

Chemical variation in minerals of the astrophyllite group

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SUMMARY. Eight new and fourteen published analyses of astrophyllites are used to examine chemical variation within the group. Al, Ca, Cs, F, Mg, Mn, Nb, Rb, Sn, Zn, and Zr may all substitute in moderate to large amounts in the unit cell, whose basic formula is $(K,Na)_3Fe_7Ti_2Si_8(O,OH)_{31}$; the natural Mn- and Nb- analogues of astrophyllite have been recorded. Ba, Cl, Cu, Li, P, Pb, Sr, and Ta are present, but in smaller amounts. The majority of specimens show appreciable cation deficiencies, up to 5 % of sites remaining vacant. Astrophyllites from undersaturated igneous rocks are characterized by higher Al, Ca, Mg, Mn, (OH+F), (K+Na), and Zr, and lower Li, Pb, and Zn contents than those from oversaturated igneous rocks. A 'high-alkali' type of astrophyllite is distinguished. A new occurrence of nigerite is noted.

ASTROPHYLLITE is a rare mineral, being restricted to alkaline, and usually peralkaline, salic rocks. It has most commonly been recorded as an accessory in peralkaline nepheline syenites and granites and their associated pegmatites, but occurs more rarely in fenites and other metasomatic rocks. Minerals of the astrophyllite group have also been found in metamorphic parageneses, such as riebeckite gneisses and pegmatites from N.W. Spain (Floor, 1961, 1966), in nepheline-syenite gneiss from Finland (Eskola and Sahlstein, 1930), and in paragneiss from Labrador (Nickel *et al.*, 1964).

Though astrophyllite has been known for nearly 130 years, having been discovered in 1844 by Weibye on the island of Låven, Norway, very few complete analyses have been made of the mineral, causing Butler *et al.* (1962) to call astrophyllite 'analytically neglected'. It is known that a number of minor elements, such as Zr, Nb, and Cs, can enter into the astrophyllite structure in moderate to large amounts, yet few published analyses contain determinations of more than one or two of these elements. As a result, it has not been possible to give a complete account of chemical variation within the group, or to comment unreservedly on such features as the approach to stoichiometry (Nickel *et al.*, 1964). Accordingly, we have analysed eight samples of astrophyllite from various localities for 26 elements, as a first step towards further elucidating the group's chemistry. We have checked that no other element is present in the specimens in more than trace amount, and feel therefore that these eight analyses can be considered practically complete.

Formula. Woodrow (1967) has shown that the structure of astrophyllite is similar to that of the trioctahedral micas, except that it contains octahedrally coordinated Ti in the tetrahedral layer. The basic unit consists of a continuous sheet of $(\text{Fe},\text{Mn})\text{O}_6$ octahedra between two sheets consisting of chains of SiO_4 tetrahedra linked by TiO_6 octahedra in the ratio 4:1. These composite sheets are separated by sheets of alkali ions, where K occurs in 13-fold coordination and Na in 10-fold coordination. The general formula has been adjusted to $(\text{K},\text{Na})_3\text{Fe}_7\text{Ti}_2\text{Si}_8(\text{O},\text{OH})_{31}$ or $A_3B_7C_2D_8X_{31}$, and unit-cell contents are based on 31 anions (Nickel *et al.*, 1964; Woodrow, 1967).

Two major substitutions have been distinguished, Mn for Fe in the B-group, resulting in the Mn-analogue of astrophyllite, *kupletskite* (Semenov, 1956), and Nb for Ti in the C-group, giving the Nb-analogue, *niobophyllite* (Nickel *et al.*, 1964). It is clear from table III (sample nos. 19–21, 22, 17) that the natural examples of kupletskite, niobophyllite, and the type astrophyllite from Låven, Norway, are rather removed from their end-member compositions, though more nearly 'pure' astrophyllites have been found in Colorado and S. Greenland (table II, nos. 1, 2, 3).

Analytical data. Eight samples of astrophyllite were available to us for this study (table I). Samples 2 and 7 were supplied pure. The relatively large crystals in specimens 1, 4, 5, and 6 were flaked from the rocks and hand-picked to purity. Pure astrophyllite in sample 3 was electromagnetically separated from amphibole with no difficulty, whereas final purification of specimen 8 from the astrophyllite/amphibole mixture supplied to us was possible only by hand-picking.

During analysis, a small amount (0.38 wt. %) of a red mineral forming hexagonal tablets, and insoluble in HF, HNO_3 , and H_2SO_4 was found in sample 7, from La Guia, Vigo, Spain. This mineral has been identified as *nigerite* $(\text{Zn},\text{Fe},\text{Mg})(\text{Sn},\text{Zn})_2(\text{Al},\text{Fe}^{3+})_{12}\text{O}_{22}(\text{OH})_2$, by Miss E. F. Fejer, Department of Mineralogy, British Museum (Natural History), to whom we extend our grateful thanks. The effect of the nigerite on the chemical determinations, especially on the Zn and Sn values, is unknown. However, the Zn content of sample 7 is low compared to most of our analyses, suggesting that contamination may not have been appreciable. All other samples were $\geq 99\%$ pure.

An initial qualitative analysis of about 0.01 g of each sample was performed using X-ray fluorescence. The presence of Nb, Rb, Zn, and Zr was confirmed in all samples, and a useful assessment of their relative quantities made by comparing appropriate peak heights on the recorder scans. The following elements were especially sought, but were not found in appreciable quantity: Bi, Ce, Ga, Ge, Mo, Sb, Th, U, W, and Yt. There may be a relatively high rare-earth content in specimen 8. The presence of B could not be confirmed using insensitive qualitative chemical tests. Be was not sought, but other elements not recorded were apparently absent.

Maxwell (1968, p. 314) has recently made a plea for more published descriptions of wet-chemical procedures used for the analysis of uncommon minerals, suggesting that these will be of use not only to intending analysts, but also in allowing an assessment of the validity of the analytical results presented. Accordingly, we have outlined in some detail the methods used here (Appendix). In some cases, these methods proved to be not entirely satisfactory, and we recommend alternative procedures that we have

not yet fully investigated. However, we believe that our results (tables I and II) are as reliable as any yet published for astrophyllite. They contain the most complete information available on Ba, Cl, Cu, Nb, Sn, Sr, Ta, and Zn in astrophyllites, and the first determinations of Pb, to our knowledge. They show that the mineral is a strong concentrator of Sn and Zn, and earlier reports that it is enriched in Cs, Nb, Rb, Ta, and Zr were confirmed on all samples.

The unit-cell contents of 14 published analyses of astrophyllite, kupletskite, and niobophyllite are given in table III. We have included here all fairly complete, reliable analyses of which we are aware. Early analyses of astrophyllite from El Paso County, Colorado by Koenig (1877) and Eakins (1891) have been omitted because new and more complete data (table I, no. 1) are now available for material from this locality.

Substitutions. These are conveniently considered in terms of replacement in the astrophyllite formula $(K,Na)_3Fe_7Ti_2Si_8(O,OH)_{31} = A_3B_7C_2D_8X_{31}$.

A-group. Ca is the most important substitute for alkalis, up to a maximum of 0.83 atoms, i.e. some 28 % of available sites, in kupletskite from Kuivchorr, Kola. Ba and Sr are both very low, Ba tending to be the more abundant. Rb is also generally low, less than 0.15 atom, though Ganzeev *et al.* (1969) report astrophyllites from Russian alkaline granites with rather higher Rb (wt. %) values than our specimens. Despite the fact that it is only a minor substituent, Rb still shows strong enrichment relative to K compared to common terrestrial rocks and minerals (Butler *et al.*, 1962). K/Rb ratios (wt.) are always less than 30, and range down to 2 (data from this paper and from Ganzeev *et al.*, 1969). There is no correlation between K and Rb.

Cs is also concentrated in astrophyllite, and a caesian specimen from alkaline granite from Dara Pioz in the Alai range, Kirgiz SSR, containing 10.80 % Cs (wt.) has been described by Ganzeev *et al.* (1969). The full analysis of this mineral has not yet been published: however, the atomic ratio 100 Cs: (Cs + Na + K) is 45.5; hence the mineral should not be given species status, for which Cs should be > Na + K. The data given in table IV indicate that many more analyses are needed to ascertain the degree of isomorphism between astrophyllite and its Cs-enriched variety.

Analyses for rare earths are very scarce. Nickel *et al.* (1964) report 1.50 % (wt.) (Ln, Yt)₂O₃ in niobophyllite with Ce and La oxides predominant. Assuming all the rare-earths to be Ce, this gave a unit-cell content of 0.123 atom. Dietrich *et al.* (1965) report semi-quantitative spectrographic results for two astrophyllites from Norwegian alkaline granites (ekerites): La, 250, 130 ppm; Nd, 700, 420 ppm; Yt 200, 250 ppm.

B-group. The most important substitution is of Mn for Fe, resulting in the Mn end-member, kupletskite, and complete solid solution almost certainly exists between astrophyllite and kupletskite (Semenov, 1956; Nickel *et al.*, 1964) (fig. 1a). Mg is also an important substitute for Fe, occupying up to 30 % of B-sites in kupletskite from the Sea of Azov region, U.S.S.R. (table III, no. 19).

Zn ranges from 0.02 atom in the Spanish astrophyllites to 0.31 atom in the Colorado specimen, which is the most Zn-enriched astrophyllite yet recorded. Borley (1963) has described the entry of Zn into riebeckite-*arfvedsonites* from the Younger Granites of

TABLE I. *New analyses of astrophyllite from various localities. M. J. Saunders, anal.*

	1	2	3	4	5	6	7	8
SiO ₂	35·41	34·71	35·79	34·18	35·99	35·86	34·81	33·93
Al ₂ O ₃	0·40	0·89	0·72	1·54	3·46	2·61	2·00	1·46
TiO ₂	9·92	8·90	9·88	9·04	8·15	10·14	10·48	8·87
ZrO ₂	0·99	1·38	1·74	3·70	4·53	1·89	0·40	1·60
Nb ₂ O ₅	2·76	2·58	1·87	1·07	1·25	0·78	1·22	3·45
Ta ₂ O ₅	0·26	0·29	0·16	0·06	0·10	0·04	0·13	0·46
SnO ₂	0·40	0·30	0·07	0·14	0·04	0·01	0·20	0·38
FeO	29·56	35·23	33·11	27·02	20·91	22·65	34·35	30·59
Fe ₂ O ₃	0·76	0·70	1·76	0·67	1·48	0·87	0·89	3·80
MnO	4·16	1·02	1·70	7·41	8·14	9·10	2·00	2·10
MgO	0·11	0·08	0·21	0·97	0·87	1·49	0·10	0·19
ZnO	1·88	0·76	0·58	0·24	0·18	0·34	0·12	0·11
PbO	0·43	0·37	0·10	< 0·01	< 0·01	< 0·01	0·15	0·06
Li ₂ O	0·181	0·051	0·050	0·036	0·016	0·015	0·198	0·028
CuO	0·005	0·010	0·013	0·005	0·017	0·004	0·012	0·022
Na ₂ O	2·97	2·72	2·83	2·19	2·46	2·57	2·15	2·00
K ₂ O	5·04	5·57	5·48	5·98	6·03	6·06	4·91	4·99
Rb ₂ O	1·10	0·38	0·19	0·31	0·41	0·20	0·36	0·49
Cs ₂ O	0·08	0·07	< 0·01	0·15	0·12	< 0·01	0·06	0·19
CaO	0·23	0·28	0·46	1·43	1·56	1·60	1·15	0·82
SrO	0·007	0·003	0·008	0·034	0·020	0·022	0·018	0·009
BaO	0·120	0·020	0·050	0·035	0·097	0·069	0·091	0·053
P ₂ O ₅	0·04	n.f.†	n.f.	0·01	0·04	0·01	n.f.	n.f.
F	1·15	1·24	1·38	1·26	1·22	1·27	1·29	0·90
H ₂ O ¹	2·70	2·60	2·49	2·80	2·91	2·71	2·79	3·37
Cl	< 0·01	< 0·01	< 0·01	< 0·01	< 0·01	< 0·01	< 0·01	< 0·01
Sum	100·66	100·15	100·64	100·28	100·00	100·31	99·88	99·87
O=(F,Cl) ₂	0·48	0·52	0·58	0·53	0·51	0·53	0·54	0·38
Total	100·18	99·63	100·06	99·75	99·49	99·78	99·34*	99·49

* Acid insoluble 0·38 %. † Not found.

Key to Tables I and II; 1, 2, 3 from oversaturated rocks, 4, 5, 6, from undersaturated, and 7, 8 from metamorphic.

1. Astrophyllite, pegmatite, St. Peter's Dome, El Paso County, Colorado. Occurs as crystals up to 7 cm × 2 cm × 1 cm embedded in quartz. The geology and mineralogy of these pegmatites have been described by Gross and Heinrich (1966), who give the following optical data for the astrophyllite: α 1·695, red-orange, β 1·725, lemon-yellow, γ 1·755, dark yellow-green; 2V_y large.
2. Astrophyllite from peralkaline granite sheet (Greenland Geol. Surv. no. 26272), Kûngnât complex, South Greenland. White homogeneous rock consisting of euhedral antiperthite (65·5 % modally), anhedral quartz (29·0), riebeckite or arfvedsonite (4·5), zircon (tr.), opaque ore (tr.), and astrophyllite (0·8). Latter has α 1·695, orange, β 1·715, yellow, γ 1·751, lemon-yellow; 2V_y 66 to 70° (B. G. J. Upton, pers. comm.).
3. Astrophyllite from peralkaline granite sill (G.G.U. no. 40595/86114), Central Complex, Tûgtutoq, South Greenland. Anhedral crystals up to 1 mm long (0·6 % modally), occur in association with alkali feldspar (76·3), quartz (18·4), riebeckite or arfvedsonite (4·7), and fluorite (trace). α bright-orange, β 1·721, orange-yellow, γ 1·751, yellow; 2V_y 69 to 75°.
4. Astrophyllite, pegmatite, Barkevîk, Langesundfjord, Norway, from the collections of the Department of Geology, University of Edinburgh. Associated minerals in hand specimen used for mineral separation include perthitic feldspar, nepheline, aegirine, riebeckite or arfvedsonite, and zircon. Astrophyllite occurs as flakes up to 7 cm × 2 cm, sometimes intergrown with pyroxene or amphibole. α orange, β 1·710, orange-yellow, γ 1·740, lemon-yellow. 2V_y large.

TABLE II. Unit-cell contents, based on 31 anions, of new analyses of astrophyllites

	1	2	3	4	5	6	7	8
Na	1.277	1.182	1.208	0.940	1.030	1.076	0.916	0.854
K	1.426	1.591	1.538	1.691	1.661	1.667	1.377	1.402
Rb	0.147	0.054	0.026	0.045	0.057	0.029	0.050	0.069
Cs	0.003	0.005	—	0.013	0.010	—	0.005	0.019
Ca	0.055	0.067	0.108	0.339	0.361	0.369	0.270	0.193
Sr	0.001	0.001	0.001	0.004	0.003	0.003	0.003	0.001
Ba	0.011	0.001	0.004	0.003	0.008	0.005	0.008	0.004
A	2.920	2.901	2.885	3.035	3.130	3.149	2.629	2.542
Fe ²⁺	5.484	6.600	6.088	5.007	3.776	4.087	6.316	5.631
Fe ³⁺	0.128	0.118	0.291	0.112	0.241	0.070	0.147	0.630
Mn	0.781	0.194	0.317	1.391	1.488	1.663	0.372	0.391
Mg	0.036	0.027	0.069	0.321	0.280	0.480	0.033	0.062
Li	0.163	0.046	0.045	0.032	0.013	0.013	0.174	0.024
Zn	0.308	0.125	0.094	0.039	0.029	0.054	0.020	0.019
Cu	0.003	0.001	0.003	0.001	0.003	0.001	0.003	0.004
Pb	0.025	0.023	0.005	—	—	—	0.009	0.004
B	6.928	7.134	6.912	6.903	5.830	6.368	7.074	6.765
Ti	1.656	1.500	1.634	1.506	1.324	1.645	1.733	1.468
Zr	0.107	0.151	0.186	0.399	0.478	0.198	0.042	0.172
Nb	0.277	0.261	0.185	0.107	0.122	0.075	0.121	0.344
Ta	0.016	0.019	0.010	0.003	0.005	0.003	0.008	0.026
Sn	0.036	0.027	0.001	0.012	0.004	0.001	0.017	0.033
C	2.092	1.958	2.016	2.027	1.933	1.922	1.921	2.043
Al	0.104	0.234	0.188	0.402	0.880	0.664	0.519	0.378
Si	7.855	7.777	7.869	7.572	7.772	7.736	7.653	7.468
D	7.959	8.011	8.057	7.974	8.652	8.400	8.172	7.846
OH	3.996	3.885	3.652	4.138	4.192	3.899	4.090	4.949
F	0.806	0.879	0.959	0.883	0.833	0.866	0.894	0.627
O	26.198	26.236	26.389	25.979	25.975	26.235	26.016	25.424
Σ cations	19.899	20.004	19.870	19.939	19.545	19.839	19.796	19.196
Fe ²⁺ /Fe ³⁺	42.84	55.9	20.9	44.7	15.7	58.4	43.0	8.9
K/Na	1.12	1.35	1.27	1.80	1.61	1.55	1.50	1.64
K/Rb (wt)	4	13	26	18	13	27	12	9
Nb/Ta (wt)	9.1	7.6	10.0	15.2	10.7	16.6	8.0	6.4

- Astrophyllite, Narssarsuk, S. Greenland (G.G.U. no. 63785A). From pegmatite cutting SI-4 syenite, Igaliko Complex (see Emelius and Harry, 1970, p. 70). Pegmatite contains abundant aegirine, perthitic alkali feldspar, natrolite (in granular aggregates), cancrinite, and (?) zircon. Optical data on astrophyllite, kindly supplied by Dr. C. H. Emelius: β 1.710, γ 1.735, $2V_{\gamma}$ $84 \pm 1.5^{\circ}$.
- Astrophyllite, microfoyaite dyke, Mirala Estate, Zomba, Malawi. (Coll. no., Malawi Geol. Surv. is K.B. 1689.) This dyke described by Bloomfield, 1965, p. 142. Dyke also contains aegirine, nepheline, alkali feldspar and alkali amphibole, titanomagnetite, fluorite, rutile, and zircon. Astrophyllite occurs as narrow, bronzy yellow flakes up to 4×40 mm in size, enclosing feldspar, and showing the pleochroic scheme α bright orange, β yellow, γ pale lemon-yellow.
- Astrophyllite from riebeckite-gneiss of Galiñeiro type, south of La Guía, Vigo, Spain (Floor, 1966, coll. no. 61 cor 20). Crystals up to 2 mm in length in association with quartz, albite, microcline ($Or_{99.6}Ab_{0.4}An_{0.0}$), riebeckite, lepidomelane, aegirine, zircon, fluorite, and trace amounts of nigerite. α orange, β 1.722, yellow, γ 1.757, lemon-yellow; $2V_{\gamma}$ 88.4° in red light, 81.9° in green light.
- Astrophyllite from non-deformed pegmatite, 10 cm thick, south of Monte Galiñeiro, Vigo, Spain (Floor, 1966, pegmatite of col 602 m., p. 59). Floor describes the geology and mineralogy of this pegmatite, which contains quartz, microcline, albite, astrophyllite, riebeckite, zircon, xenotime, and pyrochlore. Astrophyllite forms thin crystals up to 5 mm long, and with α orange-red, β 1.726, yellow, γ 1.758, lemon-yellow; $2V_{\gamma}$ 78.6° in red light, 67.2° in green light.

TABLE III. Unit-cell contents, based on 31 anions, of minerals of the astrophyllite group, calculated from published analyses (refs. below). 9—from oversaturated igneous, 10–21—from undersaturated igneous, 22—from metamorphic, parageneses; 23–24, 'high-alkali' astrophyllites

	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Na	1.274	0.936	1.265	0.983	1.259	1.264	1.177	1.259	1.352	1.308	1.211	0.892	0.892	1.079	2.146	1.860
K	1.421	1.876	1.637	1.630	1.578	1.814	1.617	1.636	1.713	1.661	1.245	1.547	1.202	1.572	1.911	1.791
Rb	—	—	—	—	—	—	—	—	—	—	—	0.052	—	—	—	—
Ca	0.158	0.282	0.375	0.402	0.298	0.239	0.296	0.169	0.273	0.293	0.242	0.335	0.830	0.173	0.253	0.966
Sr	—	—	0.007	0.005	—	—	—	—	—	—	—	—	—	—	—	—
Ba	—	—	0.013	—	—	—	—	—	—	—	—	0.027	—	—	—	—
Ln	—	—	—	—	—	—	—	—	—	—	—	—	—	0.123	—	—
A	2.853	3.094	3.297	3.020	3.135	3.317	3.090	3.064	3.338	3.262	2.698	2.853	2.924	2.947	4.310	4.617
Fe ²⁺	4.131	5.471	4.859	3.592	4.124	4.189	3.989	3.699	3.042	2.561	1.342	0.964	0.979	4.439	3.081	2.970
Fe ³⁺	1.714	0.644	0.432	1.062	0.443	0.459	0.416	0.656	0.720	0.232	0.146	1.262	—	—	0.457	0.317
Mn	0.254	0.521	1.225	1.241	1.338	1.970	2.220	2.407	2.821	2.965	3.436	4.303	5.040	1.862	0.696	0.532
Mg	0.214	0.294	0.499	0.376	0.307	0.313	0.300	0.349	0.206	0.121	2.108	0.523	0.956	0.053	1.959	1.749
Li	—	—	—	—	—	—	—	—	—	—	—	0.083	—	—	—	—
Zn	—	—	—	—	—	—	—	—	—	0.033	—	—	—	—	—	—
B	6.313	6.930	7.035	6.271	6.212	6.931	6.925	7.111	6.789	5.912	7.032	7.135	6.975	6.354	6.193	5.568
Ti	1.560	2.014	1.940	2.126	1.520	1.553	1.831	1.476	1.323	1.521	0.850	1.723	1.949	0.494	1.884	1.870
Zr	0.346	0.086	0.060	0.000	—	0.493	0.390	0.416	0.571	0.262	0.311	0.000	0.125	—	—	—
Nb	0.077	—	—	—	0.120	—	—	—	—	0.476	0.059	0.241	0.005	1.492	—	—
Ta	0.008	—	—	—	0.003	—	—	—	—	—	—	—	—	0.032	—	—
Sn	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
C	1.991	2.100	2.000	2.126	1.643	2.046	2.221	1.892	1.894	2.259	1.220	1.964	2.139	2.018	1.884	1.870
Al	0.147	0.311	0.154	0.583	1.259	0.425	0.253	0.337	0.445	0.516	1.324	0.254	0.427	0.235	0.269	0.220
Si	7.830	7.485	7.567	7.200	7.257	7.397	7.237	7.500	7.416	7.656	7.423	7.220	7.015	7.467	7.812	7.943
D	7.977	7.796	7.721	7.783	8.516	7.822	7.490	7.837	7.861	8.172	8.747	7.474	7.442	7.702	8.081	8.163
OH	3.717	4.835	4.330	5.032	5.773	5.074	5.078	5.297	5.024	4.251	5.597	5.600	5.503	5.429	4.724	4.683
F	1.104	—	0.592	0.885	0.429	—	0.673	—	0.485	0.450	0.650	—	0.830	0.325	0.293	0.331
Cl	—	—	0.129	0.000	—	—	—	—	—	—	—	—	—	—	—	0.038
O	26.179	26.165	25.949	25.083	24.798	25.926	25.249	25.703	25.491	26.299	24.753	25.400	24.667	25.246	25.983	25.948
Σ cations	19.134	19.920	20.053	19.200	19.506	20.116	19.726	19.904	19.882	19.605	19.697	19.426	19.480	19.021	20.268	20.118
Fe ²⁺ /Fe ³⁺	2.41	8.50	10.75	3.38	9.31	9.13	9.59	5.64	4.23	11.04	9.19	0.76	—	—	6.74	9.37
K/Na	1.12	2.00	1.29	1.66	1.25	1.44	1.37	1.30	1.27	1.27	1.03	1.73	1.35	1.46	0.90	0.96
K/Rb (wt.)	—	—	—	—	—	—	—	—	—	—	—	14	—	—	—	—
Nb/Ta (wt.)	4.6	—	—	—	35.6	—	—	—	—	—	—	—	—	24.2	—	—

Nigeria, where it occurs up to a maximum of 0.10 atom per unit-cell (0.93 % wt. ZnO), and has suggested that this represents an unusually large amount of Zn to be found in silicate lattices. Astrophyllite must therefore be considered a strong Zn-concentrator.

TABLE IV. *Data indicating the degree of solid substitution between astrophyllite and Cs-kupletskite.*

Locality	Cs × 100 Cs + Na + K (atomic)	
Lovozero, U.S.S.R.	0.03	Ganzeev <i>et al.</i> , 1969
Kūngnāt, S. Greenland	0.20	
Narsarssuaq, S. Greenland	0.40	This paper
Tuva, U.S.S.R.	1.18	
Burpala, U.S.S.R.	2.00	Ganzeev <i>et al.</i> , 1969
Burpala, U.S.S.R.	4.33	
Dara Pioz, U.S.S.R.	7.56	
Dara Pioz, U.S.S.R. (Cs-kupletskite)	45.51	

The Colorado specimen is also the most Pb-enriched of our samples (0.03 atom), though this element normally occurs in only very minor amounts, being below the limit of detection (0.01 % wt.) in three of the samples. Cu is also a relatively unimportant minor substituent for Fe. Koenig (1877) reported a CuO value of 0.42 % (wt.) in astrophyllite from El Paso co., Colorado, but the new data (table I) suggest that his figure may be in error. Li is present in our samples up to a maximum of 0.17 atoms in a Spanish astrophyllite, though Ganzeev *et al.* (1969) have recorded astrophyllites richer in Li from several Russian localities, ranging up to 0.59 % Li (wt.).

Fe²⁺/Fe³⁺ ratios in the new and published analyses vary widely, from 0.8 to 58.4, but the new analyses generally show the Fe to be present mostly in the divalent form.

Source of analyses used in table 3

- Specimens 9–18, astrophyllite; 19–21, kupletskite; 22—niobophyllite; 23, 24 high-alkali astrophyllite.
 9—post-Jurassic alkaline granite, Maritime Province, U.S.S.R. (Perchuk and Zyryanov, 1965, table 1, no. 10);
 10—Naujakasik, Tunugdliarfik, S. Greenland (Kunitz, 1936, table 9);
 11—Kukisvumchorr, Chibina Tundra, Kola, U.S.S.R. (Bonshtedt, 1931);
 12—Yukspor, Chibina Tundra, Kola, U.S.S.R. (Bonshtedt, 1931);
 13—Central Turkestan–Alay Range, U.S.S.R. (Perchuk, 1964, p. 204);
 14—Brevik, Norway (Kunitz, 1936, table 9);
 15—Island of Eikaholm, Norway (Brøgger, 1890);
 16—Rume, Los Archipelago (Kunitz, 1936, table 9);
 17—Låven, Langesundfjord, Norway (Gossner and Reindl, 1934, p. 165);
 18—Middle Tatarsk massif, U.S.S.R. (Sveshnikova, 1960, table 1);
 19—Sea of Azov region, U.S.S.R. (Valter *et al.*, 1965, p. 251);
 20—Mt. Nephka, Lovozero, Kola, U.S.S.R. (Semenov, 1956, 1960);
 21—Mt. Kuivchorr, Lovozero, Kola, U.S.S.R. (Semenov, 1956);
 22—Seal Lake, Labrador (Nickel *et al.*, 1964);
 23—U.S.S.R., (Peng and Ma, 1963);
 24—Pegmatite, Yukspor, Khibina, U.S.S.R. (Dorfman, 1962, p. 54).

From a spectral study of astrophyllite from El Paso County, Colorado, Manning (1969, p. 672) has suggested that Fe^{3+} ions are not located in the octahedral layer, despite the presence in Koenig's (1877) analysis of material from this locality of significant Fe_2O_3 ($\text{Fe}^{2+}/\text{Fe}^{3+}$ (atomic) = 4.4). The new analysis of Colorado astrophyllite (spec. 1) has a value of this ratio of 42.8. These features combined suggest that Fe^{3+} is relatively minor in the astrophyllite structure, and that many of the older analyses may be in error in this regard.

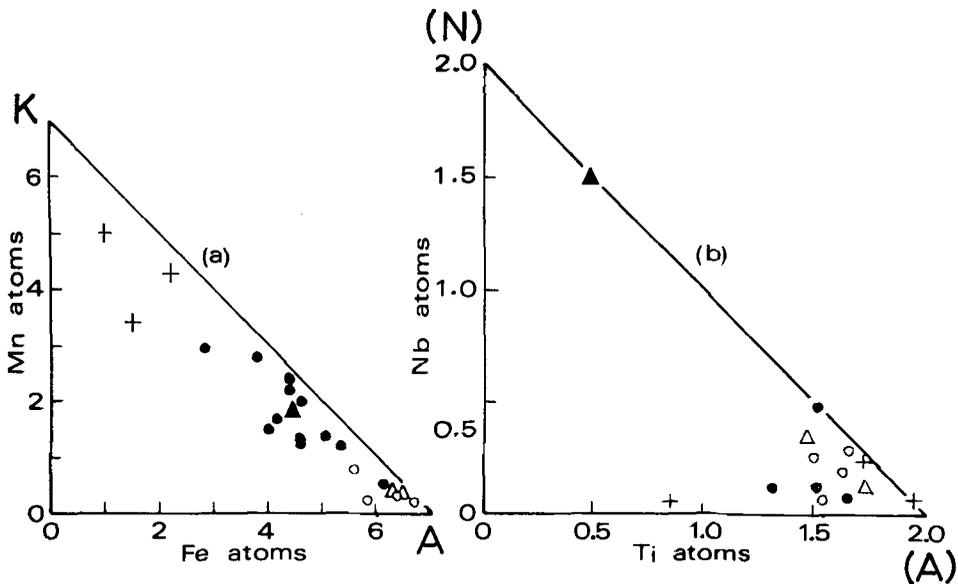


FIG. 1. Degree of solid substitution between (a) theoretical astrophyllite (A) and kupletskite (K) compositions, and (b) astrophyllite and niobophyllite (N). Open circles—astrophyllites from oversaturated rocks; closed circles—astrophyllites from undersaturated rocks; open triangles—astrophyllites from Spanish metamorphic rocks; closed triangle—niobophyllite; crosses—kupletskite.

Dietrich *et al.* (1965, table 4) found Cr, Sc, and V below the limits of detection in astrophyllite from two Norwegian ekerites, while Ni was detectable at 75 and 90 ppm.

C-group. Due to an inadequate number of available analyses, Nickel *et al.* (1964) were unable to draw any conclusions about the degree of solid solution between astrophyllite and its Nb-analogue, niobophyllite. Data now available (fig. 1b) indicate that Nb replaces Ti in astrophyllite up to some 24 % of available sites, but that there is still a considerable composition gap between astrophyllite and niobophyllite. Hansen (1968) has given values of 4.2–7.1 % Nb_2O_5 (wt.) for niobophyllite from the Ilmaussaq intrusion, S. Greenland, and, although the full analysis of this mineral has not yet been published, it seems likely that it will fall in the composition gap of fig. 1b.

Ta is a very minor substitute for Ti, occurring up to 0.03 atom (table III). The Nb/Ta ratio varies from 5 to 36 (wt. %). The importance of Zr replacing Ti in astro-

phyllite was recognized by Kunitz (1936); Zr ranges from 0.00 to 0.57 atoms, that is, it occupies up to 28 % of the theoretical C-sites. The most Zr-rich specimens are those from the nepheline syenite pegmatites of the Permian Oslofjord alkaline province.

Sn is present in only trace amounts, up to 0.04 atom. The only determination of Hf in astrophyllite is from the Kangerdlugssuaq alkaline intrusion, E. Greenland, where Brooks (1970) records Hf 0.2 %, Zr 1.13 %, and a Zr/Hf (wt.) ratio of 5.7.

D-group. Al is an important substitute for Si in the tetrahedral sites, occupying up to 16 % of the D-sites.

X-group. The main substituent is F, which reaches 1.1 atoms. Cl is very low (< 0.01 % wt.) in all our specimens. The only other determinations, in two astrophyllites from Kola, U.S.S.R (Bonshtedt, 1931), gave 0.00 and 0.35 % wt. Cl, the latter equivalent to 0.129 atom Cl in the unit cell. OH has a fairly small range, some 3.5 to 6 atoms.

Stoichiometry. Nickel *et al.* (1964) found appreciable departures from the ideal $A_3B_7C_2D_8X_{31}$ formula in kupletskite, niobophyllite, and astrophyllite from Colorado, and suggested that non-stoichiometry may be a characteristic feature of the group. This prediction appears to be borne out by the larger body of data (tables II and III). All but three of the analyses show cation deficiencies ranging up to 0.98 atoms per unit cell, or some 5 % of available sites. This feature is partly due to failure in most cases to analyse for all possible substituting elements. Of the 8 new analyses, 6 have total cations equal to or greater than 19.8 per unit cell, suggesting perhaps that many astrophyllites will prove to be nearly stoichiometric when fully analysed. However, the Spanish astrophyllite F92 (spec. 8) contains only 19.2 cations per unit cell, exhibiting one of the largest deficiencies of all specimens we have examined.

There is no preferential tendency towards either cation excess or deficiency in the A, C, and D groups, but in the B-group deficiency of cations is more common than excess. There is also no strong correlation between cation deficiency in one group and cation excess in another.

Relationship between composition and paragenesis

Igneous rocks. Systematic differences between astrophyllites found in granitic rocks (oversaturated parageneses) and those from feldspathoidal rocks (undersaturated parageneses) can be readily detected by inspection of tables II and III. Compared to the 'oversaturated' types, astrophyllites from undersaturated rocks show higher Na+K, Ca, Sr, Mn, Mg, Zr, Al, and OH+F and lower Zn, Pb, and Li contents. The data of Ganzeev *et al.* (1969) suggest that the highest concentrations of Rb and Cs are also found in astrophyllites from granitic rocks, and this is in accord with the high values for those elements found in the Colorado specimen during this study.

There is also a strong tendency for K/Na ratios to be higher in 'undersaturated' types, and the increased Na+K content usually results in a cation excess in the A-group, while 'oversaturated' astrophyllites usually have a cation deficiency in this group (tables II and III). Between 'oversaturated' and 'undersaturated' types, there is,

therefore, increasing replacement of Mn and Mg for Fe, Ca for alkalis, Zr for Ti, Al for Si, and (OH+F) for O. There is no obvious connection between the Nb-content of astrophyllite and the type of rock in which it is found.

It seems clear that the relatively open structure of astrophyllite allows it to accept a large number of minor elements; the mineral acts as a 'soak' for the residual elements during magmatic crystallization and its composition varies with the composition of the residual solutions. Ganzeev *et al.* (1969) have already suggested that the enrichment of the alkali metals in various Russian astrophyllites closely reflects the concentration of these elements in the host-rock.

Metamorphic rocks. The two Spanish astrophyllites are found in association with quartz and are generally similar in composition to the astrophyllites from oversaturated rocks, except that the contents of Ca and Al and the K/Na ratios are more similar to those from undersaturated parageneses. Both show a large cation deficiency in the *A*-group, and also Zn is particularly low. The composition of astrophyllites will depend on the composition of the host-rock, but further analyses may show that it also varies with the type of metamorphism and the pressure-temperature conditions.

Niobophyllite, found in association with albite and arfvedsonite in paragneiss (Nickel *et al.*, 1964) is as yet unique in the astrophyllite group, and perhaps owes its unusual composition to the unique nature of the Seal Lake deposit.

High alkali astrophyllites. Woodrow (1967, p. 678) has pointed out that the composition and structure of an astrophyllite studied by Peng and Ma (1963) may indicate the occurrence of several other varieties of the mineral. The analysis of Peng and Ma's specimen and that of a closely similar astrophyllite studied by Dorfman (1962), are included in table III (nos. 23 and 24). They are characterized by being very Mg-rich (up to 2 atoms per unit-cell), and by having a large excess of cations in the *A*-group, very low K/Na ratios (< 1), and an overall excess of cations per unit-cell. To distinguish them from other members of the group, we have termed them 'high-alkali' astrophyllites. The extra Na atoms and the high Mg contents have resulted in structural modifications compared to the structure of the Colorado astrophyllite studied by Woodrow (1967) and Woodrow has suggested that other varieties, with different Ti/Si ratios in the tetrahedral layers, may also be possible.

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REFERENCES

- BLOOMFIELD (K.), 1965. *Bull. Geol. Surv. Malawi*, 16.
 [BONSHTEDT (E.)], БОШТЕДТ (Э.), 1931. Зап. Росс. мин. общ. (*Mém. Soc. Russe Min.*), ser. 2, 60, 280 [MA 5-232].
 BORLEY (G. D.), 1963. *Min. Mag.* 33, 358.
 BRØGGER (W. C.), 1890. *Zeits. Krist.* 16, 1.
 BROOKS (C. K.), 1970. *Geochimica Acta*, 34, 411 [MA 21-2364].
 BUTLER (J. R.), BOWDEN (P.), and SMITH (A. Z.), 1962. *Ibid.* 26, 89.

- DIETRICH (R. V.), HEIER (K. S.), and TAYLOR (S. R.), 1965. *Skr. norske Vidensk. Akad. Mat. Naturv. Kl.*, 19.
- [DORFMAN (M. D.)] Дорфман (М. Д.), 1962. Минералогия пегматитов и зон выветривания в ийолит-уртитях Юкспор Хибинского массива [*Mineralogy of the pegmatites and areas of wind erosion in ijolite-urtite of the Yukspor peak in Khibiny mountain range*] Изд. АН СССР (Akad. nauk U.S.S.R. Press), Moscow [MA 16-557].
- EAKINS (L. G.), 1891. *Amer. Journ. Sci.*, ser. 3, **42**, 35.
- EMELEUS (C. H.) and HARRY (W. T.), 1970. *Medd. Grønland*, **186**, nr. 3.
- ESKOLA (P.) and SAHLSTEIN (Th. G.), 1930. *Bull. Comm. Géol. Finlande*, **92**, 77.
- FLOOR (P.), 1961. *Notas Com. Inst. Geol. Min. España*, **62**, 59.
- 1966. *Leidse Geol. Medd.* **36**, 1.
- [GANZEEV (A. A.), EFIMOV (A. F.), and SEMENOVA (N. G.)] ГАНЗЕЕВ (А. А.), ЕФИМОВ (А. Ф.), и СЕМЕНОВА (Н. Г.), 1969. [Геохимия, 335] transl. as *Geochem. Intern.* **6**, 295.
- GOSSNER (B.) and REINDL (E.), 1934. *Centr. Min. Abt. A*, 161.
- GROSS (E. B.) and HEINRICH (E. W.), 1966. *Amer. Min.* **51**, 299.
- HANSEN (J.), 1968. *Rept. 23rd Intern. Geol. Congr., Czechoslovakia*, **7**, 263.
- KOENIG (G. A.), 1877. *Zeits. Kryst. Min.*, **1**, 423.
- KUNITZ (W.), 1936. *Neues Jahrb. Min. Abt. A, Beil.-Bd.* **70**, 429.
- MANNING (P. G.), 1969. *Canad. Min.* **9**, 663 [M.A. 21-1553].
- MAXWELL (J. A.), 1968. *Rock and mineral analysis*. New York and London (Wiley: Interscience). [M.A. 20-1897].
- NICKEL (E. H.), ROWLAND (J. F.), and CHARETTE (D. J.), 1964. *Canad. Min.* **8**, 40.
- PENG (CHIH-CHUNG) and MA (CHE-SHENG), 1963. [*Scientia Sinica*, **12**, 272]; *Min. Abstr.* **16-611**.
- [PERCHUK (L. L.)] Перчук (Л. Л.), 1964. [*Physico-chemical petrology of the granite and alkaline intrusions of the Central Turkestan-Alay Range.*] (In Russian.) Moscow (Akad. nauk U.S.S.R. Press).
- and ZYRYANOV (V. N.) [Зырянов (В. Н.)], 1965. *Doklady Acad. Sci. U.S.S.R., Earth Sci. Sect.* **162**, 200, transl. from Докл. Акад. наук СССР, **162**, 671 [M.A. 19-139].
- [SEMENOV (E. I.)] Семенов (Е. И.), 1956. Доклады Акад. наук СССР (*Compt. Rend. Acad. Sci. USSR*), **108**, 933 [M.A. 13-384].
- [—] — 1960. Труды Инст. мин., геохим. крист. редк. элем. (*Trans. Inst. Min., Geochem. Cryst. Rare Elements*), **4**, 20.
- [SVESHNIKOVA (E. V.)] Свешникова (Е. В.), 1960. Геология и Геофизика, **2**, 142.
- [VALTER (A. A.), EREMENKO (G. K.), and LYSENKO (G. A.)] Вальтер (А. А.), Еременко (Г. К.) и Лысенко (Г. А.), 1965. Мин. Сборник Львов геол. общ. (*Min. Mag. Lvov Geol. Soc.*), **19**, 248.
- WOODROW (P. J.), 1967. *Acta Cryst.* **22**, 673.

Appendix on analytical methods

M. J. SAUNDERS

(Brief notes are given on the analytical procedure for each element. Details of the procedures, instrumental conditions, standard materials, etc., may be obtained from M. J. Saunders.)

Sample attack. Samples were easily and completely attacked by evaporating with HF, HNO₃, and H₂SO₄ in the usual manner. Residues were easily soluble in dil. H₂SO₄ to give a clear solution initially, but after a few minutes, especially with more prolonged heating, Sn, Ta, and Nb precipitated.

If HF, HNO₃, and HClO₄ were used, although attack appeared to be complete, the residues produced were often insoluble in dil. HCl, a white precipitate presumably containing Ta, Nb, Ti, and Sn remaining. Some MnO₂ was produced with sample weights of 0.1 g and over for those samples with high Mn. It was dissolved by adding dil. H₂O₂.

Silicon. This was determined using the Jeffery and Wilson (1960) method. The method was slightly modified, only 0.3-0.4 g sample being used, to keep Ti below the level at which it interfered. A Palau crucible was used for the Na₂CO₃ fusion. The melt was dissolved in 9 ml HCl. Impure SiO₂ was ignited at 1200 °C before weighing. The residue after volatilization of SiO₂ was large, containing

most of the Sn, Ti, Nb, and Ta present; it was therefore ignited at the same temperature as the impure SiO_2 before weighing. It was fused with the minimum quantity of KHSO_4 , the melt dissolved by warming with 1 ml HCl and water (Sn, Nb, and Ta remain insoluble here and were ignored), and added to the filtrate from the gravimetric SiO_2 determination which was then diluted to 200 ml. The residue containing Nb, Ta, Sn, Pb, and Ba was allowed to settle and SiO_2 in the filtrate determined colorimetrically as soon as possible after the gravimetric determination. Small amounts of Sn and Pb present in the samples should not affect the accuracy of this determination.

Aluminium, calcium, magnesium, and manganese. These were determined in the filtrate from the SiO_2 determination. The insoluble material containing Nb, Pb, Sn, Ta, and Ba was allowed to settle before taking aliquots.

Al_2O_3 . LaCl_3 was added to a 25 ml aliquot which was then diluted to 50 ml. Standards contained LaCl_3 , NaCl, and HCl in similar concentrations to those in sample solution. Determination was by A.A. using a $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame.

MnO. An aliquot of between 25 and 50 ml of the silica filtrate was diluted to 100 ml and Mn determined by A.A. using an air- C_2H_2 flame. NaCl was not added to standards. As a check on the accuracy of these determinations in the samples containing most Mn, Mn was also determined colorimetrically as permanganate using periodate as an oxidizing agent (Sandell, 1959, p. 608), and by the titrimetric method of Lingane and Karplus (1946).

The results by the three methods for MnO in sample 4 were: A.A. 7.33 %. Colorimetric 7.41, 7.51 %. Titrimetric 7.44 %.

CaO, MgO. For Ca a 25 ml, and for Mg a 5 or 10 ml aliquot of the SiO_2 filtrate were used. Aliquots were diluted to 100 ml and Ca and Mg determined by A.A. using $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ and air- C_2H_2 flames respectively. Sample and standard solutions contained like amounts of LaCl_3 , NaCl, and HCl.

Iron. This was determined using SnCl_2 reduction (Mercy and Saunders, 1966). A 0.08 to 0.1 g sample was attacked with HNO_3 , HF, and HClO_4 in a P.T.F.E. crucible. The crucible and residue were placed in a conical beaker, 5 ml of HCl and 20 ml water added, and the beaker and contents heated to give maximum solution. The insoluble residue was ignored and Fe^{3+} reduced with SnCl_2 in a CO_2 atmosphere in the usual manner. $\text{K}_2\text{Cr}_2\text{O}_7$ (0.03 N) was used to titrate Fe^{2+} ; sodium diphenylamine sulphinate was used as indicator and a blank was determined.

SnCl_2 reduction is probably quite accurate applied to astrophyllite analysis as there is no V or Mo present. Results obtained suggested that there was no reduction of Nb and Ta present in the insoluble residue.

Titanium. This was determined colorimetrically as the peroxide. A 0.025 g sample was attacked with HF, HNO_3 , and H_2SO_4 . The residue was dissolved in dilute H_2SO_4 and the peroxide immediately developed. The final volume of dilution was 50 ml. Sulphuric acid (7 ml 1 + 1) was added to sample and standard solutions to buffer any effect due to sulphate in sample solutions. Phosphoric acid (10 ml 25 %) was added to all solutions to decolorize Fe. Tests showed that it was not fully effective and Fe equivalent to 30 % Fe_2O_3 in a sample gave an absorbance equivalent to about 0.05 % TiO_2 .

In the presence of Fe, H_3PO_4 , and H_2SO_4 similar in concentration to those in sample solutions, the Nb interference was proportional to the concentration of Nb, 0.25 mg Nb_2O_5 being equivalent to 0.021 mg TiO_2 . To make a valid correction for this interference Ti-peroxide was developed before Nb hydrolysed. Nb is then kept in solution as the peroxide.

Niobium was determined colorimetrically as the peroxide (Palilla *et al.*, 1953), after separation from Ta and Ti, etc., using ion-exchange according to the Kallman *et al.* (1962) method. 0.1 g of sample was attacked with HF, HNO_3 , and H_2SO_4 , dissolved in HF-HCl mixture and transferred to a column of Amberlite CG 400 resin, 12 inches long, contained in a flexible PVC tube of 1 cm internal diameter and supported by a disc of Perspex. The maximum flow rate possible with this column was slower than that described by the above workers. The column was washed with HF-HCl to elute Ti, Zr, Fe, etc., from Nb and Ta. Niobium was eluted from Ta by washing with NH_4Cl -HF mixture, H_3BO_3 and 10 mg Zr (as ZrOCl_2) added to the eluate and Nb+Zr precipitated with cupferron. Paper pulp was added and the precipitate filtered on a Whatman No. 40 paper and ignited in a Vitreosil crucible. The use of paper pulp here left ignited oxides easily attacked subsequently by fusing with 1.5 g of KHSO_4 ; the melt was dissolved in concentrated H_2SO_4 , transferred to a 50 ml flask and Nb determined as the peroxide in 96 % H_2SO_4 . The absorbance of a reagent blank containing KHSO_4 was also

measured. Tin, the only element present in astrophyllite that accompanies Nb through the ion-exchange separation was assumed not to interfere in the peroxide determination.

Tantalum was eluted from the resin column using $\text{NH}_4\text{Cl-NH}_4\text{F}$ mixture and determined colorimetrically using pyrogallol (B.I.S.R.A. 1967). 10 mg of Zr (as ZrOCl_2) were added to the eluate and Ta+Zr precipitated using cupferron. Paper pulp was added, the precipitate filtered, ignited in a Vitreosil crucible, and attacked, fusing with 1.5 g of KHSO_4 . The melt was dissolved in 4% ammonium oxalate and the colorimetric procedure applied. The sensitivity of this procedure is adequate for the determination of Ta in astrophyllite; 0.25 mg $\text{Ta}_2\text{O}_5/50$ ml gave an absorbance of 0.4 in 4 cm cells at 400 nm. A reagent blank containing KHSO_4 and Zr was measured, and found to be about 0.17, decreasing the accuracy of the Ta results obtained. Only Bi accompanies Ta through the ion exchange separation and it was absent in astrophyllite.

Iron, ferrous. Fe^{2+} was determined using a slightly modified version of Wilson's (1955) method. About 0.1 g NH_4VO_3 , accurately weighed, and 10 ml HF were added to 0.1 g sample in a Pt crucible, and the mixture left for 2 days. The crucible and contents were placed in $\text{H}_2\text{SO}_4\text{-H}_3\text{BO}_3$ solution, avoiding a washing operation, and unreduced NH_4VO_3 titrated with ferrous ammonium sulphate in the presence of H_3PO_4 , using sodium diphenylamine sulphonate as the indicator.

Zirconium was determined gravimetrically as the phosphate using the method described by Kolthoff and Sandell (1952, p. 725), with a little modification.

About 0.1 to 0.2 g of sample (depending on availability) were fused with K_2CO_3 in a Palau crucible and the melt extracted with water; Zr remains in the residue, and most of the Nb, Ta, Pb, and Sn present should pass into solution (cf. Schoeller and Powell, 1955, p. 200). The residue was dissolved in H_2SO_4 . If necessary Ba and Sr sulphates were filtered off, and Zr phosphate precipitated in the usual way in the presence of a very large excess of H_2O_2 to keep Ti and possible traces of Nb and Ta in solution. Precipitation was allowed to take place overnight. Paper pulp was added before filtration and the precipitate ignited in a Pt crucible taking the usual precautions in the presence of phosphate.

Qualitative X.R.F. analyses of the Zr phosphate precipitates indicated that only traces of Nb, Ta, and Ti were present, the major contaminant being iron, which must have been present only in small amounts as the precipitates were pure white.

Copper, zinc, potassium, lithium, sodium (manganese). A 0.1 g sample (0.05 g if material is scarce) was attacked with HF, HNO_3 , and H_2SO_4 , dissolved in dilute H_2SO_4 and diluted to 50 ml (25 ml if using the smaller sample wt.). Cu, Zn, and Li were normally determined in this solution, though the concentration of Zn was in some cases too high. A 10 ml aliquot was diluted to 100 ml for Na and K determinations, and for Zn where appropriate.

Na_2O and K_2O were determined directly using the EEL flame photometer. The concentrations of Na and K in the sample solutions were such that their mutual enhancement could be ignored.

For Na_2O determination, Ca interferes only if there is more than 2% CaO in the sample. Cs, Fe, and Mn can interfere but probably not in the concentrations found in astrophyllite; any enhancement due to Rb was ignored.

There are few interferences in the potassium determination. A correction was made for rubidium emission passing through the K filter (a wide spectral band-width gelatine filter was used). Interference in the determination of from 10 to 15 ppm K_2O was proportional to the Rb concentration, 1 ppm Rb_2O was equivalent to 0.6 ppm K_2O . Any enhancement due to Rb and Cs was ignored.

ZnO was determined using A.A. and a C_2H_2 -air flame. It was assumed that there were no interferences (Abbey, 1967, p. 14), but it is not known whether Nb or Zr interfere.

CuO was determined by A.A. using a C_2H_2 -air flame. There should be few interferences (Slavin, 1968, p. 103).

Li_2O was determined using A.A. and a C_2H_2 -air flame. It was assumed that there were no interferences (Slavin, 1968, p. 123). Standard solutions contained Na and K equivalent to 2.5% Na_2O and 5.5% K_2O in a sample.

MnO can be easily determined using A.A. in the solution used for Na and K analyses.

Rubidium and caesium were determined using the Unicam SP 900 flame photometer (C_2H_2 -air flame). We would have preferred to use propane as fuel, but did not possess a suitable burner. 0.1 g of sample was attacked with HF, HNO_3 , and H_2SO_4 , dissolved in HCl, diluted to 40 ml and a double precipitation of the R_2O_3 group made with NH_4OH in the presence of NH_4Cl (Peck, 1964), with the reagent

quantities scaled down. The filtrate was evaporated to small bulk and ammonium salts destroyed with HNO_3 (Smith, 1853), as the NH_4^+ ion interferes (Dean, 1961, p. 178). The residue was fumed with H_2SO_4 to remove nitrates, dissolved in dilute H_2SO_4 , and diluted to 25 ml.

For Rb, standard solution contained Na and K equivalent to 2.5 % Na_2O and 5.5 % K_2O in a sample.

Cs standards also contained Na and K in appropriate amounts. The background radiation when measuring Cs in samples was rather high, probably due to Ca and Mg, which are not separated using NH_4OH precipitation.

Cs_2O contents below 0.01 % could not be detected. Duplicate determinations agreed for sample 4.

Little Rb and Cs should be lost in the double NH_4OH precipitation in the presence of excess NH_4Cl (cf. Kolthoff and Sandell, 1952, p. 312).

Water was determined using the rapid method of Shapiro and Brannock (1955, 1962), but with the more efficient flux recommended by Peck (1964, p. 18). Sample weights of 0.1–0.2 g were used. Duplicate determinations using a small and large weight of sample agreed; results were precise to within 0.1 % H_2O absolute. Fluorine should not interfere, as it will be held by the flux.

Fluorine was determined by the method of Huang and Johns (1967) with modification to the procedure for measuring the absorbance of coloured solutions. 0.025 g of sample were attacked as described by the above workers and the sample solution diluted to 50 ml. A 5 ml aliquot was taken for the colour determination.

The following results were obtained over a period for % F in astrophyllite 2 using a variety of methods:

Titrimetric (Kolthoff and Sandell, 1952, p. 721)	1.20
Colorimetric (Huang and Johns), modified	1.28
Colorimetric (Peck and Smith, 1964)	1.24

Results reported here for % F in astrophyllite are therefore probably accurate to within ± 0.10 % absolute. The method used was selected because of its sensitivity, so that only a small sample weight was required, and because Cl may be easily determined at the same time.

Chlorine was sought using the method of Huang and Johns (1967) but was not detected in any of the samples.

Lead, barium, and strontium were determined in the same solution to conserve sample. A 0.05 g sample was attacked with HNO_3 , HF, and HClO_4 and the residue dissolved in HCl. LaCl_3 and 0.01 g NaCl (KCl may precipitate K perchlorate) were added and the solution diluted to 10 ml. Any insoluble material was allowed to settle before A.A. determinations.

PbO was determined using A.A. and a C_2H_2 -air flame. Standards contained appropriate amounts of NaCl and LaCl_3 . If there is sufficient sample the determination is best made in the absence of NaCl and LaCl_3 as they tend to cause unsteady readings. The absorbance of 10 ppm Pb, similar to the highest sample concentration of Pb measured, added to a solution of sample 6 which contains negligible Pb, was compared with that of a pure 10 ppm Pb solution. A relative enhancement of about 7.5 % was indicated under the conditions of the determination. Results for Pb were corrected by this factor.

BaO was determined by A.A. using a $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame. NaCl and LaCl_3 were added to standard solutions. Calcium may interfere (Kerber and Barnett, 1969), but it was assumed that interference was negligible as Ca is low in astrophyllite.

SrO was determined using A.A. and a $\text{N}_2\text{O}-\text{C}_2\text{H}_2$ flame. NaCl and LaCl_3 were added to standard solutions.

Tin was determined colorimetrically using 2:3:7 trihydroxy-9-phenyl-6-fluorone following the method of Luke, described by Sandell (1959, p. 862). From 0.01 to 0.02 g of sample containing less than 40 μg Sn were attacked with proportionately small volumes of HNO_3 , HF, and H_2SO_4 , dissolved in H_2SO_4 and the whole of the solution taken for the colour determination. The calibration graph, 0 to 80 μg Sn taken through the procedure, was linear to 40 μg Sn, then flattened quickly. The absorbance of a reagent blank taken through the whole procedure was measured. Best quality reagents (such as 'Aristar' grade) are necessary to keep the blank absorbance low.

Phosphorus was determined using the method of Murphy and Riley (1958) in samples where there was plenty of material. A turbidity developed in coloured solution on standing overnight. The precipitate, presumably of Sn, Ta, Nb, was allowed to settle before absorbance measurements.

Rare earths. These were sought in sample 5 by standard methods (Schoeller and Powell, 1955; Groves, 1951) using the silica filtrate after determining Al, Ca, Mg, and Mn and the eluate from the determination of Nb. Rare earth contents were too low for their determination gravimetrically. An X.R.F. qualitative comparison of Ln contents indicated that similarly low amounts were present in all samples.

REFERENCES

- ABBEY (S.), 1967. *Geol. Surv. Canada, Paper 67-37*, 35 pp. [M.A. 21-1064].
B.I.S.R.A., 1967. Open report MG/D/556/67.
DEAN (J. A.), 1960. *Flame Photometry*. New York (McGraw-Hill).
GROVES (A. W.), 1951. *Silicate Analysis*, 2nd edn, London (Allen and Unwin).
HUANG (W. H.) and JOHNS (W. D.), 1967. *Anal. Chim. Acta*, **37**, 508.
JEFFREY (P. G.) and WILSON (A.D.), 1960. *Analyst*, **85**, 478-86.
KALLMAN (S.), OBERTHIN (H.), and LIU (R.), 1962. *Anal. Chim. Acta*, **34**, 609.
KERBER (J. D.) and BARNETT (W. B.), 1969. *Perkin Elmer Atomic Absorption Newsletter*, **8**, 113.
KOLTHOFF (I. M.) and SANDELL (E. B.), 1952. *A textbook of quantitative inorganic analysis*, 3rd edn, New York (Macmillan).
LINGANE (J. J.) and KARPLUS (R.), 1946. *Ind. Eng. Chem. Anal. Ed.* **18**, 191.
MERCY (E. L. P.) and SAUNDERS (M. J.), 1966. *Earth Planet. Sci. Letters*, **1**, 169.
MURPHY (J.) and RILEY (J. P.), 1958. *Journ. Marine Biol. Ass. U.K.* **37**, 9.
PALILLA (F. C.), ADLER (N.), and HISKEY (C. F.), 1953. *Anal. Chem.* **25**, 926.
PECK (L. C.), 1964. *Bull. U.S. Geol. Surv.* **1170**.
— and SMITH (V. C.), 1964. *Talanta*, **11**, 1343.
SANDELL (E. B.), 1959. *Colorimetric determination of traces of metals*, 3rd edn, New York and London (Wiley: Interscience).
SCHOELLER (W. R.) and POWELL (A. R.), 1955. *The analysis of minerals and ores of the rarer elements*, 3rd edn, London (Griffin).
SHAPIRO (L.) and BRANNOCK (W. W.), 1955. *Anal. Chem.* **27**, 560.
— — — 1962. *Bull. U.S. Geol. Surv.* **1114-A**, 46.
SLAVIN (W.), 1968. *Atomic absorption spectrometry*. New York (Interscience).
SMITH (J. L.), 1853. *Amer. Journ. Sci.*, ser. 2, **15**, 234.
WILSON (A. D.), 1955. *Bull. Geol. Surv. Gt. Britain*, **9**, 56.

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