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COMPOSITIONAL HETEROGENEITY OF POLLUCITE FROM HIGH GRADE DYKE, MASKWA LAKE, SOUTHEASTERN MANITOBA

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ABSTRACT

Primary pollucite from the High Grade Dyke pegmatite of the Maskwa Lake group in southeastern Manitoba occurs with spodumene, microcline, quartz, elbaite, albite, and lepidolite. Pollucite is replaced *en masse* by microcline and lepidolite + quartz, veined by a sequence of spodumene, lepidolite, late spodumene and adularia, and replaced at a late stage by clay minerals. The primary homogeneous pollucite has locally evolved to a mosaic of Na-enriched and Cs-enriched domains 20–300 μm across, cross-cut by 1- to 15-μm veinlets of quartz-containing Cs-rich pollucite rimmed by Na-rich pollucite. This homogeneous pollucite has an average composition of $Na_{0.149}Ca_{0.016}Cs_{0.581}Rb_{0.043}Al_{0.860}Si_{2.153}O_6$ per anhydrous subcell. The primary homogeneous pollucite has $2.45 < Si/Al < 2.55$ and a molar proportion of the pollucite end-member CRK = (Cs + Rb + K) × 100/(cation sum) between 76 and 81, in contrast with the Cs-enriched blebs ($2.10 < Si/Al < 2.40$, $82 < CRK < 90$), Na-enriched blebs ($2.30 < Si/Al < 2.50$, $74 < CRK < 80$), veinlets of Cs-rich pollucite ($2.00 < Si/Al < 2.40$, $84 < CRK < 92$) and their Na-rich rims ($2.50 < Si/Al < 2.90$, $58 < CRK < 78$). Na contents and Si/Al are highest adjacent to the margin of the Cs-rich veinlet, and decrease over 30–70 μm into homogeneous pollucite. The above sequence indicates re-equilibration of primary pollucite at decreasing temperature into a two-phase subsolvus assemblage of Cs- and Na-rich compositions. An overall positive correlation of Al contents with CRK is noted throughout the homogeneous pollucite, the blebby domains, and veinlets plus their rims. Extrapolation of the Cs enrichment to CRK = 100 suggests that the ideal composition of a fully exsolved pollucite phase, not encountered in nature to date, is $(Cs >> Rb,K)_xAlSi_2O_6$; x will equal 1 if Li or H have no crystallochemical role in this structure.

Keywords: pollucite, granitic pegmatite, cesium, exsolution, Manitoba.

SOMMAIRE

La pollucite primaire du filon pegmatitique dit de High Grade, dans le groupe du lac Maskwa, dans le sud-est du Manitoba, coexiste avec spodumène, microcline, quartz, elbaïte, albite et lépidolite. La pollucite est massivement remplacée par microcline et lépidolite + quartz, recoupée par des veinules contenant la séquence spodumène, lépidolite, spodumène tardive, et adulaire, et enfin remplacée tardivement par des argiles. La pollucite homogène primaire a ici et là été transformée en une mosaïque de domaines de 20 à 300 μm enrichis soit en Na, soit en Cs, le tout recoupé par des veinules de 1 à 15 μm de largeur contenant quartz + pollucite riche en Cs avec un liseré de pollucite riche en Na. La pollucite primaire homogène possède une composition anhydre de $Na_{0.149}Ca_{0.016}Cs_{0.581}Rb_{0.043}Al_{0.860}Si_{2.153}O_6$. Elle possède un rapport Si/Al entre 2.45 et 2.55, et une proportion molaire du terme CRK de la pollucite [= (Cs + Rb + K) × 100/(somme des cations)] de 76 à 81, en contraste avec les lamelles enrichies en Cs ($2.10 < Si/Al < 2.40$, $82 < CRK < 90$), en Na ($2.30 < Si/Al < 2.50$, $74 < CRK < 80$), les veinules riches en Cs ($2.00 < Si/Al < 2.40$, $84 < CRK < 92$), et leur bordure riche en Na ($2.50 < Si/Al < 2.90$, $58 < CRK < 78$). La teneur en Na et le rapport Si/Al sont les plus élevés le long de la bordure de chaque veinule riche en Cs, et diminuent sur 30–70 μm vers la pollucite homogène. Cette séquence indiquerait un ré-équilibrage de la pollucite primaire lors de son refroidissement à un assemblage subsolvus, à deux phases (riche en Cs ou Na). L'ensemble des compositions semble indiquer une corrélation des teneurs en Al et de la proportion CRK. D'après une extrapolation de l'enrichissement en Cs jusqu'à CRK = 100, la composition idéale d'une pollucite exsolvée, pas encore rencontrée dans la nature, serait $(Cs >> Rb,K)_xAlSi_2O_6$; x sera égal à 1 si Li ou H ne joue aucun rôle cristallochimique dans cette structure.

(Traduit par la Rédaction)

Mots-clés: pollucite, pegmatite granitique, cesium, exsolution, Manitoba.

INTRODUCTION

Pollucite was first discovered on the island of Elba in 1846 by Breithaupt; since then, nearly 80 localities have been reported. Cesian analcime was described relatively recently, in 1972 by Černý. Cs-enriched minerals of the analcime–pollucite series are restricted in occurrence to the most fractionated granitic pegmatites of the rare-element class. Primary pollucite crystallizes at near-solidus temperatures in central parts of these pegmatites (Černý 1982). Henderson & Martin (1985) confirmed that pollucite is a near-solidus phase in experimental Cs- and F-enriched haplogranitic melts. Most bulk compositions of pollucite fall into a CRK [= 100 X (Cs + Rb + K)/(cation sum)] range from 70 to 88. In contrast, cesian analcime ranging in CRK from 5 to 50 occurs in low-temperature "alpine vein" assemblages (terminology of Ginsburg 1960), in cavities and fissures formed by leaching in pegmatites bearing the primary pollucite (Černý 1972).

Černý (1974) reviewed the chemistry and physical properties of minerals in the analcime–pollucite series. Minerals in the series are consistent with Beger's (1969) structural model; however, poor covariations of bulk chemical composition and physical parameters, particularly with index of refraction, were noted. These observations prompted a re-examination of the analcime–pollucite series with the electron-microprobe technique.

A reconnaissance study of primary pollucite from several localities revealed widespread compositional heterogeneity (Teertstra *et al.* 1989), which suggests a gradual breakdown of primary homogeneous pollucite into Na- and Cs-enriched components. This feature, never reported before, is persistent in most of the occurrences examined, although developed to different extents in individual pegmatites. Thus we undertook a detailed examination of pollucite from a locality, the High Grade Dyke (Bristol 1962, Černý & Bristol 1972), that shows a full range of the features observed to date.

Besides explaining the discrepancies between physical properties of pollucite and its composition based on "bucket" analysis, detailed examination of pollucite using a microbeam technique has additional, and much more significant, implications. In conjunction with experimental studies, the textural and compositional heterogeneity of pollucite should contribute to an understanding the near-solidus and subsolidus history of consolidation in highly fractionated pegmatites. Also, subsolidus behavior of natural pollucite provides important information about relative stability of synthetic analcime–pollucite phases utilized in deep-seated storage of solid nuclear wastes.

GEOLOGICAL SETTING

Regional framework

The High Grade Dyke spodumene-bearing granitic pegmatite, near Donner Lake in southeastern Manitoba, lies approximately 210 km east-northeast of Winnipeg and is accessible on foot 10 km from Highway 314. The High Grade Dyke occurs in the westernmost exposed portion of the English River subprovince of the Superior province of the Canadian Shield. The High Grade Dyke is part of the Cat Lake – Maskwa Lake pegmatite district, north of the Winnipeg River district, which contains the Tanco granitic pegmatite at Bernic Lake (Černý *et al.* 1981).

The High Grade Dyke is the only pollucite-bearing type of pegmatite in a closely spaced swarm of three types of geochemically related granitic pegmatites comprising the Maskwa Lake pegmatite series. Most abundant are unzoned spodumene-bearing pegmatites, and a single unzoned petalite-bearing dyke also is present. The host rocks are the tonalites of the Maskwa Lake batholith and pillow basalts of the Lamprey Falls formation (Černý *et al.* 1981).

The parent pegmatite

The pollucite-bearing High Grade Dyke has sharp contacts with the host metabasalt along the exposed length of 18 m. It strikes 170° and dips 65° west. The dyke has variable thickness from 0.6 m to a maximum of 1.2 m. It is not systematically zoned, but contains primary assemblages of blocky K-feldspar + quartz, blocky quartz + spodumene, and pollucite + lath spodumene. Superposed, in part metasomatic assemblages include widespread albite-rich units that replace K-feldspar, and sporadic assemblages of lepidolite + quartz (± spodumene) that locally penetrate spodumene and K-feldspar. Patches of holmquistite occur locally at the wallrock contact. Other minerals in the dyke include microcline, beryl, microlite, columbite–tantalite, topaz(?), garnet, and biotite.

The granitic pegmatite is highly fractionated, as indicated by the above mineral assemblage and by relevant geochemical parameters. High to extreme fractionation is shown by K-feldspar (K/Rb 5.6–3.4, K/Cs 69–36, Rb/Cs 12–10), lepidolite (K/Rb 2.4, K/Cs 8.3, Rb/Cs 3.4, Li_2O 3.23 wt.%), and garnet [Mn/(Fe+Mn) 0.93] (Černý *et al.* 1981).

Properties, association and alteration of pollucite

Pollucite at the High Grade Dyke is found as essentially monomineralic, equidimensional pods and lenses up to 15 cm long in association with spodumene, quartz, lepidolite, albite, and polychromatic elbaite. The pollucite is anhedral, and fills interstices between spodumene laths (5 to 10 cm long) and equant, coarsely perthitic microcline crystals (4 to 5 cm in size). Finer grains of pollucite (1 to 5 mm across) are found in association with spodumene, up to 5 cm from the main pods and lenses. Irregularly distributed blocky quartz tends to rim pollucite pods and lenses where pollucite is not in direct contact with spodumene and microcline.

The pollucite is clear and colorless; it is for the most part isotropic, but a slight birefringence is found in small areas where pollucite has replaced other minerals. The index of refraction is variable in thin section. Crushed grains show a conchoidal fracture, though a poor cubic parting can be seen in thin section. The centers of the pollucite pods are essentially monomineralic, whereas inclusions of other minerals are more abundant toward the margins.

Scattered, 1- to 2-cm-long laths of spodumene are partly penetrated by pollucite, with the lath tips corroded into sheafs of very thin parallel needles. Abundant clear and colorless, to pink and grey translucent elbaite rods up to 1 cm wide and 5 cm long are not altered, and extend in random orientation through the pollucite. The pollucite contains small amounts of euhedral, equidimensional apatite crystals 0.2 mm in size.

Alteration of the pollucite at the High Grade Dyke is widespread. The alteration of pollucite has been noted by many authors at other localities; the sequence of alteration phenomena was examined by Quensel (1938, 1945), Shaub & Schenck (1954), and Černý & Simpson (1978). On the basis of these investigations, Černý (1979, 1982) constructed a generalized sequence of alteration features. The consistency of this pattern of alteration allowed recognition of clay pods pseudomorphous after pollucite even at localities without relics of the original mineral (Černý 1978).

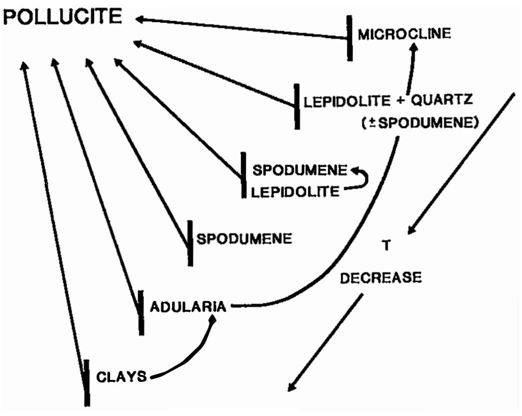


FIG. 1. Schematic sequence of alteration products replacing pollucite in High Grade Dyke, from early microcline to late clay minerals. Arrows also indicate replacements among the alteration products.

The relative ease of alteration of pollucite preserves a record of late-stage, low-temperature hydrothermal processes within complex granitic pegmatites. At the High Grade Dyke, an extensive portion of the generalized sequence of alteration is observed (Fig. 1), superposed on the preceding breakdown of primary pollucite described below in "Features of compositional heterogeneity". Several specific features of this sequence, such as the Rb,Cs-rich adularia, will be dealt with at a later date.

COLLECTION AND TREATMENT OF DATA

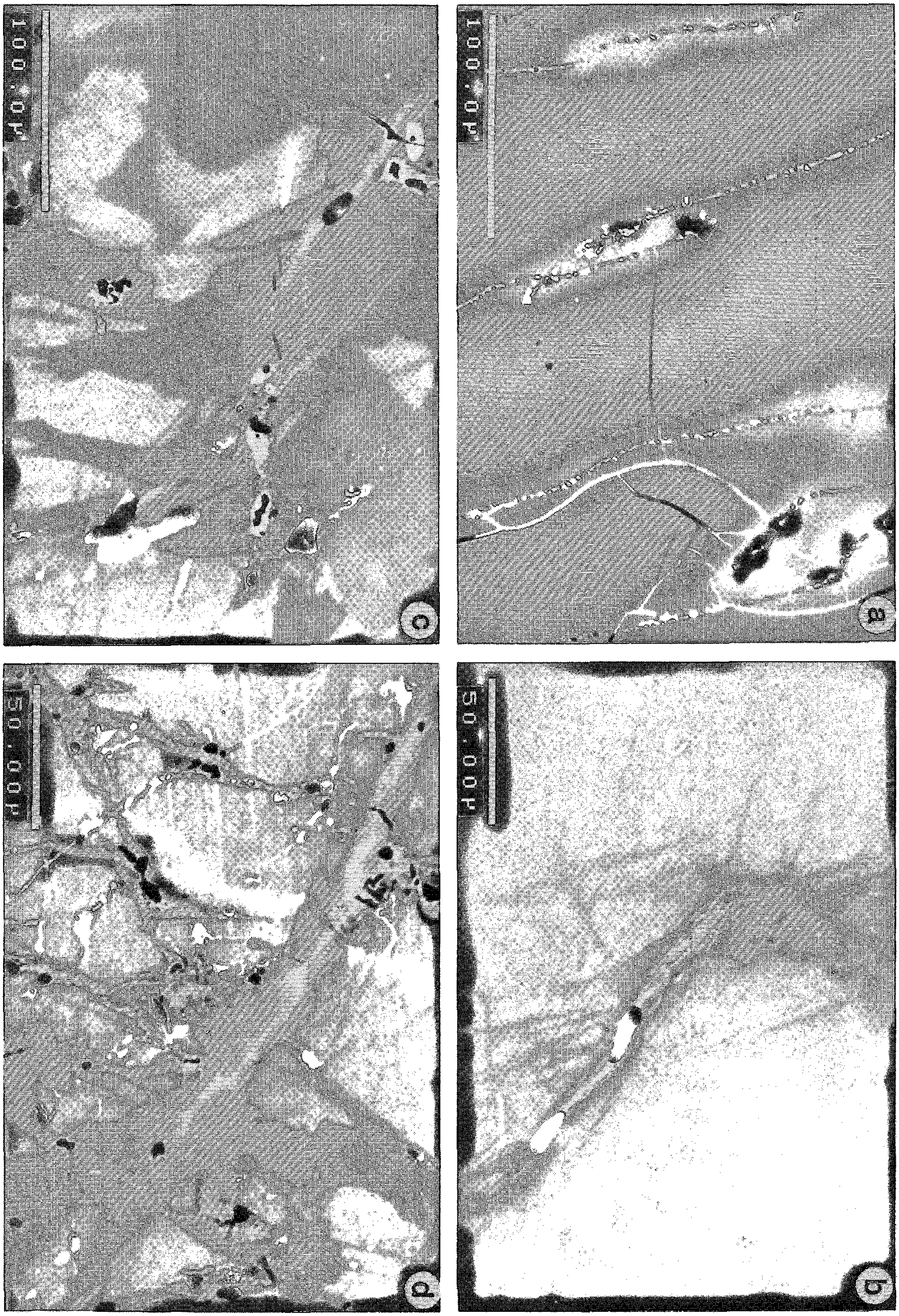
Seven specimens from the High Grade Dyke were sectioned and analyzed with a CAMEBAX SX-50 electron microprobe, using the "PAP" procedure of data reduction (Pouchou & Pichoir 1985). Back-scattered electron imaging was used to select points for analysis. Concentrations of major elements were measured using 15 kV, 20 nA, beam size 5 μm, and count times of 20 s (background 10 s). The following standards were used: pollucite (Al$K\alpha$, Si$K\alpha$, and Cs$L\alpha$), and albite (Na$K\alpha$). Minor elements were determined using 15 kV, 40 nA, beam size 5 μm, and count times of 50 s (background 25 s). Standards used were rubidian microcline (Rb$L\alpha$), orthoclase (Fe$K\alpha$ and K$K\alpha$), anorthite (Ca$K\alpha$), hornblende (Mg$K\alpha$), and vanadium diphosphate (P$K\alpha$). Detection limits for minor oxides were (in wt.%) 0.02 for Fe_2O_3, 0.01 for P_2O_5, K_2O, CaO and MgO, and 0.07 for Rb_2O.

Results of the analyses were recalculated to atomic contents on the basis of six atoms of oxygen per anhydrous subcell. The molar percentage of the pollucite end-member was calculated as the "CRK" index, defined as (Cs + Rb + K) X 100/cation sum (Černý 1974). The CRK index is based on assignment of Cs, Rb, and K to the larger 16*b* site, and of Li, Na, Ca, Mg and any other minor cations to the smaller 24*c* site [*cf.* Beger (1969) for description of the crystal structure].

FEATURES OF COMPOSITIONAL HETEROGENEITY

Textural relationships

Pollucite from High Grade Dyke shows a compositional heterogeneity expressed in a range of textural features: a homogeneous matrix locally grades into a blebby mosaic of Na-enriched and Cs-enriched domains, which are cross-cut by quartz-bearing Cs-rich veinlets rimmed on either side by Na-rich pollucite. Textural combinations of homogeneous areas, blebby mosaics, and Cs-rich veinlets are observed, as well as blebby mosaics and Cs-rich veinlets occurring individually in homogeneous pollucite. The considerable dif-


a
100.0µ
b
50.00µ
c
100.0µ
d
50.00µ

ference in electron density between Na and Cs dominates the back-scattered electron (BSE) images of pollucite. This difference overshadows the weak influence exerted by variations in Si, Al and H_2O. Consequently, BSE images of pollucite can be interpreted as reflecting directly the variations in Na and Cs.

Figure 2a shows a set of subparallel veinlets of Cs-rich pollucite, 1 to 3 μm in width and containing quartz grains 1 to 3 μm in size. The veinlets seem to follow fractures along most of their length. The veinlets occur in a relatively large area of homogeneous pollucite, which becomes Na- and Si-rich near the veinlets.

Figure 2b shows a stringy veinlet of Cs-rich pollucite associated with two quartz grains, in an area of homogeneous pollucite. The very thin veinlets are interwoven around islands of homogeneous pollucite, giving it a brecciated appearance.

Figure 2c shows a blebby mosaic of domains of pollucite that are Na-enriched or Cs-enriched relative to homogeneous pollucite (which surrounds this area just outside the field of view). The blebs are 20 to 300 μm in size, generally elliptical in shape, and are not closely associated with quartz grains. In contrast, the quartz grains are closely associated with incipient development of veinlets of Cs-rich pollucite.

Figure 2d shows two distinct generations of veinlets of Cs-rich pollucite: a 20- to 30-μm wide, quartz-free veinlet of Cs-rich pollucite, and a cross-cutting set of veinlets 1 to 10 μm wide that are more Cs-enriched than the early, coarser veinlets. The smaller veinlets contain quartz grains 1 to 6 μm in size. The wide veinlets of Cs-rich pollucite typically show an internally developed blebby structure that is not readily observed in the smaller quartz-containing veinlets of Cs-rich pollucite.

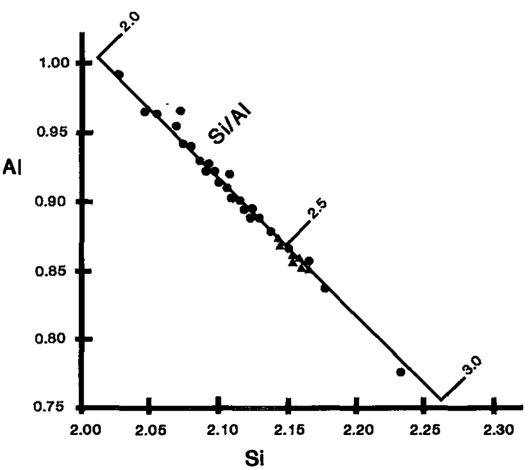


FIG. 3. Al *versus* Si (atoms p.f.u.) in homogeneous (▲), and in other textural types (•) of pollucite. The homogeneous pollucite has a limited range of Si/Al from 2.45 to 2.55. Data are plotted along the line of best fit (slope 1.00 ± 0.06).

Compositional trends

The electron-microprobe analysis of the various textural manifestations of pollucite in the High Grade Dyke has revealed a relatively wide range of compositions. Figure 3 compares the variation of Al with Si in atoms p.f.u. (per formula unit, based on 6 oxygen atoms) in homogeneous pollucite with the variation seen in the blebs and veinlets. Corresponding values of Si/Al are plotted along the line of best fit. Overall, there is a wide range in Si/Al from near 2.0 to 2.9, yet the homogeneous pollucite has a limited range of Si/Al from 2.45 to 2.55. Only trace amounts of Fe or P were detected.

Figure 4 shows Si/Al as a function of CRK for the various textural components. The homogeneous pollucite is restricted to a CRK of 76 to 81. Examples of this range, and the average composition of the homogeneous pollucite, are given in Table 1. A wider compositional range is seen, however, within the blebby mosaic and among the various generations of veinlets: CRK varies in them from 58 to 93 (examples in Table 2).

The Na-enriched blebs have Na contents only slightly higher than the adjacent homogeneous pollucite, yet they are compositionally distinguishable by the tendency to slightly lower values of

FIG. 2. Back-scattered electron images of textural features seen in pollucite from High Grade Dyke. Levels of grey do not correlate between images. a) Subparallel Cs-rich veinlets 1 to 3 μm in width containing small quartz grains, occurring in a relatively large area of pollucite, which is Na-rich near the veinlets. b) A stringy Cs-rich veinlet associated with two quartz grains located in an area of homogeneous pollucite. c) Blebby mosaic with domains of pollucite that are Na-enriched, and Cs-enriched, relative to the homogeneous pollucite (which surrounds this area just outside the field of view). The blebs show no regular relationship to the distribution of quartz grains that are, however, closely associated with the cross-cutting Cs-rich veinlets. d) Cs-rich quartz-free veinlets 20 to 30 μm wide, are cross-cut by a set of 1- to 10-μm wide, quartz-bearing veinlets with elevated Cs content. Veinlets of the first generation show an internal blebby structure not apparent in the narrower veinlets.

TABLE 1. COMPOSITION OF PRIMARY POLLUCITE

No.	14	17	61	Average
SiO_2 wt.%	48.04	48.25	47.21	47.57 (.38)
Al_2O_3	16.09	16.15	16.32	16.12 (.12)
Fe_2O_3	0.01	0.01	0.00	0.00
P_2O_5	0.00	0.00	0.00	0.00
Na_2O	1.47	2.00	1.65	1.69 (.12)
K_2O	0.01	0.00	0.02	0.013 (.007)
Rb_2O	1.12	0.69	1.66	1.48 (.15)
Cs_2O	30.25	30.19	29.93	30.07 (.24)
CaO	0.26	0.28	0.42	0.35 (.07)
MgO	0.00	0.00	0.00	0.00
sum, less H_2O	97.25	97.55	97.20	97.29 (.45)
Si	2.166	2.161	2.142	2.153 (.0057)
Al	0.856	0.852	0.873	0.860 (.0055)
Na	0.128	0.173	0.145	0.149 (0.10)
Ca	0.013	0.014	0.021	0.016 (.0028)
Rb	0.032	0.020	0.048	0.043 (.0046)
Cs	0.582	0.577	0.579	0.581 (.0060)
Σ cat. charge	0.769	0.798	0.814	0.806 (.013)
Si/Al	2.531	2.536	2.454	2.504 (.022)
CRK	81.4	76.1	79.1	79.1 (1.1)

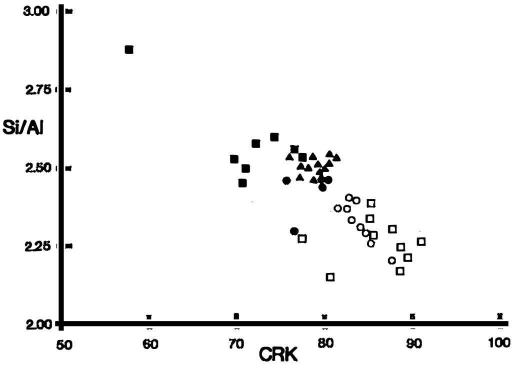


FIG. 4. Si/Al *versus* CRK [100 × (Cs + Rb + K)/cation sum] in homogenous pollucite (▲), Na-enriched blebs (•), Cs-enriched blebs (○), Na-rich borders of of Cs-rich veinlets (■) and Cs-rich veinlets (□).

Si/Al and CRK. In comparison, the Cs-enriched blebs have Cs contents distinctly higher than that of the homogeneous pollucite, as well as lower values of Si/Al. Cs-enriched blebs have Si/Al from 2.00 to 2.40 and CRK from 82 to 90. Na-enriched blebs have Si/Al from 2.30 to 2.50 and CRK from 74 to 80. There is minimal variation in composition within blebs; however, adjacent Na-enriched and Cs-enriched blebs differ in CRK by 3 to as much as 10.

The veinlets of Cs-rich pollucite have Si/Al from near 2.00 to 2.40, and CRK from 84 to 92 (Fig. 4). The Na-rich pollucite adjacent to the Cs-rich pollucite has compositions that overlap the range of homogeneous pollucite (Fig. 4); however, Na contents are usually higher, with CRK from 58 to 78, and Si contents are usually elevated, with Si/Al from 2.50 to 2.90. There are relatively large compositional variations along veinlets in both the Na-rich and the Cs-rich phases; adjacent phases have differences in CRK from 7 to as much as 19.

In general, Figure 4 shows a strong trend of Al increasing with CRK, a compositional feature of the analcime–pollucite minerals that was never noticed before, either at a single locality or in an assembly of data from different localities (*cf.* Fig. in Černý 1974).

A compositional cross-section of a veinlet of Cs-rich pollucite with Na-rich margins is shown in Figures 5a and b. The most Na-rich pollucite occurs immediately adjacent to the sharp boundary with the Cs-rich veinlet, and Na contents gradually decrease over 30 to 70 μm into homogeneous

TABLE 2. COMPOSITION OF EXSOLVED POLLUCITE PHASES

	Cs-enriched blebs				Na-enriched blebs				Cs-rich veinlets				Na-rich margins of Cs-rich veinlets			
No.	40	44	63	68	30	35	56	65	4	22	48	80	6	16	21	47
SiO_2 wt.%	45.59	43.26	44.72	46.85	47.56	47.13	47.54	47.11	43.28	44.63	43.62	45.43	47.55	47.82	52.02	49.54
Al_2O_3	16.14	16.67	16.56	16.58	16.40	17.44	16.37	16.39	16.26	16.64	17.26	16.17	15.95	16.57	15.35	16.18
Fe_2O_3	0.01	0.01	0.02	0.01	0.00	0.00	0.02	0.02	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	1.24	0.76	1.03	1.51	2.08	1.99	1.55	1.58	0.73	2.02	1.57	1.28	1.84	2.58	3.69	2.13
K_2O	0.01	0.01	0.02	0.02	0.02	0.02	0.01	0.02	0.00	0.01	0.03	0.00	0.01	0.01	0.01	0.01
Rb_2O	1.47	1.41	1.56	1.61	1.24	1.18	1.61	1.64	0.83	0.76	0.97	0.15	0.67	0.01	0.63	1.15
Cs_2O	31.83	34.30	32.56	31.21	29.79	29.86	29.97	30.14	36.18	31.15	30.42	36.38	30.40	29.70	22.52	28.66
CaO	0.54	0.65	0.65	0.46	0.28	0.26	0.43	0.42	0.11	0.14	0.20	0.18	0.28	0.19	0.15	0.35
MgO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.01
sum, less H_2O	96.84	97.06	97.12	98.24	97.36	97.87	97.49	97.31	97.40	95.36	94.06	99.61	96.71	96.87	94.35	98.03
Si	2.124	2.073	2.098	2.127	2.142	2.109	2.146	2.139	2.092	2.097	2.073	2.118	2.159	2.142	2.231	2.176
Al	0.887	0.942	0.915	0.887	0.871	0.920	0.871	0.877	0.926	0.922	0.966	0.888	0.854	0.875	0.776	0.837
Na	0.112	0.070	0.094	0.133	0.182	0.173	0.135	0.139	0.069	0.184	0.145	0.116	0.163	0.225	0.306	0.181
Ca	0.027	0.034	0.033	0.023	0.014	0.012	0.021	0.021	0.006	0.007	0.010	0.009	0.014	0.009	0.007	0.017
Rb	0.044	0.043	0.047	0.047	0.035	0.034	0.047	0.048	0.026	0.023	0.030	0.005	0.020	0.000	0.018	0.032
Cs	0.633	0.701	0.652	0.604	0.572	0.570	0.577	0.583	0.746	0.624	0.616	0.724	0.589	0.567	0.411	0.537
Σ cation charge	0.843	0.883	0.858	0.830	0.818	0.801	0.801	0.813	0.852	0.845	0.812	0.863	0.800	0.810	0.749	0.783
Si/Al	2.396	2.201	2.290	2.399	2.460	2.292	2.461	2.437	2.259	2.275	2.145	2.384	2.528	2.449	2.874	2.599
CRK	83.0	87.8	84.7	80.8	75.7	76.6	80.1	79.8	91.1	77.2	80.7	85.3	77.6	70.8	57.8	74.2

CRK = (Cs+Rb+K)x100/(cation sum)

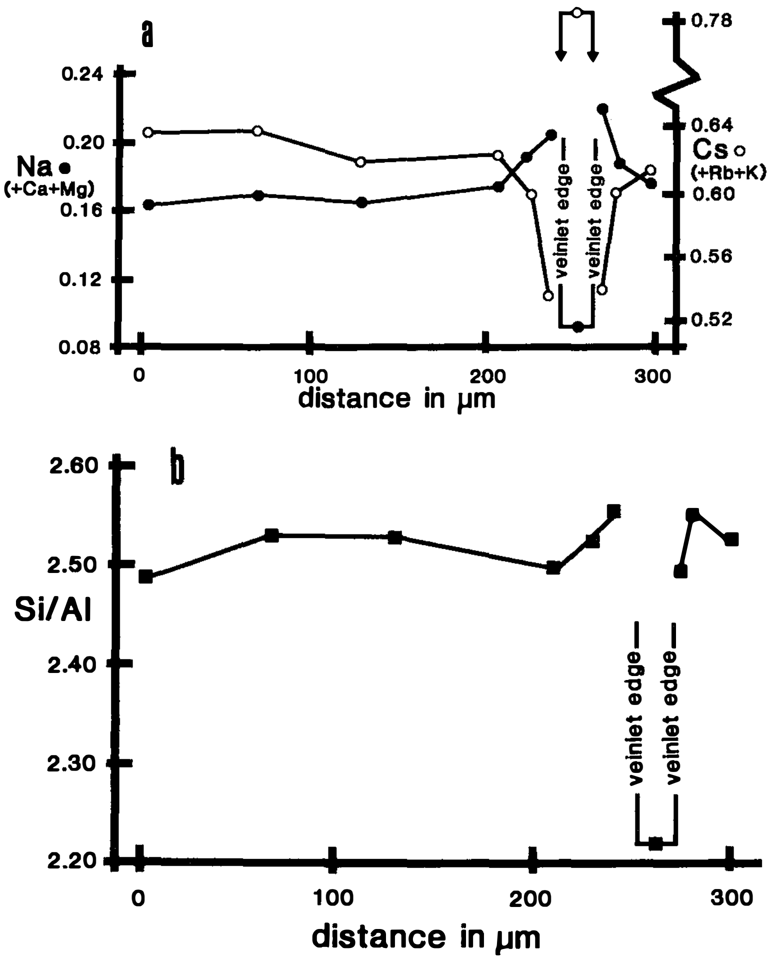


FIG. 5. a) Na (+ Ca + Mg) (atoms p.f.u.), and Cs (+ Rb + K) (atoms p.f.u.), and b) Si/Al, in a traverse across a 20-μm wide Cs-rich veinlet rimmed by Na-rich pollucite, which cuts across an area of homogeneous pollucite.

pollucite. Si/Al increases toward the Cs-rich veinlet, in which Na contents and Si/Al are lower.

Scattered grains of quartz (and rarely albite) in pollucite that are not immediately associated with blebs or veinlets have locally a rim of Cs-rich pollucite. Typical grain-size of this quartz ranges from 10 to 30 μm. The composition of this Cs-rich pollucite is similar to that of the Cs-rich veinlets; compared to homogeneous pollucite, it has higher Cs contents, and lower Si/Al (one analysis gave CRK 85.8 and Si/Al 2.30). The Cs-rich pollucite around the quartz grains is rimmed by Na-rich pollucite, which has Na and Si/Al higher than that of the surrounding homogeneous pollucite.

Laths of spodumene that occur at the margins of pollucite pods and lenses contain pollucite as fracture-fillings and inclusions. The fracture-fillings are typically 1 to 10 μm in width, whereas the inclusions are 5 μm up to 5 mm in size. This pollucite has highly variable but Cs-rich compositions. For example, fracture-filling pollucite occurring with K-feldspar has, on one side of the feldspar grain, CRK = 78 and Si/Al = 2.39 and, on the other side, CRK = 88 and Si/Al = 2.04. Late fracture-filling pollucite has more Cs than pollucite in earlier fractures. The larger inclusions of pollucite contain abundant grains of quartz (<20 μm in size); a typical composition has CRK = 93 and Si/Al = 2.12.

Pollucite near spodumene recrystallized to Cs-rich compositions, and has a "brecciated" texture of broken grains "cemented" by thin seams of

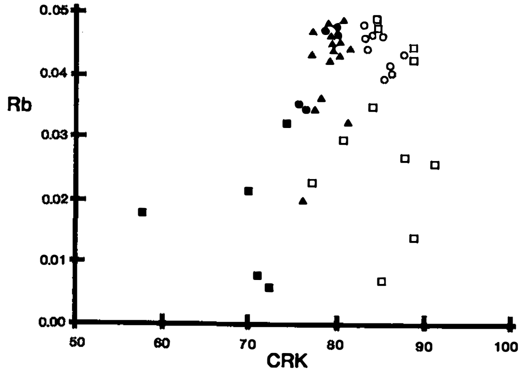


FIG. 6. Rb (atoms p.f.u.) *versus* CRK [100×(Cs + Rb + K)/cation sum] in homogeneous pollucite, Na-enriched blebs, Cs-enriched blebs, Na-rich borders of Cs-rich veinlets, and Cs-rich veinlets. Symbols as in Fig. 4.

more Cs-enriched pollucite. Inclusions of quartz are abundant.

Round inclusions of pollucite 5 to 10 μm in diameter are found in quartz. This pollucite appears to be more Cs-rich than the main, homogeneous pollucite.

In addition to the major cations Na and Cs, pollucite from the High Grade Dyke contains minor Rb and Ca, and negligible K and Mg. Figure 6 shows Rb (as atoms p.f.u.) as a function of CRK for the various textural features. Homogeneous pollucite has Rb variable from 0.020 to 0.050 atoms p.f.u. Rb contents of Na-enriched blebs fall within

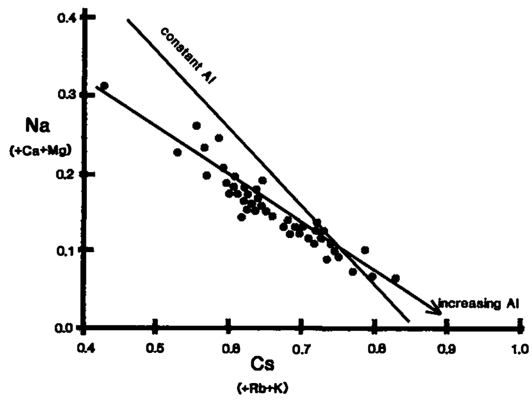


FIG. 8. Na (+ Ca + Mg) *versus* Cs (+ Rb + K) (atoms p.f.u.). The "constant Al" line is for the average Al = 0.86 of the primary pollucite, the other one for the trend of Al increasing with CRK [100 X (Cs + Rb + K)/cation sum] among all the various textural variants.

the same range, whereas Cs-enriched blebs have from 0.040 to 0.050 Rb p.f.u. The veinlets of Cs-rich pollucite have from below the detection limit up to 0.050 Rb p.f.u., whereas adjacent Na-rich material has up to 0.030 Rb p.f.u.

Figure 7 shows Ca as a function of CRK for the different varieties of pollucite. Homogeneous pollucite has from 0.012 to 0.022 Ca p.f.u. The Na-enriched blebs fall in the same range, but Cs-enriched blebs have 0.018 to 0.034 Ca p.f.u. Veinlets of Cs-rich pollucite have from below the detection limit to 0.035 Ca p.f.u.,

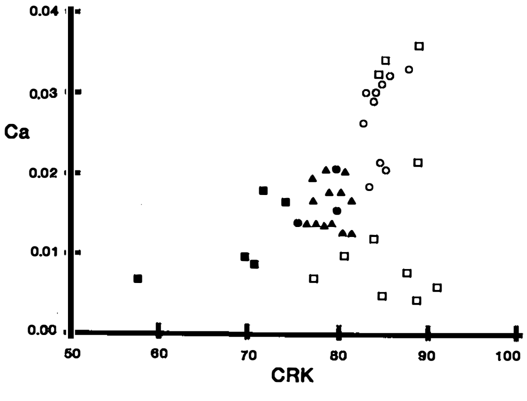


FIG. 7. Ca (atoms p.f.u.) *versus* CRK [100X(Cs + Rb + K)/cation sum] in homogeneous pollucite, Na-enriched blebs, Cs-enriched blebs, Na-rich borders of Cs-rich veinlets, and Cs-rich veinlets. Symbols as in Fig. 4.

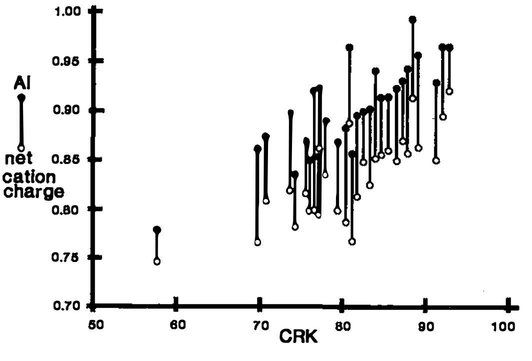


FIG. 9. Al and cation charge sum (atoms p.f.u.) *versus* CRK [100 X (Cs + Rb + K)/(cation sum] for High Grade Dyke pollucite. An 8 to 10% deficiency in cationic charges (relative to Al) is seen in each analysis.

whereas adjacent Na-rich material has up to 0.017 Ca p.f.u.

Figure 8 shows Na (+ Ca + Mg) plotted against Cs (+ Rb + K), both as atoms p.f.u. Scatter in this plot is due to the substitution of cation(s) that could not be analyzed for (such as Li or some form of hydrogen), possible substitution of a single cation into both Na and Cs sites, Al contents variable among different compositions, and analytical error. Note that the data deviate from a trend characteristic of constant Al; the sum of cations, and consequently Al, increase with enrichment in Cs, as apparent in Figure 4.

Figure 9 shows Al and the corresponding sum of cationic charges p.f.u. plotted against CRK. An 8 to 10% deficiency in cationic charges (relative to Al) is noted in all analytical results, independent of variations in CRK.

DISCUSSION

Composition and physical properties

The range of compositions of heterogeneous pollucite from High Grade Dyke ($58 < CRK < 93$) covers the range of most compositions of pollucite established by bulk wet-chemical analysis, $53 < CRK < 87$, and extends it to slightly higher values. This heterogeneity is responsible for the poor covariance of bulk chemical composition with physical properties observed previously in studies of the analcime–pollucite series. Determination of index of refraction should be particularly erratic in this respect, more so than density.

Notes on crystal chemistry

Černý (1974) reviewed the members of the analcime–pollucite series and concluded that the basic requirements of Beger's (1969) structure model were correct: $Cs + H_2O = 1$; $Na < H_2O$; thus $Cs + Na < 1$, and therefore $Al < 1$ and $Si/Al > 2$ (all atoms p.f.u.). The compositional heterogeneity represented by the range of textural features seen in pollucite from High Grade Dyke is in agreement with these requirements (Tables 1, 2).

The closeness of the data points to a line of best fit on a plot of Al *versus* Si (Fig. 3) suggests that all minor elements substituting for Si have been determined; only trace amounts of Fe and P are present in High Grade Dyke pollucite. The slope of this line is 1.00 ± 0.06, as expected for the single tetrahedrally coordinated site in this framework structure.

The compositional trend of Al with CRK (Fig. 9) suggests an Al content of near 1.0 for a CRK of 100. Since pollucite compositions with the highest CRK have Si/Al approaching 2.0, the compositional trends imply that a fully exsolved pollucite phase will have an ideal formula of $(Cs >> Rb,K)_xAlSi_2O_6$, with $x = 1$ if Li or H has no crystal-chemical role in such an end member. Published results of thermodynamic calculations (Bennington *et al.* 1983) and data available from synthesis of Na-free (and H_2O-free?) pollucite do not clarify possible differences in stabilities of phases with variable Si/Al ratio. Thus we can only speculate that the trend toward the simple composition $CsAlSi_2O_6$ may possibly suggest a much greater stability of this stoichiometric, potentially fully ordered composition, which has not been encountered in nature to date.

No clear trend of either Rb or Ca with CRK has been established; however, both Rb and Ca are relatively depleted in the most Na-rich compositions (Figs. 6, 7).

Textural and compositional heterogeneity

Blebby mosaic structures appear to have developed from homogeneous pollucite strictly by local migration of H_2O, Na, Cs, Al, and Si. Likewise, veinlets of Cs-rich low-(Si/Al) pollucite + quartz rimmed by Na-rich, high-(Si/Al) pollucite appear to have developed *in situ*. This arrangement suggests a local mass-balance controlled by three principal mechanisms, the first two being dominant:

(i) exsolution into (Na,Si)-enriched and (Cs,Al)-enriched pollucite compositions,

$$(Na_xCs_y)Al_{x+y}Si_{3-x-y}O_6\bullet xH_2O \rightarrow (Na_{x+z}Cs_{y-z-n})Al_{x+y-n}Si_{3-x-y+n}O_6 \bullet (x+z)H_2O + (Na_{x-z}Cs_{y+z+n})Al_{x+y+n}Si_{3-x-y-n}O_6 \bullet (x-z)H_2O,$$

where $0 < x+y+z \leq 1$;

(ii) liberation of quartz, leading to Si-poor, cation- and Al-enriched pollucite,

$$(Na_xCs_y)Al_{x+y}Si_{3-x-y}O_6\bullet xH_2O \rightarrow (Na_xCs_y)Al_{x+y}Si_{3-x-y+m}O_{6-2m}\bullet xH_2O + mSiO_2,$$

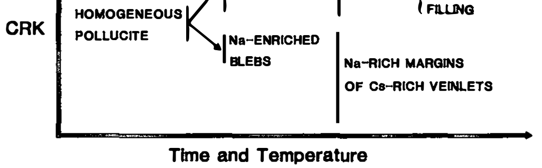


FIG. 10. Schematic general sequence of exsolution products of primary, homogeneous pollucite at High Grade Dyke.

where $0 < x+m \leq 1$, Si/Al ≥ 2, and Na/Cs is constant;

(iii) cation exchange, which modifies the Na/Cs ratio but does not affect Si/Al,
$(Na_xCs_y)Al_{x+y}Si_{3-x-y}O_6 \bullet xH_2O \rightarrow (Na_{x-z}Cs_{y+z})Al_{x+y}Si_{3-x-y}O_6 \bullet (x-z)H_2O + Na_{x-z}Cs_{y-z})Al_{x+y}Si_{3-x-y}O_6 \bullet (x+z)H_2O$,
where $0 < z \leq 1$.

In contrast to the smaller quartz-containing veinlets, veinlets of Cs-rich pollucite greater than about 10 μm in width appear to be of fracture-filling origin. They could have been produced by fluid transport of the Cs-enriched pollucite separated from its Na-enriched counterpart, or, less likely, from a late fluid more or less independent of the breakdown of primary pollucite.

Despite uncertainties about the origin of some of the veinlets of secondary pollucite, the breakdown of homogeneous primary pollucite to (Na,Si)-rich and (Cs,Al)-rich compositions is essentially an exsolution process, commonly combined with separation of quartz, and rarely modified by cation exchange. It is generally progressive with decreasing temperature (Fig. 10). Our observations indicate the presence of a solvus, peaking asymmetrically in the CRK range of about 60 to 80, and at a temperature of less than approximately 500°C.

Pollucite was estimated to crystallize in the temperature range 600 to 300°C (Černý 1979), and was found to be a solidus phase in experiments with granitic bulk compositions at 620 to 540°C (Henderson & Manning 1984, Henderson & Martin 1985). The temperature of precipitation of pollucite in natural (B, F, Li, H_2O)-rich pegmatite-forming melts is probably somewhat below this range. Experimental data are not available for the critical temperature range close to and somewhat below 500°C, somewhat above the solidus of highly fractionated granitic pegmatites, a temperature at which pollucite crystallizes following the termination of the precipitation of petalite or primary spodumene (*e.g.*, Tanco; London 1990). The data of Sebastian & Lagache (1990) do not apply to the observed exsolution, as they pertain to a silica-oversaturated system in which albite is stabilized.

The variations in Na and Cs among the various textural variants are virtually always accompanied by changes in Si/Al, which suggests that complete recrystallization generates the exsolved phases, whereas cation exchange alone plays a negligible role. In the more advanced stages of exsolution, the process is accompanied by liberation of silica from the Cs-enriched phase, compounding the decrease of its Si/Al ratio. This trend of parallel enrichment in Cs and Al may be conditioned by stability relationships of the potential end-member (*cf.* "Notes on crystal chemistry").

Recommendations for future research

Investigations of crystal structure are required to examine the possibility of lower-than-cubic symmetry in birefringent pollucite, and to investigate the nature of the potential deficiency of alkalis relative to Al. In this latter respect, studies of the vibrational spectra of water in homogeneous pollucite may be useful.

Laboratory synthesis of pollucite has been successful over a wide range of pressure and temperature conditions, from 80° to 1400°C at 1 bar (Barrer & McCallum 1953, Vance *et al.* 1982), to 620°C at 1 kbar (Henderson & Martin 1985), and 800°C at 30 kbar (Suito *et al.* 1974). However, the stability fields of end-member pollucite, of pollucite with variable Si/Al, or of pollucite and cesian analcime with compositions similar to natural material have not been adequately established. Research into the experimental formation of homogeneous sodian pollucite and the extent of its two-phase field are highly desirable.

The relationship of the alteration sequence observed in pollucite to late-stage hydrothermal processes in complex granitic pegmatites remains to be evaluated in terms of the types of fluids precipitating low-temperature mineral assemblages, producing exomorphic effects, and invading consolidated pegmatites from their host rocks.

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