Mineral chemistry and paragenesis of astrophyllite from Egypt
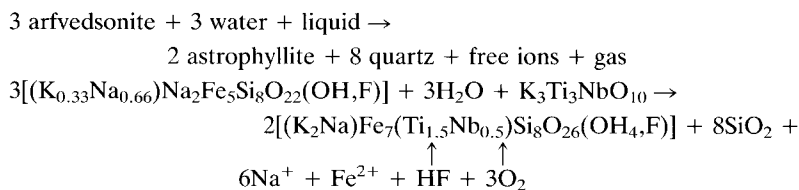
ABDEL-FATTAH M. ABDEL-RAHMAN*

Department of Geological Sciences, McGill University, 3450 University Street, Montreal, Quebec, Canada, H3A 2A7

Abstract

Astrophyllite is a rock-forming mineral (3.4 vol.%) in the metasomatized wallrocks within 2 to 3 km of the contact with the Mount Gharib A-type complex in northeastern Egypt. In the peralkaline A-type granites of the main complex, astrophyllite occurs in accessory amounts (0.1 to 0.5 vol.%), mostly in association with arfvedsonite. Eighteen chemical analyses of astrophyllite from both rock units have been used to discuss mineral chemistry, compositional variations and isomorphism.

Substitutions in the astrophyllite unit cell $[(Na,K)_3Fe_7Ti_2Si_8(O,OH)_{31}]$ involve F, Ca, Mn, Zn, Mg, Nb, Zr, Sn and Al. The contents of the unit cell depart from ideal stiochiometry. Unusually high Nb contents (up to 5 wt.% Nb_2O_5) characterize the Egyptian astrophyllites. The replacement of Ti by Nb is balanced by cation vacancies ($Nb^{5+} \rightarrow Ti^{4+} + \square$). The niobophyllite–astrophyllite relationship and the structure of astrophyllite in relation to mica and biopyriboles are discussed.

Astrophyllite may have been formed at the expense of alkali amphiboles by metasomatic reactions involving Ti–Nb-rich alkaline fluids and arfvedsonite;

$$3 \text{ arfvedsonite} + 3 \text{ water} + \text{liquid} \rightarrow$$
$$2 \text{ astrophyllite} + 8 \text{ quartz} + \text{free ions} + \text{gas}$$
$$3[(K_{0.33}Na_{0.66})Na_2Fe_5Si_8O_{22}(OH,F)] + 3H_2O + K_3Ti_3NbO_{10} \rightarrow$$
$$2[(K_2Na)Fe_7(Ti_{1.5}Nb_{0.5})Si_8O_{26}(OH_4,F)] + 8SiO_2 +$$
$$6Na^+ + Fe^{2+} + \overset{\uparrow}{HF} + 3O_2$$

Most astrophyllite reported in the literature occurs in association with alkali amphiboles, particularly arfvedsonite, thus suggesting that similar metasomatic reactions were responsible for the formation of astrophyllite in many other localities in the world.

KEYWORDS: astrophyllite, A-type granite, arfvedsonite, metasomatic reactions, Egypt.

Introduction

ASTROPHYLLITE $[(Na,K)_3Fe_7Ti_2Si_8(O,OH)_{31}]$ is the Ti end-member of the astrophyllite mineral group which comprises three minerals. The two other end-members are niobophyllite and kupletskite, the Nb and Mn analogues of astrophyllite, respectively. One significance of these minerals relates to their ability to host large concentrations of the rare and alkali-metals.

Astrophyllite minerals generally occur as accessories, and rarely as rock-forming minerals, mostly hosted in alkaline and peralkaline igneous

rocks that range in composition from nepheline syenites to saturated and oversaturated syenites, peralkaline granites and pegmatites. They also occur in fenites and other metasomatic rocks such as the wallrocks reported here. Less commonly, they occur in metamorphic rocks such as the astrophyllite-riebeckite gneiss reported by Floor (1966) from Vigo, Spain, and the niobophyllite paragneiss of Labrador, Canada (Nickel et al., 1964).

Astrophyllite has received relatively little attention and only a few complete analyses have been reported in the literature; several aspects of its structure and crystal chemistry remain unclear. The scarcity of information is partly due to its rarity, and partly to its optical similarity to mica,

* Present address: Department of Geology, Concordia University, Loyola Campus, 7141 Sherbrooke Street West, Montreal, Quebec, Canada, H4B 1R6.

which may have led some investigators to mis-identify it. This is the first report on astrophyllite in the Nubian Shield of NE Africa.

Aspects of the structure and chemistry of astrophyllite are given by Semenov (1956), Peng and Ma (1963), Woodrow (1967), Ganzeyev *et al.* (1968), Macdonald and Saunders (1973), and Layne *et al.* (1982), but the mineral's paragenesis has not been previously investigated. Here we discuss the chemical variations and substitution schemes in astrophyllite from Egypt, and propose a paragenesis that could serve as a general model for the origin of astrophyllite.

General geology

Astrophyllite is hosted in two rock units; the Mount Gharib A-type peralkaline granite complex and its metasomatized wallrocks. The Mount Gharib complex, located in the northern Nubian Shield, NE Egypt (Fig. 1), was emplaced 476±2 Ma ago (Abdel-Rahman and Doig, 1987) into the voluminous calc–alkaline granodiorite–adamellite suite of Pan-African age (552±7 Ma) the latter is a typical I-type orogenic suite, formed on an active continental margin (Abdel-Rahman and Martin, 1987).

The emplacement of this A-type granite complex following the terminal stages of the Pan-African orogeny was associated with lithospheric extension, expressed by regional dyke swarms, caused by cooling, fracturing and relaxation of the thin, newly formed, mostly granodiorite–adamellite Pan-African crust (Abdel-Rahman and Martin, 1990a). During the emplacement of this A-type complex, a metasomatized aureole developed in the calc-alkaline host rocks. The peralkaline granite intrudeq two swarms of mafic to felsic dykes (some are alialine), and sends apophyses of a fine-grained arfvedsonite-rich variety of the peralkaline granite into the surrounding rocks, including the metasomatized
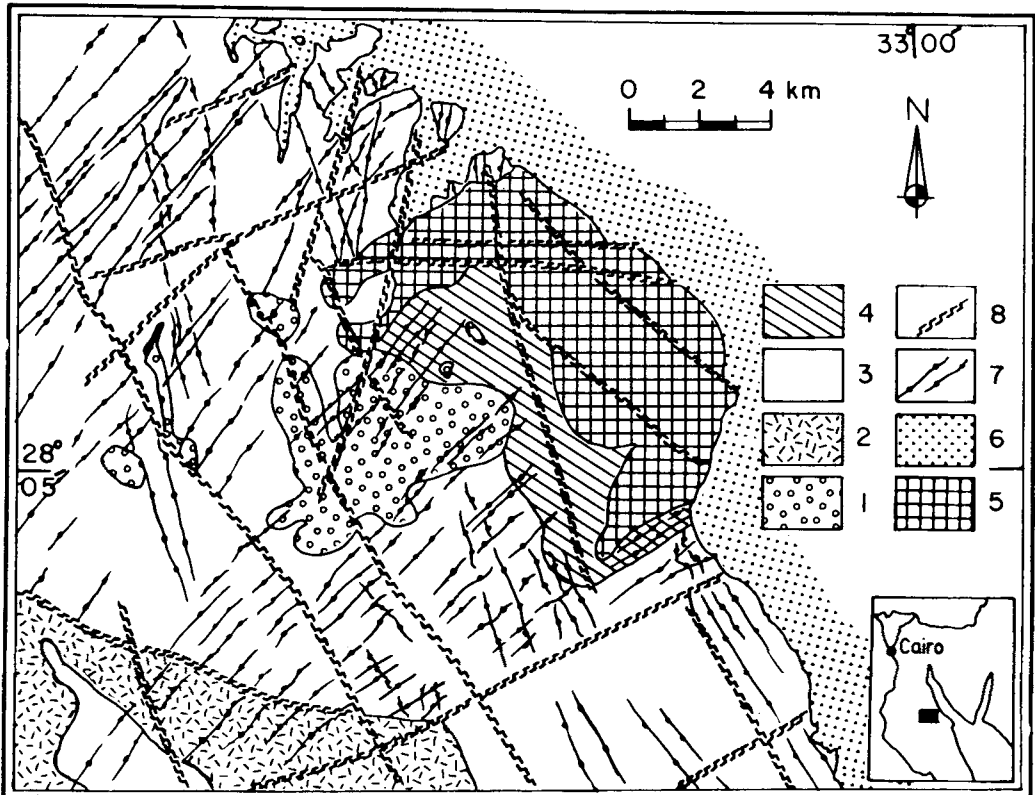

FIG. 1. Geological map of the Mount Gharib anorogenic alkaline complex and its host rocks in the northern Nubian Shield, NE Egypt. Units: 1, diorite-tonalite; 2, 'Dokhan' volcanic rocks; 3, Pan-African granodiorite-adamellite; 4, metasomatized wallrocks; 5, peralkaline granite; 6, Phanerozoic sedimentary cover; 7, dyke rocks; and 8, fault.

wallrocks. The region is intersected by four major sets of faults (Fig. 1).

Petrography of the astrophyllite host rocks

Astrophyllite forms bronzy-yellow to yellowish-red flakes up to 5 mm across. In the peralkaline granite, it commonly occurs in accessory amounts, forming subhedral to anhedral, highly pleochroic, yellowish-orange grains, found mostly in association with alkali amphiboles. It frequently occupies the exterior and the interior of arfvedsonite grains, and less commonly forms small individual grains near perthite grain margins. Astrophyllite ranges from 0.1 to 0.5% (by volume) in the peralkaline granite, which also contains perthite, quartz, and alkali amphibole (ferro-richterite to arfvedsonite: Abdel-Rahman, 1987), with accessory zircon, fluorite, apatite, allanite, aenigmatite, elpidite (?), and ilmenite. The texture of the peralkaline granite ranges from sparsely miarolitic and coarse-grained at the lowest level of exposure to vacuolar and fine-grained with acicular arfvedsonite in the roof facies.

The metasomatized wallrocks occur within 2 to 3 km of the contact with the peralkaline granite (Fig. 1) and are buff to reddish, inequigranular, texturally complex rocks, containing up to 3.4 vol.% astrophyllite (i.e. in rock-forming mineral proportions). Other minerals include highly turbid perthitic feldspar, interstitial quartz grains of variable size, secondary albite and alkali amphibole, with accessory fluorite, zircon, allanite, apatite, and opaque iron oxides.

Astrophyllite occurs as subhedral individual grains, interstitial fine aggregates, or as shreds either rimming or occurring within the alkali amphiboles (Fig. 2a). It is distinctly associated with (secondary) pure albite that replaces perthite, and occasionally occurs in filamentous overgrowth with both albite and arfvedsonite (Fig. 2b). The amphiboles in the metasomatized suite is virtually end-member fluor-arfvedsonite (Abdel-Rahman, 1986, 1987). Localized replacement of arfvedsonite by astrophyllite is common (Fig. 2). The pleochroic scheme of astrophyllite in both units is; α bright red-orange, β orange-yellow, and γ lemon-yellow with greenish tint.

Petrology of host rocks

Details of the petrology and petrogenesis of the astrophyllite host rocks are given in Abdel-Rahman and Martin (1990a). Here, we outline some chemical features to support field and mineralogical distinctions. A plot of (Na + K)

versus Si (Fig. 3) illustrates the range of composition of the two rock units; the metasomatized wallrocks are restricted to high silica values (75 to 77 wt.% SiO_2; Table 1 of Abdel-Rahman and Martin, 1990a), whereas the peralkaline granites of the main complex and its roof facies exhibit a wider range of SiO_2 values (69 to 77 wt.%). The wallrocks also exhibit lower (Na + K) values than peralkaline granites of similar Si-contents (Fig. 3), and are predominantly metaluminous (cf. Fig. 5 of Abdel-Rahman and Martin, 1990a).

The peralkaline granite of the main complex is enriched in large-iron lithophile- (LIL; K, Rb, Ba) and high field-strength elements (HFS; Zr, Nb, Y, and REE) and has a high initial $^{87}Sr/^{86}Sr$ ratio (0.711; Abdel-Rahman and Doig, 1987),
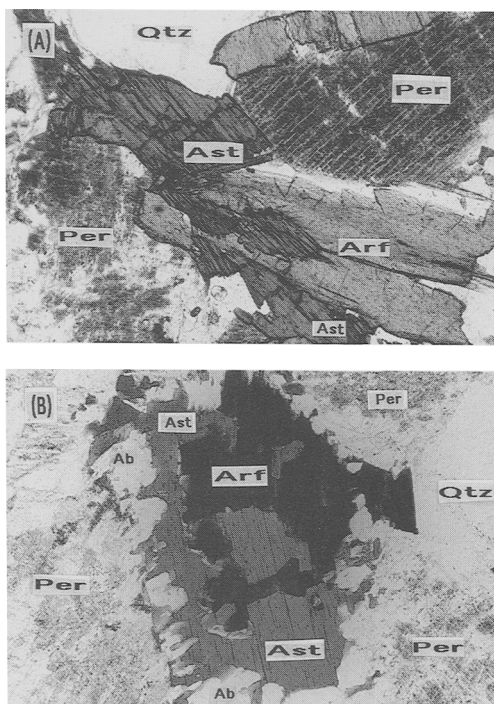
FIG. 2. (a) astrophyllite (Ast; dark grey with one set of cleavage) replacing arfvedsonite (Arf; light grey). Note the 56–124° cleavages of arfvedsonite at its upper margin; the other two minerals are quartz (white) and K-feldspar (cloudy). Crossed polars, field of view 2.6 mm. (b) filamentous overgrowth of astrophyllite (Ast; dark grey with one set of cleavage), arfvedsonite (Arf; black), and secondary albite (light grey) at the contact with perthite (cloudy) in the metasomatized wallrocks. Minute quartz granules (white) occur at the arfvedsonite–astrophyllite interface. Note the astrophyllite and associated secondary albite invading arfvedsonite and perthite. Crossed polars, field of view 2.05 mm.

FIG. 3. Compositions of astrophyllite host rocks in terms of Si versus (Na + K); values in cation percent. Symbols: the peralkaline granites (closed circles) and the metasomatized wallrocks (squares).

and trace-element abundances characteristic of 'within plate' granites. A fine-grained acicular-amphibole-bearing roof facies shows further enrichment in LIL and HFS elements, whereas the relatively astrophyllite-rich metasomatized wallrocks contain levels of the LIL and HFS elements intermediate between those in the main complex and its roof facies.
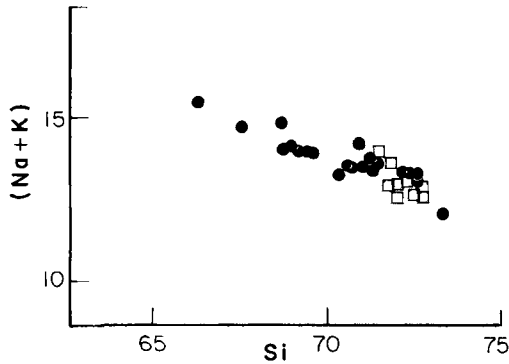
Analytical techniques

Eighteen astrophyllite samples were analysed using the Cameca Camebax/micro computer-automated electron microprobe at McGill University. The microprobe was operated using the wavelength-dispersion mode (WDS), with an accelerating voltage of 15kV, and a beam current of about 5nA. Counting time was 30 seconds, and the standards used (McGill internal lab standards) were run for three periods.

The number of atoms in the unit cell were calculated on the basis of 31 anions [based on the formula $W_3X_7Y_2Z_8O_{26}(OH)_5$]. Note that the total number of (OH, F, Cl) atoms that replace oxygen atoms in the unit cell should be 5 (cf. Macdonald and Saunders, 1973) and not 7 as given in Layne et al. (1982). If calculations are to be done on the basis of the number of oxygen atoms instead (due to the lack of F and/or OH analyses), calculations should be made on the basis of 28.5 O, and not 28 O as given in Wallace et al. (1990). Chemical analyses given in Table 1 are presented with H_2O contents calculated from ideal stoichiometry; note that the totals for most of the samples depart only slightly from 100%,

which is considered a reasonable measure of the accuracy of analysis.

Results and discussion

Astrophyllite: a sheet-silicate or a biopyribole?

Astrophyllite is structurally related to micas (Fig. 4a); both comprise tetrahedral and octahedral sheets in layers linked by alkali ions. In the structure of astrophyllite, determined by X-ray diffraction (Woodrow, 1967), the basic unit consists of a continuous sheet of Fe (Mn, Mg) octahedra between two sheets, each consisting of chains of Si (Al) tetrahedra linked by TiO_6 octahedra in the ratio (Si:Ti = 4:1; Fig. 4b). These composite sheets are separated by sheets of alkali ions, mostly K in 13-fold coordination and Na in 10-fold coordination. Thus, the astrophyllite structure differs from that of mica (TOT structure; Bailey, 1984) only in the presence of TiO_6 octahedra in the tetrahedral layer, and in its unit cell content, which is based on 31 anions.

On the basis of (1) the characteristic presence of net cation deficiency in most analyses (Nickel et al., 1964; Macdonald and Saunders, 1973), and (2) the presence of structural disorder in the b direction interpreted from Weissenberg photographs (reported by Woodrow, 1967) showing streaking parallel to b*, Layne et al. (1982) have suggested a modification to the structure of astrophyllite. They have considered its structure in the context of the biopyribole series described first by Veblen et al. (1977).

The structure of biopyribole is a continuum between the single-chain (pyroxene) and the double-chain (amphibole) and sheet (mica) silicates that may occur in a variety of stacking sequences. The structure of jimthompsonite, for example (Fig. 4d; after Veblen and Burnham, 1978), is in the form of I-beams consisting of triple silicate chains and wide octahedral strips are connected in the stacking sequence. Disordered zones in biopyribole structures, comprising random arrangements of different chain widths, produce a characteristic streaking parallel to b* on X-ray photographs (Veblen et al., 1977; Veblen and Burnham, 1978). By adding a pyroxene-type chain $(Si_2O_6)n$ to the $(Si_4O_{12})n$ chain in astrophyllite, a new type of (triple) chains and a new repeat unit with Si:Ti ratio of 6:1 rather than 4:1 is produced (Fig. 4c; Layne et al., 1982), thus showing some resemblance to the biopyribole (jimthompsonite) structure (Fig. 4d).

Woodrow (1967) has also suggested that astrophyllite varieties with different Si:Ti ratios in the tetrahedral layers may also be possible. As in the new biopyribole mineral, chesterite, which is

Table 1. Chemical composition of astrophyllite from Egypt, and the number of atoms in the unit cell calculated on the basis of 31 anions.

Sample #	R1180 1	R1200 2	R1201 3	R1202 4	R3090 5	R1730 6	R1731 7	R1732 8	R2180 9	R2181 10	R2340 11	R2341 12	R2342 13	R1440 14	R1441 15	R1442 16	R1443 17	R1444 18
SiO_2	35.61	35.74	34.98	35.03	35.50	34.82	35.06	34.53	35.26	35.02	35.33	35.28	35.99	35.41	35.77	35.53	34.40	34.51
Al_2O_3	1.10	0.69	0.88	0.98	0.43	0.97	1.00	1.06	0.84	0.75	1.05	1.01	0.71	0.69	0.44	0.56	0.87	0.86
TiO_2	6.65	9.74	8.22	8.07	9.23	6.92	7.38	7.44	8.91	7.63	6.98	7.99	8.80	8.11	9.48	8.03	7.93	7.69
ZrO_2	2.57	2.24	2.13	2.11	1.61	2.92	2.62	2.99	1.64	1.77	1.85	1.72	1.46	2.44	2.84	3.30	2.30	2.34
Nb_2O_5	3.82	1.50	4.00	4.28	2.01	3.73	3.44	3.29	3.82	4.64	4.87	4.00	3.16	3.57	2.49	3.37	3.74	3.96
SnO_2	0.20	0.16	0.18	0.21	0.44	0.19	0.08	0.09	0.12	0.17	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
FeO	35.26	34.54	34.79	35.82	34.42	34.91	34.85	34.98	35.07	34.99	35.53	35.61	35.79	34.47	34.63	35.41	35.30	35.00
MnO	1.46	1.37	1.36	1.32	1.55	1.55	1.23	1.63	1.39	1.31	1.42	1.42	1.36	1.32	1.39	1.43	1.04	1.08
MgO	0.03	0.02	0.08	0.01	0.02	0.04	0.04	0.03	0.02	0.03	0.02	0.02	0.02	0.03	0.01	0.02	0.02	0.01
ZnO	0.31	0.39	0.33	0.52	0.89	0.31	0.57	0.53	0.20	0.34	0.28	0.34	0.38	0.01	0.25	0.11	0.35	0.28
CaO	0.16	0.35	0.26	0.11	0.24	0.50	0.52	0.45	0.25	0.13	0.22	0.25	0.24	0.44	0.30	0.30	0.61	0.42
Na_2O	2.86	2.73	2.93	2.68	3.14	2.59	2.39	2.33	2.62	2.72	2.51	2.56	2.79	2.37	2.68	2.66	2.51	2.42
K_2O	6.29	6.23	6.31	6.12	5.72	6.26	6.45	6.28	6.60	6.60	6.34	6.21	6.19	6.47	6.16	6.28	6.57	6.53
F	0.92	1.46	1.35	0.81	1.77	0.78	1.06	1.17	1.46	1.67	0.90	0.98	1.82	0.63	1.27	1.29	1.70	1.21
H_2O*	2.93	2.69	2.74	3.01	2.52	2.96	2.84	2.78	2.70	2.57	2.95	2.92	2.55	3.06	2.80	2.78	2.53	2.75
Total	100.16	99.85	100.54	101.08	99.49	99.25	99.53	99.58	100.9	100.34	100.25	100.29	101.26	99.02	100.51	101.07	99.87	99.06
Si	7.841	7.790	7.649	7.665	7.775	7.767	7.765	7.668	7.658	7.675	7.775	7.738	7.746	7.857	7.772	7.738	7.590	7.686
Al	0.286	0.175	0.227	0.252	0.111	0.255	0.261	0.277	0.215	0.194	0.272	0.261	0.180	0.180	0.112	0.144	0.226	0.226
Z	8.127	7.965	7.876	7.917	7.886	8.022	8.026	7.945	7.873	7.869	8.047	7.999	7.926	8.037	7.884	7.882	7.816	7.912
Ti	1.101	1.597	1.352	1.328	1.520	1.161	1.229	1.242	1.455	1.257	1.155	1.318	1.424	1.353	1.549	1.315	1.316	1.288
Zr	0.276	0.236	0.227	0.225	0.172	0.318	0.283	0.324	0.174	0.189	0.198	0.184	0.153	0.264	0.301	0.351	0.247	0.254
Nb	0.380	0.147	0.395	0.423	0.199	0.376	0.344	0.330	0.375	0.460	0.484	0.396	0.307	0.358	0.332	0.332	0.373	0.398
Sn	0.018	0.013	0.016	0.018	0.038	0.017	0.007	0.008	0.010	0.015	—	—	—	—	—	—	—	—
Y	1.775	1.993	1.990	1.994	1.929	1.872	1.863	1.904	2.014	1.921	1.837	1.898	1.884	1.975	2.094	1.998	1.936	1.940
Fe	6.491	6.297	6.361	6.554	6.304	6.512	6.454	6.495	6.369	6.412	6.538	6.531	6.441	6.395	6.292	6.448	6.513	6.518
Mn	0.273	0.249	0.252	0.245	0.287	0.255	0.230	0.300	0.256	0.244	0.264	0.259	0.248	0.248	0.256	0.264	0.195	0.203
Mg	0.009	0.013	0.026	0.003	0.007	0.013	0.013	0.009	0.007	0.009	0.007	0.007	0.006	0.009	0.003	0.007	0.007	0.003
Zn	0.050	0.065	0.054	0.084	0.143	0.051	0.093	0.087	0.031	0.055	0.045	0.055	0.061	0.001	0.040	0.018	0.057	0.045
X	6.823	6.624	6.693	6.886	6.741	6.831	6.790	6.898	6.663	6.720	6.854	6.852	6.756	6.653	6.591	6.737	6.772	6.769
Ca	0.038	0.079	0.060	0.026	0.057	0.119	0.124	0.107	0.057	0.030	0.052	0.058	0.056	0.104	0.069	0.069	0.144	0.100
Na	1.220	1.152	1.243	1.136	1.334	1.120	1.027	1.003	1.104	1.156	1.071	1.089	1.164	1.018	1.128	1.123	1.074	1.044
K	1.767	1.728	1.760	1.709	1.597	1.780	1.823	1.780	1.829	1.846	1.780	1.737	1.699	1.832	1.707	1.745	1.848	1.855
W	3.025	2.959	3.063	2.871	2.988	3.019	2.974	2.890	2.990	3.032	2.903	2.884	2.919	2.954	2.904	2.937	3.066	2.999
F	0.640	1.008	0.934	0.560	1.226	0.551	0.742	0.822	1.002	1.157	0.627	0.680	1.239	0.443	0.872	0.888	1.186	0.852
OH	4.307	3.902	3.991	4.394	3.674	4.404	4.197	4.112	3.916	3.755	4.329	4.270	3.662	4.522	4.057	4.040	3.717	4.078
A	4.947	4.910	4.925	4.954	4.900	4.955	4.939	4.934	4.918	4.912	4.956	4.950	4.901	4.965	4.929	4.928	4.903	4.930

Samples 1 to 4 metasomatized wallrocks, and 5 to 18 peralkaline granite.

n.a. not determined.

* H_2O calculated from ideal stoichiometry (see text for details).

Z refers to (tetrahedral cations), Y (octahedral cations), X (8 coordinated cations), W (10 to 13 coordinated cations), and A (anions).
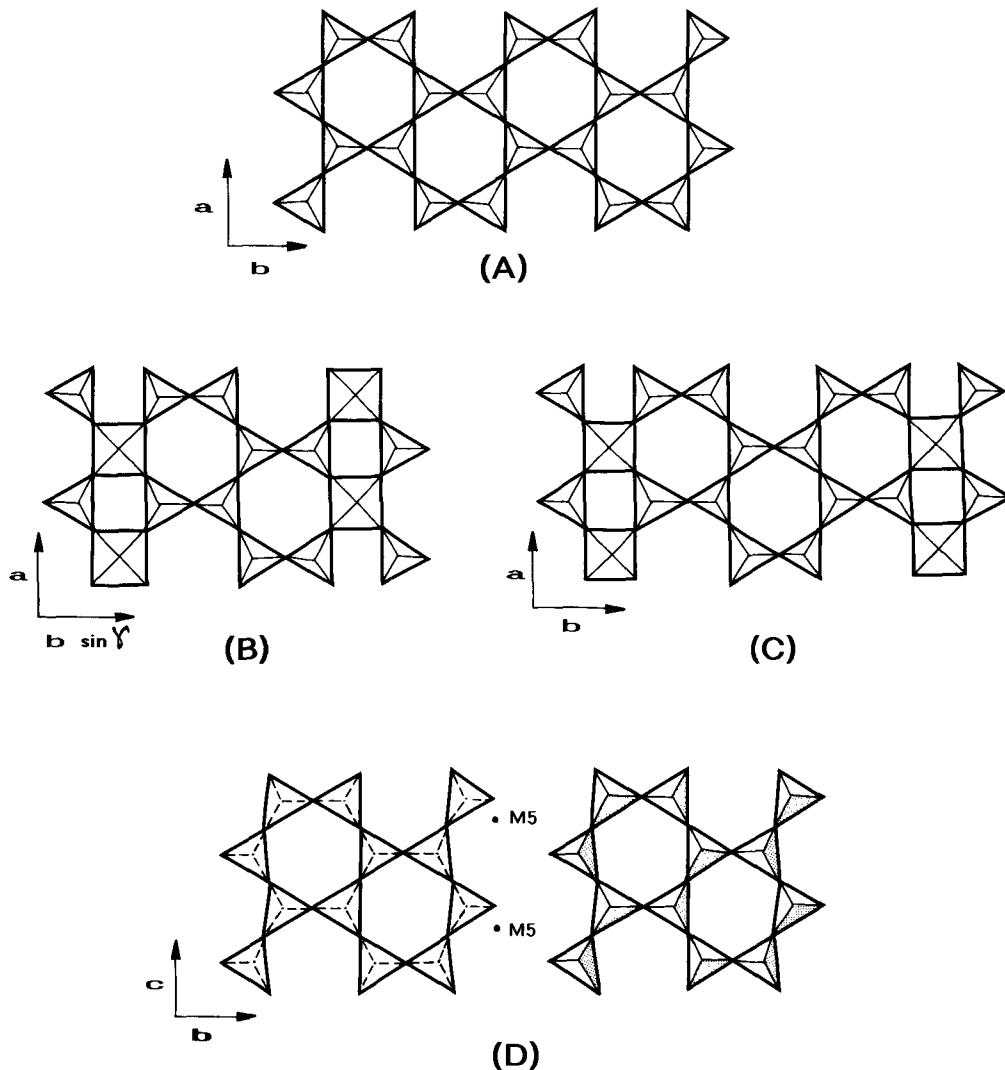
FIG. 4. Simplified diagram showing astrophyllite structure in comparison to the structures of mica and biopyribole: (A) simplified projection of mica structure; (B) projection of the astrophyllite structure (after Woodrow, 1967), showing the arrangement of a sheet of SiO_4 tetrahedra and TiO_6 octahedra with Si:Ti = 4:1; (C) postulated astrophyllite structure (Layne *et al.*, 1982) showing triple-chain arrangement for astrophyllite in which Si:Ti = 6:1; and (D) simplified triple A-chain of the biopyribole (jimthompsonite), projected onto (100), forming triple-chain I-beams; the inner parts of the chain are straight while the outer parts are slightly O-rotated, and *M*5 is the outer *M*-site which is a distorted octahedron (after Veblen and Burnham, 1978). See text for details.

structually composed of alternating double and triple chains, Layne *et al.* (1982) have proposed that there may be $(Si_6O_{18})n$ (triple) chains mixed with $(Si_4O_{12})n$ (double) chains in the astrophyllite structure. Detailed invetigations using high-resolution transmission electron microscopy (HRTEM) are essential to evaluate the validity of these postulated structures.

Mineral chemistry and isomorphism

Chemical variations and isomorphism in astrophyllite can be conveniently considered in terms of the general formula $(W_3X_7Y_2Z_8A_{31})$. Over 25 elements reside in these structural sites, allowing a considerable range of isomorphism. The unit-cell contents, calculated on the basis of 31 anions

(Table 1), clearly show departure from ideal stoichiometry, as the majority of specimens exhibit appreciable cation deficiencies (between 1 and 5% of sites remaining vacant). The X (8-coordinated) structural sites, in particular, exhibit higher cation deficiencies than the other cationic sites. Cation deficiency is considered to be a characteristic feature of both astrophyllite and niobophyllite structures (Nickel et al., 1964; Macdonald and Saunders, 1973; Layne et al., 1982).

The main substitution in the A-group (anionic sites) is F for OH, occupying up to 25% of theoretical A-sites (F reaches 1.24 atoms in unit cell; Table 1). We did not analyse for Cl, but in general, it is a minor component in astrophyllite (less than 0.01 wt.%; Macdonald and Saunders, 1973). The calculated OH atoms per unit cell range from 3.66 to 4.52.

In the Z-group (tetrahedral cations) Al substitution of Si is minor, and ranges only from 0.11 to 0.29 atoms per unit cell (1 to 4% of the tetrahedral sites).

In the Y-group (octahedral cations), the Ti–Nb substitution is quite important as it could produce the Nb-analogue of astrophyllite (niobophyllite; Nickel et al., 1964). These authors reported that niobophyllite contains 1.49 atoms of Nb, or 75% of octahedral structural sites, with Ti occupying 25%. Nb concentrations in the Egyptian astrophyllites are higher than those from various localities around the world (Fig. 5), thus suggesting that the mineral is a niobian astrophyllite. Concentrations of Nb_2O_5 range from 2 to 5 wt.% (0.15 to 0.48 atoms per unit cell; Table 1); Nb replaces Ti for up to 26% of available sites.

Macdonald and Saunders (1973) have used 8 complete analyses from 8 different localities, to evaluate the degree of solid solution between astrophyllite and niobophyllite. Their data show that Nb replaces Ti only up to 24% of the Y-octahedral sites, indicating a considerable compositional gap between the two minerals. Data plotted in Fig. 6 confirm the existence of a wide gap. The data do not plot directly on the astrophyllite–niobophyllite join. This is due largely to (i) Zr substitution for Ti, and (ii) cation deficiency in the Y group (Table 1).

The substitution of Nb^{5+} for Ti^{4+} results in charge excess, but this may be balanced, in part, by coupled substitutions such as Al for Si or Na for Ca. The relatively low contents of Ca and Al in both astrophyllite and niobophyllite, and the relatively large deviations from stoichiometry in both suggest that the Nb–Ti substitution may alternatively be balanced by vacancies

$(Nb^{5+} \rightarrow Ti^{4+} + \square)$. The smooth variation between Ti and Nb (Fig. 6) supports this substitution scheme.

Hansen (1968) has reported 4.2 to 7.1 wt.% Nb_2O_5 in niobophyllite from the Ilimaussaq intrusion, South Greenland. In his terminology, sample nos. 4, 10 and 11 (containing 4.3–4.9 wt.% Nb_2O_5) are niobophyllites. However, the main difference between niobopyllite and astrophoyllite is in optic orientation; in niobophyllite Z (c-axis) is normal to the cleavage, giving negative elongation (length fast), whereas in astrophyllite X (c-axis) is normal to the cleavage giving positive elongation (length slow; Nickel et al., 1964). All Egyptian samples exhibit positive elongation and are astrophyllite.

Ta, which normally substitutes for Ti, was not detected in any sample, but up to 0.5 wt.% Ta_2O_5 was reported in astrophyllite from Vigo, Spain (Floor, 1966; Macdonald and Saunders, 1973). Significant contents of Zr commonly substitute for Ti; Zr atoms per unit cell in the Egyptian astrophyllite range from 0.15 to 0.35 (8 to 18%) of octahedral sites (Table 1). The Zr enrichment in this astrophyllite is comparable with that displayed at several other localities, but is substantially less than Zr in astrophyllite from Låven, Norway (Gossner and Reindl, 1934; Fig. 5), where Zr substitutes for more than 30% of octahedral sites, perhaps suggesting the possible existence of a Zr-astrophyllite end-member. In end-member astrophyllite, Ti occupies 100% of octahedral sites (2 atoms per unit cell); in this Nb–Zr-rich astrophyllite Ti ranges from 1.1 to 1.6 atoms per unit cell.

In the X-group (8-coordinated cations), a major substitution of Mn for Fe could ultimately produce the Mn analogue of astrophyllite (kupletskite; Semenov, 1956). Semenov (1956), Nickel et al. (1964) and Macdonald and Saunders (1973) have documented the existence of a complete solid solution between the two minerals. In the Egyptian astrophyllite, Mn concentration is notably low; Mn substitutes some 0.26 atoms (only about 4% of available sites). Mg also occurs in very minor amounts (Table 1). Earlier reports that astrophyllite is a strong concentration of Zn were confirmed on most samples; Zn reaches 0.143 atom in the unit cell (2% of available sites).

In the W-group (10 to 13 coordinated cations), Ca is the main substitute for alkalis, with unit cell contents ranging from 0.026 to 0.144 atoms (1 to 5% of W-sites). Na occupies some 35–41% of W-sites leaving about 60% of these sites occupied by K, with a relatively constant K:Na ratio (about 3:2). Note that Na does not substitute for K; this
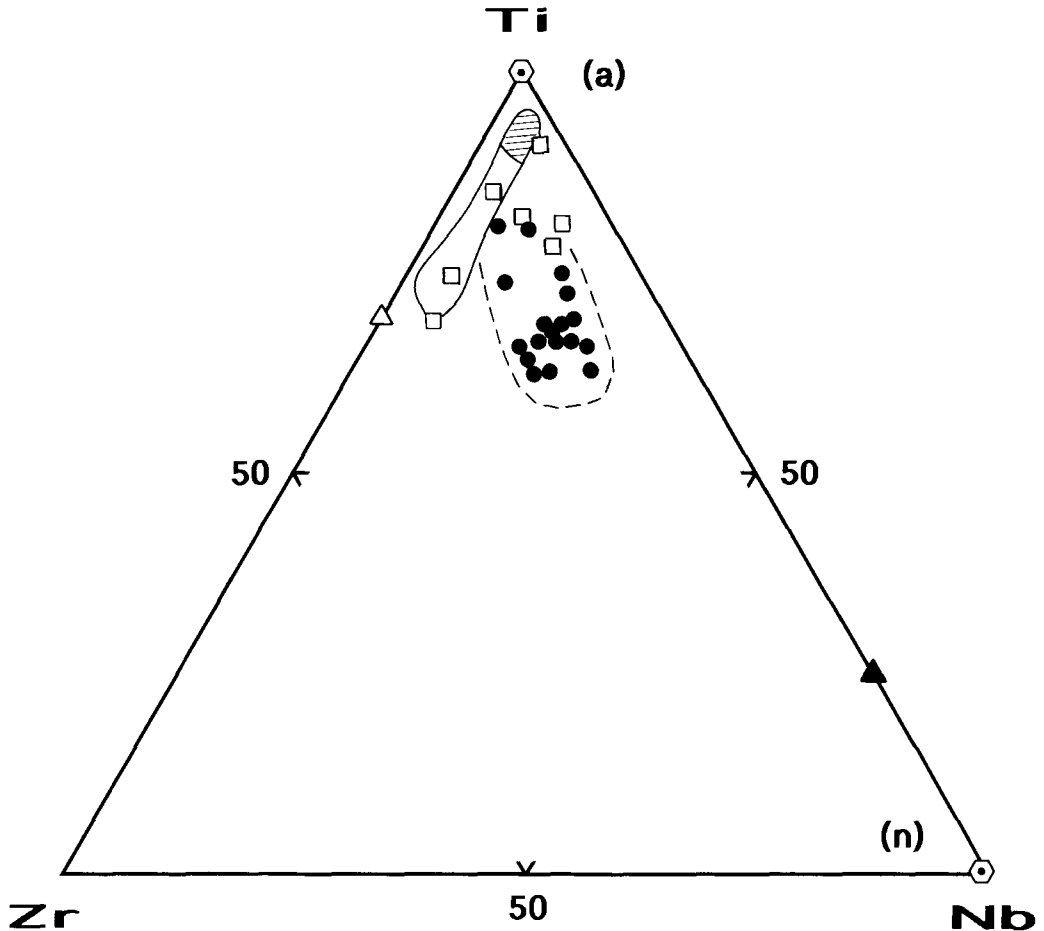
Fig. 5. Triangular plot of Ti–Zr–Nb (atoms per unit cell) for the Egyptian astrophyllites (closed circles), in relation to astrophyllite from East Greenland [area defined by a solid line containing astrophyllite from silica oversaturated rocks (unshaded area) and silica oversaturated rocks (shaded area); after Layne *et al.*, 1982], and astrophyllite from various other localities around the world (squares; after Macdonald and Saunders, 1973). Note the relatively higher Nb values of the Egyptian astrophyllite. The closed triangle represents natural niobophyllite (Nickel *et al.*, 1964) and the open triangle represents Zr-rich astrophyllite from Låven, Norway (Gosner and Reindl, 1934). The open hexagons represent end-members astrophyllite (a) and niobophyllite (n).

is because a K atom is surrounded by 13 oxygen atoms, while a Na atom is surrounded by only 10 (Peng and Ma, 1963; Woodrow, 1967). The structure appears to be stable only if K and Na (or equivalent cations) enter simultaneously at the appropriate lattice nodes.

Unlike Na, both Rb and Cs are common substitutes for K. We did not analyse for Cs, but the concentration of Rb (as well as Ba) in all samples was below detection. In a study on the isomorphism of the alkali metals (Rb, Cs, and Li) in astrophyllite, Ganzeyev *et al.* (1969) reported unusually high Rb and Cs concentrations reaching 2.1 and 10.8 wt.%, respectively.

Astrophyllite paragenesis

Chemical and petrographic data on the astrophyllite reported here, combined with detailed petrological information on its host rocks (Abdel-Rahman, 1986; Abdel-Rahman and Martin, 1990a), allow an interpretation of the mineral's paragenesis.

Most hypersolvus A-type alkaline plutonic suites, such as the Mount Gharib peralkaline complex, typically reach water-saturation during late stages of magmatic crystallization, where exsolved, commonly F-bearing alkali-rich deuteric fluids cause autometasomatism within these
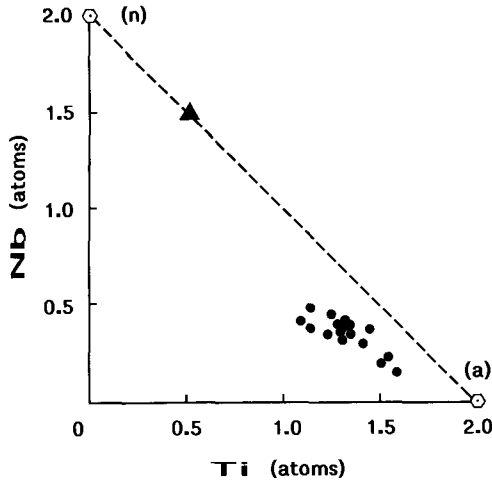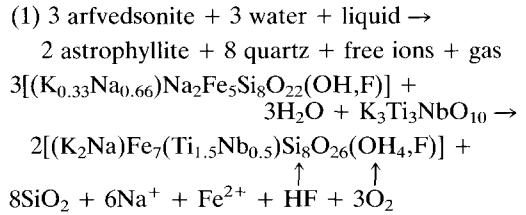
FIG. 6. Plot of Ti versus Nb (atoms per unit cell) for the investigated astrophyllite (closed circle). The diagram illustrates the degree of solid solution between end-members astrophyllite (a), and niobophyllite (n). Other symbols as in Fig. 5.

complexes, and, in some cases, produce meta-somatic contact aureoles. Significant subsolidus Na- and K-metasomatic alteration has been documented in numerous anorogenic alkaline complexes; the Deloro alkaline igneous complex of SE Ontario provides a clear example of extensive post-magmatic Na-, that was followed by K-metasomatism at a lower temperature (Abdel-Rahman and Martin, 1990*b*).

The abundance of miarolitic cavities and peg-matitic pods in the Mount Gharib anorogenic peralkaline complex reflect local saturation of the melt in H_2O during crystallization (e.g. Jahns and Burnham, 1969). Evidence suggesting the active role of late metasomatizing fluids in this complex includes; (1) a cover of strongly peralkaline, fine-grained, albitized roof rocks containing long, acicular, pure end-member fluor-arfvedsonite, pure albite and fluorite, was formed by vapour phase transfer via alkali fluoride complexes (Abdel-Rahman and Martin, 1990*a*), and (2) the presence of a metasomatized aureole within 2 to 3 km of its contact, where astrophyllite occurs in rock-forming mineral proportions, along with chessboard-twinned domains of hydrothermal pure albite, abundant interstitial seriate-textured secondary quartz granules and fluor-arfved-sonite. The restricted occurrence of astrophyllite mostly in metasomatic- and alkaline igneous rocks, clearly suggests the significance of an alkali-rich medium for its stability.

On the basis of (i) the higher abundance of

astrophyllite particularly in the metasomatized wallrocks, (ii) the petrographic evidence of astro-phyllite replacing arfvedsonite,with the develop-ment of secondary albite in filamentous over-growth (Fig. 2), and (iii) the nature of the mineral assemblage where the association (astrophyllite + arfvedsonite + albite + fluorite) characterizes astrophyllite host rocks globally, I suggest that the mineral may form at the expense of arfved-sonite metasomatically. A possible reaction in-volving arfvedsonite and alkali-rich fluids is as follows:

(1) 3 arfvedsonite + 3 water + liquid →

2 astrophyllite + 8 quartz + free ions + gas

$3[(K_{0.33}Na_{0.66})Na_2Fe_5Si_8O_{22}(OH,F)] +$
$\qquad\qquad 3H_2O + K_3Ti_3NbO_{10} \rightarrow$

$2[(K_2Na)Fe_7(Ti_{1.5}Nb_{0.5})Si_8O_{26}(OH_4,F)] +$
$\qquad\qquad\qquad\uparrow\qquad\quad\uparrow$
$8SiO_2 + 6Na^+ + Fe^{2+} + HF + 3O_2$

The presence of coexisting Ti-rich minerals such as aenigmatite and ilmenite indicates that the rocks were enriched in Ti. In the silica undersaturated rocks of Namibia, Marsh (1975) has shown that aenigmatite commonly coexists with arfvedsonite and astrophyllite, and has suggested that the latter may show a reaction relation with aenigmatite.

The release of Na^+ ions in reaction (1) was probably followed by ion-exchange reactions with the original perthitic K-feldspar ($6Na^+ + KAlSi_3O_8 \rightleftharpoons 6NaAlSi_3O_8 + 6K^+$), producing the extensive albitization in the host rocks. This is supported by the presence of astrophyllite–albite filamentous overgrowths at arfvedsonite–perthite grain margins (Fig. 2*b*).

Alternatively, both astrophyllite and albite may have been formed through a single reaction involving the interaction between fluids and arfvedsonite + K-feldspar as follows:

(2) 3 arfvedsonite + 6 K-feldspar +
$\qquad\qquad\qquad 3$ water + liquid →

2 astrophyllite + 6 albite + 8 quartz +
$\qquad\qquad\qquad\qquad$ free ions + gas

$3[(K_{0.33}Na_{0.66})Na_2Fe_5Si_8O_{22}(OH,F)] +$
$\qquad\qquad 6KAlSi_3O_8 +3H_2O + KTi_3NbO_9 \rightarrow$

$2[(K_2Na)Fe_7(Ti_{1.5}Nb_{0.5})Si_8O_{26}(OH_4,F)] +$
$\qquad\qquad\qquad\qquad\qquad\uparrow$
$6NaAlSi_3O_8 + 8SiO_2 + 4K^+ + Fe^{2+} + HF +$
$\uparrow$
$2.5O_2$
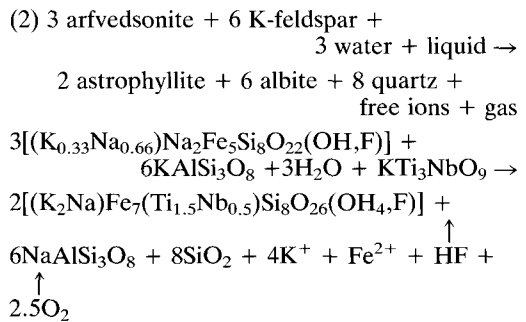
The O_2 gas released may have caused the formation of minor riebeckitic rims surrounding alkali amphiboles (Abdel-Rahman, 1987). The abundance of fine-grained, secondary quartz

granules, particularly in the astrophyllite-rich metasomatized wallrocks with high silica values (75–77 wt.% SiO_2; Fig. 3), is consistent with the formation of quartz in reactions (1) and (2). The Fe^{2+} ions released may have later precipitated at grain margins, cleavages, micro-fractures, perthitic lamellae-host interfaces, and even at micropermeable miarolitic cavities, giving the buff-reddish colour characteristic of the host rocks. Some Fe^{2+} ions may have contributed to the formation of ilmenite as given in this metasomatic reaction:

(3) 3 arfvedsonite + 3 water + liquid →

2 astrophyllite + ilmenite + 8 quartz +

free ions + gas

$$3[(K_{0.33}Na_{0.66})Na_2Fe_5Si_8O_{22}(OH,F)] + 3H_2O + K_3Ti_4NbO_{12} \rightarrow$$

$$2[(K_2Na)Fe_7(Ti_{1.5}Nb_{0.5})Si_8O_{26}(OH_4,F)] +$$

$$FeTiO_38SiO_2 + 6Na^+ + HF + 2.5O_2$$

I conclude that the Egyptian astrophyllite was formed at the expense of arfvedsonite through metasomatic reactions (1, 2 or 3). The postulated pattern of subsolidus metasomatic alteration from arfvedsonite (double-chain structure) to astrophyllite (biopyribole, or sheet structure) seems structurally and chemically a logical sequence of phases when compared to the more common alteration pattern from pyroxene to amphibole to mica. The close association between those two minerals (astrophyllite and arfvedsonite), and the similarity in both the nature of astrophyllite host rocks and the associated mineral assemblages found in most other reported occurrences suggest a wider application for our proposal.

References

Abdel-Rahman, A. M. (1986) Ph.D. Thesis, McGill University, Montreal, 326 pp.

—— (1987) *Neues. Jahrb. Mineral. Abh.*, **157**, 319–35.

—— and Doig, R. (1987) *J. Geol. Soc. London*, **144**, 577–86.

—— and Martin, R. F. (1987) *Geol. Jour.*, **22**, 281–301.

—— —— (1990a) *Contrib. Mineral. Petrol.*, **104**, 173–83.

—— —— (1990b) *Can. Mineral.* **28**, 267–85.

Bailey, S. W. (1984) In *Micas; Reviews In Mineralogy*, **13** (S. W. Bailey, ed.), 1–12.

Floor, P. (1966) *Leidse Geol. Medd.*, **36**, 1–17.

Ganzeyev, A. A., Yefimov, A. F., and Semenova, N. G. (1969) *Geochem. Intern.* **6**, 295–300.

Gosner, B. and Reindl, E. (1934) *Centr. Min.*, Abt. Ã, 161.

Hansen, J. (1968) *Rept. 23rd Inter. Geol. Congr., Czechoslovakia*, **7**, 263–73.

Jahns, R. H. and Burnham, C. W. (1969) *Econ. Geol.*, **64**, 843–64.

Layne, G. D., Rucklidge, J. C., and Brooks, C. K. (1982) *Mineral. Mag.*, **45**, 149–56.

Macdonald, R. and Saunders, M. J. (1973) Ibid., **39**, 97–111.

Marsh, J. S. (1975) *Contrib. Mineral. Petrol.*, **50**, 135–44.

Nickel, E. H., Rowland, J. F., and Charette, D. J. (1964) *Can. Mineral.*, **8**, 40–52.

Peng, C.-C. and Ma, C.-S. (1963) *Sci. Sinica*, **12**, 272.

Semenov, Ye. I. (1956) *Dokl. Akad. Nauk. USSR*, **108**, 933–6.

Veblen, D. R. and Burnham, C. W. (1978) *Am. Mineral.*, **63**, 1053–73.

—— Busck, P. R., and Burnham, C. W. (1977) *Science*, **198**, 359–65.

Wallace, G., Whalen, J. B., and Martin, R. F. (1990) *Can. Mineral.*, **28**, 251–66.

Woodrow, P. J. (1967) *Acta Crystallogr.*, **22**, 673–8.