	0.39	0.63	4.16	1.18	0.32	
Fe <sub>2</sub> Õ3	27.85	30.66	30.05	27.00	26.78	31.56	31.98	
Feð	2.21	0.82	-	1.11	-	-	-	
MgO	-	-	-	-	0.48	~-	-	
MnO	0.43	0.38	0.30	0.71	2.07	0.46	0.30	
Ca0	1.02	0.95	0.80	2.44	0.90	0.78	0.90	
Na <sub>2</sub> 0	13.27	13.25	13.81	12.78	13.65	13.50	13.39	
Sum	100.60	100.28	100.11	99.19	100.37	100.16	99.34	
	Ato	omic Pro	portions	on the	Basis of	6 Oxygens.		
Si	1.994	1.981	2.035	2.035	1.974	1,990	1.983	
Zr	0.011	0.011	0.003	0.009	0.009	0.004	0.009	
Al	-		0.043	0.048	0.004	0.023	0.035	
Ti	0.086	0.058	0.011	0.018	0.119	0.034	0.009	
Fe <sup>3+</sup>	0.800	0.886	0.858	0.780	0.769	0.909	0.931	
Fe <sup>2+</sup>	0.071	0.026	-	0.035	-	-	-	
Mg		-	-		0.029	-	-	
Mn	0.014	0.012	0.010	0.023	0.067	0.015	0.010	
Ca	0.042	0.039	0.033	0.100	0.037	0.032	0.037	
Na	0.982	0.986	1.016	0.951	1.010	1.002	1.005	
0	6.000	6.000	6.000	6.000	6.000	6.000	6.000	
Cation	1 000	3 000	(		( 63.6			
Sum	4.000	3.999	4.009	3.999	4.018	4.009	4.019	
	1.	. Kraem	ers Isla	nd, Zone	3 (2714	1A)		
	2.	. Kraem	ers Isla	nd, Zone	e 4 (2714	lF)		
	<ol><li>Bagnaesset, Zone A (40552B)</li></ol>							
	<ol> <li>Bagnaesset, Zone A (40552C)</li> <li>Bagnaesset, Zone B (27019A)</li> </ol>							
	<ul> <li>Bagnaesset, Zone C (27019B)</li> </ul>							
	/. Bagnaesset, Zone D (27019C)							

Notes: Fe $^{3+}$  and Fe $^{2+}$  have been calculated from Fe on the basis of ideal stoichiometry. Specimen numbers refer to the University of Copenhagen collection.

significant variations in the chemistry of the W, X, and Y groups. However, none of these are so large as to suggest a reason for the profoundly different habits of the mineral at the two localities. A feature which is common to all the analyses is the departure from the ideal values for the sums of the atomic proportions, in particular for the Y and Z groups. These should ideally be 2 and 8, with the former made up primarily of Ti and the latter of Si. The experimentally determined values are consistently low for both groups, but by different amounts, and it is worth spending some time to speculate what implications this may have for the crystal structure.

Woodrow (1967) has described the structure of astrophyllite based on an X-ray diffraction study. There is a certain similarity to the mica structure, with the difference that the basic structural unit is a layer of SiO<sub>4</sub> tetrahedra and TiO<sub>6</sub> octahedra in a ratio of 4:1. The ideal arrangement of this layer is shown in fig. 3A, with the SiO<sub>4</sub> tetrahedra forming infinite (Si<sub>4</sub>O<sub>12)n</sub> chains parallel to the x-axis linked through TiO<sub>6</sub> octahedra.

The repeat distance of the octahedral layer is greater than that of the  $(Si_4O_{12})_n$  chains. In the x direction a fit is apparently achieved by the contraction of the octahedra parallel to the x-axis. In the

y direction matching seems to entail a corrugation of the octahedral layer and attachment of the chains to the resulting concave surfaces.

Some variation on this basic structural scheme has already been described. Peng and Ma (1963) examined a type of so-called 'high alkali' astrophyllite to which they assigned the formula,  $(K_2Na_2)$  $(Fe_5Mg_2)Ti_2S_8(O,OH)_{31}$ . The presence of the smaller Mg atoms in the octahedral layer seems to have produced a more symmetrical stacking arrangement, generating a flat octahedral layer. In this type of astrophyllite the TiO<sub>6</sub> octahedra on both sides of the 'sandwich' are attached to the same octahedron of the Fe-Mg layer. The extra Na is then accommodated by replacing the Na atom apical to each TiO<sub>6</sub> octahedron with two Na atoms symmetrically disposed about this site in a direction perpendicular to x.

Zvyagin and Vrublevskaya (1976) have described a naturally occurring monoclinic polytype of astrophyllite, based on a similar arrangement of  $TiO_6$ octahedra attached to the same (Fe,Mg) octahedron. Rather than assigning an extra Na atom in the above fashion, however, they suggested that the 'non-uniform' distribution of  $TiO_6$  octahedra in the structure might necessitate the entry of Na into octahedral sites in order to balance the charge distribution.



F1G. 3. (A) Arrangement of a sheet containing a 'double chain' ( $Si_4O_{12}$ ) of  $SiO_4$  tetrahedra and combined with a single chain of  $TiO_6$  octahedra in astrophyllite (after Woodrow, 1967). Si: Ti = 4:1. (B) Postulated triple chain arrangement for astrophyllite in which Si: Ti = 6:1.

The apparent flattening of the corrugations in the octahedral layer with the presence of Mg led Woodrow (1967) to suggest the possibility of continuous tetrahedral layers with other ratios of Ti:Si, such as 1:2 found in bafertisite.

All analyses of astrophyllite presented here show a net cation deficiency. The sum of (Na, K, Ca) cations slightly exceeds 3.0 in some analyses but this total is probably artificially high and may be the result of omitting F from the calculation of atomic proportions.

Woodrow (1967) reports that Weissenberg photographs of astrophyllite show streaking parallel to  $b^*$ , indicating structural disorder in the *b* direction. These two considerations, characteristic cation deficiency and apparent disorder in the *b* direction, have suggested a hypothetical modification to the structure of astrophyllite.

The structure of astrophyllite may be considered in the context of the biopyribole series described by Veblen et al. (1977 and subsequently). Studies of chain and sheet silicates using electron diffraction and high-resolution transmission electron microscopy (HRTEM) have shown that there actually exists a form of continuum between the single-chain (pyroxene), double-chain (amphibole) and sheet (mica) silicates as a result of variations in chain width. Veblen et al. (1977) have described two new minerals, both of which involve 'triple' chains, essentially a combination of a double amphibole chain with a single pyroxene chain. The new mineral jimthompsonite is comprised entirely of these triple chains whereas another new mineral chesterite is composed of alternating double and triple chains. Other stacking sequences, as well as chain widths of up to 60, have been noted, appearing sporadically in some chain silicates. Disordered zones, comprising random arrangements of different chain widths, produce a characteristic streaking parallel to b\* on X-ray photographs.

The  $(Si_4O_{12})_n$  chain in astrophyllite may be considered as a short of 'reciprocal' double chain. Fig. 3B shows a hypothetical triple chain produced by adding another pyroxene type chain. This produces a new type of repeat unit in the Si-Ti layer with an Si:Ti ratio of 6:1 rather than 4:1. Even larger chain widths could be produced, of course, by adding additional pyroxene-type chains. A structure containing a proportion of these triple chains will modify the Si:Ti ratio, changing it from 4 towards 6. In Table I it is seen that this ratio (described as Z/Y, to take account of small isomorphous substitutions for Si and Ti) varies between 4.33 and 4.12, thus implying that there may be a variable number of 6:1 chains present in the structure. The number N of 6:1 (triple) chains relative to one 4:1 (double) chain required to produce a given Z/Y ratio is given by N = (Z/Y-4)/(6-Z/Y). This index N is given in Table I, and it can be seen that there is a tendency for higher values (mean 0.14) to be associated with the Kraemers Island astrophyllites than with the Bagnaesset samples (mean 0.01). This suggests that astrophyllites from the silica-saturated pegmatite have a greater proportion of triple chains and can be imagined to approximate more closely a sheettype structure. This may be the reason that these samples have adopted a platy habit in contrast to the prismatic crystals from the undersaturated Bagnaesset dyke. These observations are also consistent with the silica content of the oversaturated dykes being the greater.

This proposal that there may be  $(Si_6O_{18})_n$  (triple) chains mixed with  $(Si_4O_{12})_n$  (double) chains in the astrophyllite structure is based mainly on the cation deficiencies in the electron microprobe analyses. If such a state exists, it could be either ordered or disordered, and this parameter might have an even more profound effect on the crystal habit. A similar process has been suggested to account for fibrous habit in amphiboles (Veblen, 1980). To substantiate the idea that such processes occur, it would be necessary to look at the material in an electron microscope. This is beyond the scope of the present study, but a preliminary TEM examination has been made of the astrophyllite from zone 2 on Kraemers Island by Dr G. L. Nord of the US Geological Survey, Reston, Va. This sample was selected as being the most nonstoichiometric, and therefore having the highest triple-chain content. The electron diffraction pattern showed no evidence of disorder, and the image was quite normal, though the lattice parameters have not been measured. At this stage there is no more direct experimental evidence to support the hypothesis of the triple chains, but work is planned to make a more detailed study of these and other astrophyllite samples. In view of the fact that multiple- and variable-width chains are now being found to proliferate in the chain silicates, it would be surprising if astrophyllite proved to be an exception.

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