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THE OCCURRENCE AND ORIGIN OF ZABUYELITE (Li_2CO_3) IN SPODUMENE-HOSTED FLUID INCLUSIONS: IMPLICATIONS FOR THE INTERNAL EVOLUTION OF RARE-ELEMENT GRANITIC PEGMATITES

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ABSTRACT

Solid – liquid – vapor fluid inclusions in spodumene in rare-element granitic pegmatites commonly contain one or more high-birefringence minerals. Optical examination and laser Raman spectroscopic analyses of over 500 crystal-rich fluid inclusions in spodumene from Bikita and Kamativi, Zimbabwe, and Bernic Lake (Tanco), Manitoba, indicate that the high-birefringence phase is zabuyelite (Li_2CO_3). Laser Raman spectra were also obtained from fluid inclusions in a wafer of spodumene from the Tanco pegmatite reported to contain the type samples of diomignite ($Li_2B_4O_7$). In every fluid inclusion, the high-birefringence phase was shown to be zabuyelite; no phase yielding the Raman spectrum of $Li_2B_4O_7$ was observed. Petrographic analysis indicates that the inclusions are secondary in origin and are trapped within healed fractures and cleavage planes. Essentially all fluid inclusions exhibit extensive necking after the crystallization of solid phases. The dominant solid phases are quartz and zabuyelite. Other minerals such as cookeite, calcite, a cesium-rich phase, apatite and several unidentified minerals were found in fewer than 5% of the fluid inclusions examined. An estimate of the bulk composition of the fluid entrapped within spodumene at Tanco was obtained by averaging the contents of several hundred coeval fluid inclusions, and the composition of individual fluid inclusions was determined using laser Raman spectroscopy, synchrotron X-ray fluorescence and laser ablation – inductively coupled plasma – mass spectrometry. The results indicate that the inclusions in spodumene, like those in the quartz component of SQUI, entrapped a low-salinity (*ca*. 7 wt.% NaCl equiv.), alkali-rich, aqueous carbonic fluid. We propose that the solid – liquid – vapor inclusions in spodumene from Tanco, Bikita and Kamativi are the products of a reaction between the low-density aqueous carbonic fluid and the host spodumene during the late stages of pegmatite evolution; therefore, they do not represent the products of a complex borosilicate melt as suggested previously.

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Keywords: zabuyelite, lithium carbonate, granite pegmatite, spodumene, spodumene–quartz intergrowths after petalite (SQUI), daughter mineral, fluid inclusion, laser Raman spectroscopy, diomignite, Tanco, Manitoba, Bikita, Kamativi, Zimbabwe.

SOMMAIRE

Les inclusions fluides contenant solide – liquide – vapeur piégés dans le spodumène des pegmatites granitiques enrichies en éléments rares contiennent couramment au moins un minéral à biréfringence élevée. Un examen optique et l'analyse des spectres Raman obtenus avec laser de plus de 500 inclusions fluides contenant de tels cristaux dans le spodumène provenant des pegmatites de Bikita et de Kamativi, au Zimbabwe, et du lac Bernic (Tanco), au Manitoba, indiquent que la zabuyelite (Li_2CO_3) est cette phase solide à biréfringence élevée. Nous avons aussi obtenu des spectres Raman d'inclusions fluides dans une lame mince de spodumène de la pegmatite de Tanco réputée contenir les échantillons-types de diomignite ($Li_2B_4O_7$). Dans chacune des inclusions fluides étudiées, la phase à biréfringence élevée s'avère être la zabuyelite; nous n'avons pas trouvé de phase ayant le spectre de Raman du composé $Li_2B_4O_7$. Une analyse pétrographique indique que les inclusions sont secondaires, piégées dans des fissures cicatrisées et des plans de clivage. La grande majorité des inclusions fluides font preuve de remplissage sélectif suite à l'apparition des phases solides, dont le quartz et la zabuyelite prédominent. Nous signalons la présence aussi de cookeïte, calcite, une phase césique, apatite, et plusieurs minéraux non identifiés dans moins de 5% de la population d'inclusions fluides examinée. Nous avons pu établir la composition globale de la phase fluide piégée dans le spodumène à Tanco en prenant la moyenne du contenu de plusieurs centaines d'inclusions fluides contemporaines, et la composition d'inclusions fluides individuelles a été établie par spectroscopie Raman avec laser, analyse par fluorescence X avec synchrotron, et analyse par ablation au laser suivie de spectrométrie de masse du plasma à couplage inductif. Les résultats montrent que les inclusions dans le spodumène, tout comme celles dans le quartz faisant partie d'une intercroissance avec le spodumène (SQUI), ont piégé une phase fluide aqueuse carbonique riche en alcalins, de faible salinité (*ca*. 7% par poids de NaCl ou son équivalent). A notre avis, les inclusions de type solide – liquide – vapeur dans le spodumène provenant de Tanco, Bikita et Kamativi résulteraient d'une réaction entre une phase fluide aqueuse carbonique de faible densité avec le spodumène hôte au cours des stades ultimes de l'évolution de ces pegmatites. Elles ne représenteraient donc pas un assemblage résultant du piégeage d'un liquide borosilicaté complexe, comme on l'a conclu antérieurement.

(Traduit par la Rédaction)

Mots-clés: zabuyelite, carbonate de lithium, pegmatite granitique, spodumène, intercroissance spodumène–quartz par déstabilisation de la pétalite (SQUI), minéral fille, inclusion fluide, spectroscopie de Raman au laser, diomignite, Tanco, Manitoba, Bikita, Kamativi, Zimbabwe.

INTRODUCTION

Crystals of spodumene in granitic pegmatites commonly host numerous elongate fluid inclusions that are aligned parallel to the *c* axis of the host. These inclusions usually contain variable amounts of solid phases, which may comprise up to 80% of the inclusion volume. Previous researchers have generally interpreted such crystal-rich inclusions to be either primary or pseudo-secondary in origin and to represent the products of a hydrous silicate melt or "solution-melt" that was entrapped during the crystallization of spodumene (Fersman 1940, Bazarov 1975, Makagon 1973, Rossovskii *et al.* 1978, London 1986, Doria *et al.* 1989, Charoy *et al.* 1992, Zagorsky *et al.* 1994), or during the isochemical breakdown of petalite to spodumene-plus-quartz intergrowths (SQUI).

The recognition of lithium carbonate (zabuyelite) as a common and widespread solid phase in spodumene-hosted fluid inclusions from three major Li-rich pegmatites (Anderson *et al.* 1994) raises new questions about the origin and significance of these inclusions. In this paper, we re-examine the petrography and composition of spodumene-hosted inclusions from the Tanco pegmatite, Manitoba, and the Bikita and Kamativi pegmatites, Zimbabwe, by using complementary microanalytical techniques. The results indicate that spodumene entrapped a low-salinity carbonic fluid during the late stages in the evolution of the pegmatite. The carbonic fluid reacted with the spodumene host to produce a quartz–carbonate (± alkali aluminosilicate) assemblage. Protracted necking of the inclusions, after the precipitation of the solid phases, resulted in wide variations in the solid – liquid – vapor phase proportions. Using a thermodynamic approach, we demonstrate that zabuyelite-generating reactions are probable during late-stage hydrothermal processes in Li-rich granitic pegmatites. The implications of our alternative interpretation of the spodumene-hosted inclusions for the internal evolution of the Li-rich pegmatites are discussed.

PREVIOUS STUDIES OF SPODUMENE-HOSTED FLUID INCLUSIONS

In the Tanco granitic pegmatite, eastern Manitoba, fluid inclusions in spodumene display broad variations from crystal-rich to crystal-absent, the absence being ascribed to necking of large fluid inclusions after the crystallization of daughter minerals (London 1986). However, localized populations of fluid inclusions in spodumene that have nearly uniform proportions of crystal to liquid and phase assemblages have been reported (London 1986). These apparently unmodified inclusions were interpreted to represent trapped homogeneous fluid, now represented by an equilibrium assemblage of daughter crystals comprising albite, cookeite, pollucite–analcime, quartz and diomignite ($Li_2B_4O_7$), together with a low-salinity aqueous fluid. In addition, a carbonate phase was reported to occur in some inclusions near the tips of coarse-grained spodumene laths. On the basis of a bulk composition calculated using the estimated volume percentages of the phases in the inclusions, London (1986) suggested that spodumene in the Tanco pegmatite crystallized in the presence of a dense hydrous alkali borosilicate fluid containing up to 12 wt.% B_2O_3.

Unlike spodumene-hosted inclusions, the majority of the fluid inclusions in the quartz component of SQUI in the Tanco pegmatite, and in other Li-rich pegmatites, contain only a low-salinity (*ca.* 7 wt.% NaCl equiv.) aqueous fluid (London 1985, Thomas & Schmidt 1986, Whitworth & Rankin 1989, Doria *et al.*1989, Channer *et al.* 1999). A relatively small percentage of fluid inclusions in quartz in granitic pegmatites contain solid phases, and these are interpreted to be either accidentally trapped minerals (London 1985), or the products of devitrification of trapped silicate melt (*e.g.*, Thomas *et al.* 1988, Zagorsky *et al.* 1994, Gatter *et al.* 1999). London (1985) suggested that spodumene and coeval quartz trapped two very different types of fluids at different times in the evolution of the pegmatite, and that quartz did not trap primary fluid inclusions. In contrast, Doria *et al.* (1989) proposed that fluid immiscibility or the mixing of fluids was responsible for the differences between fluid inclusions within contemporaneous minerals in the spodumene-rich zones of the Li-rich pegmatites from the Covas de Barroso area of northern Portugal.

Investigations of spodumene-hosted fluid inclusions from the Tanco pegmatite using proton-induced gamma-ray emission (PIGE) analysis and laser Raman spectroscopy (Anderson *et al.* 1989, 1994, MacArthur *et al.* 1990) showed that the borate diomignite is neither widespread nor abundant in the fluid inclusions. Moreover, zabuyelite (Li_2CO_3) rather than diomignite was confirmed to be the major high-birefringence phase in fluid inclusions in spodumene from the Tanco pegmatite, as well as in three other large Li-rich pegmatites, Bikita and Kamativi, in Zimbabwe, and Kings Mountain, in North Carolina (Anderson *et al.* 1994). Lesser amounts of calcite and other carbonates also were discovered.

ZABUYELITE: PROPERTIES AND PARAGENESIS

Zabuyelite was discovered by Zheng & Liu (1987) in the Zabuye Salt Lake, Nagri, Tibet, where it occurs as small (1.5 to 20 μm long) crystals embedded in halite and as doubly terminated crystals (up to 1.2 mm in length) in near-shore precipitates. The occurrence of zabuyelite in granitic pegmatites was first recognized by Anderson *et al.* (1994) using laser Raman spectroscopy. Lithium carbonate is clear and colorless and exhibits a vitreous luster. It has monoclinic symmetry, space group *C*2/*c*, with cell parameters: *a* 8.39, *b* 5.00, *c* 6.21 Å, β = 114°5' (Zemann 1957: synthetic lithium carbonate) and *a* 8.356, *b* 4.964, *c* 6.185 Å, β = 114°36' (Zheng & Liu 1987: zabuyelite). Zabuyelite is twinned on (100), and displays one perfect cleavage {100} and a second {011} cleavage of moderate quality. It is slightly soluble in water (Linke 1965) (Fig. 1) and effervesces in dilute HCl (Zheng & Liu 1987). The solubility of lithium carbonate in carbonic acid solutions as a function of CO_2 pressure at temperatures up to 250°C was reported by Marshall *et al.* (1958). They showed that the solubility of lithium carbonate at constant temperature increases greatly as the pressure of CO_2 is raised. The optical properties of synthetic lithium carbonate are given in Table 1.

Zabuyelite is readily identified in unopened fluid inclusions by its high birefringence (Fig. 2) and distinctive laser Raman spectrum. Raman spectra obtained from spodumene and zabuyelite crystals in spodumene are shown in Figure 3, and the vibrational frequencies for synthetic lithium carbonate and a zabuyelite crystal extracted from an inclusion are listed in Table 2. Infrared frequencies for synthetic lithium carbonate and zabuyelite from the type locality (Zheng & Liu 1987) are given in Table 3.

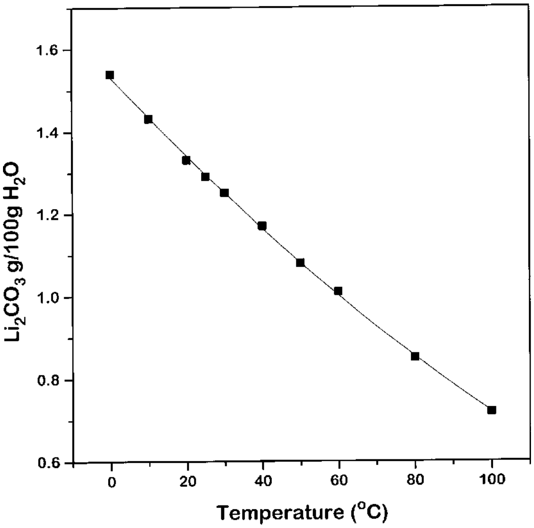

FIG. 1. The solubility of lithium carbonate in H_2O as a function of temperature.

TABLE 1. OPTICAL PROPERTIES OF SYNTHETIC Li_2CO_3, SYNTHETIC $Li_2B_4O_7$ AND ZABUYELITE

	Synthetic Li_2CO_3 Mallard (1892)	Synthetic Li_2CO_3 Chaplygina & Itkina (1968)	Zabuyelite (Li_2CO_3) Zheng & Liu (1987)	Synthetic $Li_2B_4O_7$ London *et al.* (1987)
Indicatrix	biaxial (–)	biaxial (–)	biaxial (–)	uniaxial (–)
Indices of refraction	$\gamma = 1.572$ $\beta = 1.567$ $\alpha = 1.428$	$\gamma = 1.583$ $\beta = 1.572$ $\alpha = 1.428$	$\gamma = 1.5743$ $\beta = 1.5672$ $\alpha = 1.4285$	$\omega = 1.612(1)$ $\varepsilon = 1.554(2)$
Birefringence	$\delta = 0.144$	$\delta = 0.155$	$\delta = 0.146$	$\delta = 0.058(4)$

TABLE 2. RAMAN VIBRATIONAL FREQUENCIES (cm^{-1}) FOR Li_2CO_3 AND THE HIGH-BIREFRINGENCE MINERAL

Li_2CO_3 standard (measured)	Synthetic Li_2CO_3 (Brooker & Bates 1971)	Mineral extracted from fluid inclusion[1]
1461.1	1459 (0.041)	1460.4
1090	1091 (1.0)	1090.0
750.3	748 (0.05)	751.2
n.d.[2]	711 (0.038)	n.d.[2]
192.1	192 (0.48)	192.1
156.2	156 (0.50)	156.2
126	126 (0.16)	126.5
94.8	95 (1.25)	95.9

[1] extracted from spodumene from the Tanco pegmatite, Bernic Lake, Manitoba.
[2] not detected.

TABLE 3. INFRARED VIBRATIONAL FREQUENCIES (cm^{-1}) IN ZABUYELITE AND SYNTHETIC Li_2CO_3

Zabuyelite (Li_2CO_3) Zheng & Liu (1987)	Synthetic Li_2CO_3 Brooker & Bates (1971)
259 (m)	–
–	380 (sh)
414 (s)	410 (m)
–	440 (w, sh)
488 (s)	500 (s)
713 (w)	713 (w)
739 (w)	740 (m)
–	847 (w)
862 (m)	867 (m)
1088 (w)	1088 (m)
1430 (vs)	1420 (m)
1473 (s, sh)	–

Intensity abbreviations: w, weak; m, medium; s, strong; very strong, vs; sh, shoulder.

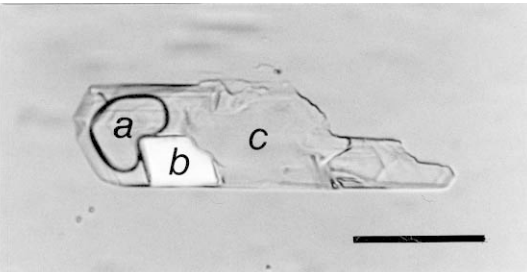

FIG. 2. Spodumene-hosted fluid inclusion from the Tanco pegmatite. At room temperature this inclusion contains a) a vapor bubble, b) zabuyelite, and c) spodumene. The scale bar represents 15 μm. The photomicrograph was taken with partially crossed polarizers.

ANALYTICAL METHODS

Petrography of the inclusions

Doubly polished wafers ($n = 30$) were prepared from both spodumene laths and spodumene + quartz intergrowths (SQUI) from three major Li-rich granitic pegmatites: Bikita and Kamativi, Zimbabwe, and Bernic Lake (Tanco), Manitoba. A polished wafer of spodumene from the Tanco pegmatite, reported to contain the type samples of diomignite ($Li_2B_4O_7$) (London *et al.* 1987), was also obtained for study from the Smithsonian Institution collection (catalogue #164236).

A modified spindle stage (Anderson & Bodnar 1993) was used to examine the shapes of individual inclusions, and to measure the angular relations between planar arrays of fluid inclusions and cleavage planes of spodumene. The dimensions and cross-sectional areas of the fluid inclusions, and the vapor and solid phases they contain, in three groups of coeval fluid inclusions ($n = 460$), were measured using a BIOQUANT OS/2 image-analysis system and petrographic microscope. The volume percentage of various phases was obtained by measuring the ratio of the total area of an inclusion and that occupied by the vapor and solid phases. This ratio is considered to be a close approximation of the volume ratios because of the bladed or tabular shape of most of the inclusions.

Microthermometry

Microthermometric measurements were carried out on a LINKAM THMSG 600 heating and freezing stage calibrated with synthetic fluid inclusions at the triple point of CO_2, the triple point of H_2O, and the critical point of H_2O. The accuracy over the temperature range of interest is estimated to be ±0.4°C. The microthermometric characteristics of inclusions in spodumene from the Tanco pegmatite and other rare-element pegmatites have been reported previously (*e.g.*, Bazarov 1975, Rossovskii *et al.* 1978, London 1986, Doria *et al.* 1989, Zagorsky *et al.* 1994). In this study, measurements were

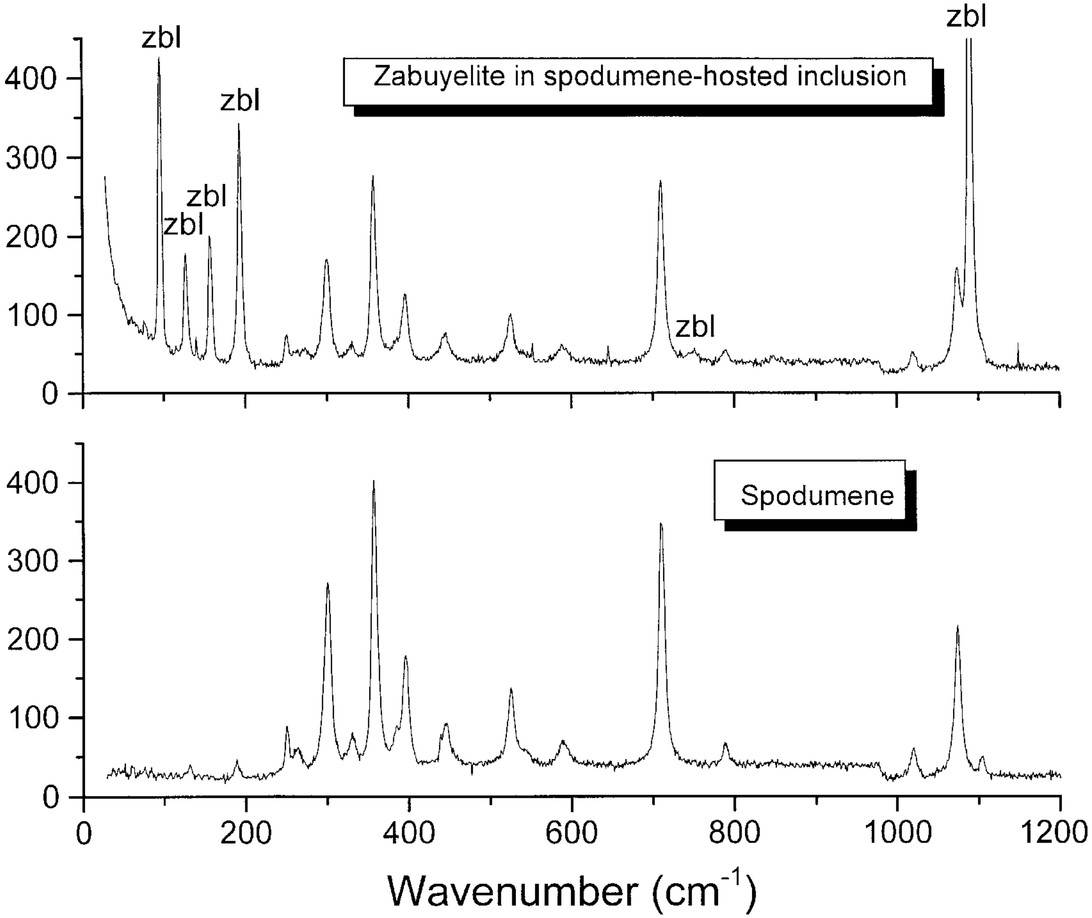

FIG. 3. Laser Raman spectrum of a zabuyelite crystal in a spodumene-hosted fluid inclusion, and of an inclusion-free spodumene host. Vibrational frequencies attributed to zabuyelite are designated by zbl.

made mainly on crystal-rich and crystal-absent inclusions within cogenetic populations in order to assess the role of post-entrapment modifications *versus* heterogeneous entrapment (Loucks 2000).

Laser micro-Raman specrotroscopy

Laser Raman analyses were carried out on solid phases within 500 unopened fluid inclusions in spodumene and quartz using a Dilor Raman microprobe housed in the Department of Chemistry, University of Toronto, an ISA U1000 multichannel Raman microprobe and a Dilor X–Y Raman Microprobe at the Fluids Research Laboratory, Virginia Polytechnic Institute and State University, and an ISA Labram Raman microprobe at the Department of Chemistry at Memorial University of Newfoundland. All instruments are fully confocal from 0 to 1100 nm, and the main excitation beam is the green line at 514.5 nm. The instruments were calibrated using mercury light at 1122.7 cm^{-1} and silicon at 520.1 cm^{-1}. The accuracy is within 0.5 cm^{-1}.

The location of each "spot" analysis within a fluid inclusion was recorded on photographs. Spectra were also collected from an isolated lithium carbonate crystal that was extracted from an inclusion using the method described by Zolensky & Bodnar (1982). Reference spectra were acquired from samples of reagent-grade lithium carbonate, beryllium carbonate, sodium carbonate, sodium bicarbonate, lithium tetraborate and sodium tetraborate. Reference spectra were also collected from minerals reported to occur in fluid inclusions from rare-element pegmatites (see Roedder 1984).

SEM–EDS analysis

The composition of solid phases in opened fluid inclusions in quartz and spodumene was investigated using an Electroscan Environmental Scanning Electron Microscope at the Bedford Institute of Oceanography, Dartmouth, Nova Scotia. All spectra were collected in the point mode at an accelerating voltage of 20 kV using a Si(Li) energy-dispersion detector. A thin (0.3 nm) polymer window on the detector permitted detection of light elements such as carbon and oxygen. An additional advantage of the Environmental SEM is that a conductive coating of gold or carbon on the sample was unnecessary.

Synchrotron X-ray-fluorescence analysis (SXRF)

The synchrotron X-ray microprobe (X26A) at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, New York, was used for *in situ* analyses of regions within ten unopened crystal-rich fluid inclusions. White synchrotron radiation was focused to a 10 μm spot on the sample using Kirkpatrick–Baes mirrors with a flux of about 1×10^5 photons/second. The X-ray fluorescence signal from the sample was collected using a Si(Li) energy-dispersion detector positioned at 90° to the incident beam, with an integration time of 120 seconds. For a description of the X-ray microprobe, the reader is referred to Rivers *et al.* (1991) and Sutton *et al.* (1994).

Laser ablation – inductively coupled plasma – mass spectrometry

The laser ablation – inductively coupled plasma – mass spectrometry (LA–ICP–MS) technique was used to analyze 30 individual fluid inclusions in spodumene and quartz from the Tanco pegmatite. The ICP–MS used was a VG PQII+ AS enhanced-sensitivity quadrupole-based instrument (VG/Thermo, Winsford, U.K.) in the Department of Earth Sciences, Memorial University of Newfoundland. A Quantel 1064 nm Q-switched Nd:YAG laser with a frequency of 266 nm was used for mineral ablation. The LA–ICP–MS technique destroys the fluid inclusion, but has the advantage of high sensitivity, especially for low-Z elements that are difficult or impossible to detect by SXRF due to severe attenuation of X-rays. A review of the LA–ICP–MS technique and a description of the instrumental design used in this study can be found in Günther *et al.* (1999) and Jackson *et al.* (1992), respectively.

Thermodynamic analysis

Phase relations in the system $LiAlSiO_4$–SiO_2–H_2O–CO_2 were explored in order to identify possible subsolidus zabuyelite-generating reactions. The thermodynamic data and sources used in this study are listed in Table 4. All thermodynamic constants for the compounds of interest were obtained from the literature, except for the heat capacity Cp(T) coefficient for Li_2CO_3. In this case, the data on heat capacity in Chase *et al.* (1974) were fitted to the function: $Cp(T) = k_0 + k_1T^{-0.5} + k_2T^{-2} + k_3T^{-3}$ (Berman & Brown 1985) using the computer program *Table Curve*. The heat capacity of Li_2CO_3 was then calculated as: $Cp(T) = 866.992 - 221.036 \bullet 10^2 T^{-0.5} + 878.062 \bullet 10^5 T^{-2} - 1268.38 \bullet 10^7 T^{-3}$. An identical procedure was employed by Vidal & Goffé (1991) to calculate the Cp(T) coefficients for spodumene and cookeite. The density of Li_2CO_3 as a function of temperature is given in Janz & Lorenz (1961), which permits calculation for molar volume as a function of temperature.

RESULTS AND DISCUSSION

Petrography and thermometric behavior

Examination of spodumene-hosted inclusions in three dimensions show that essentially all fluid inclu-

TABLE 4. THERMODYNAMIC DATA FOR MINERAL PHASES EMPLOYED IN THE STUDY

Mineral	H^o_f kJ/mol	S^0 J/mol*K	V^0 cm^3	k_0	$k_1 \times 10^2$	$k_2 \times 10^{-5}$	$k_3 \times 10^{-7}$	$V_1 \times 10^6$ K^{-1}	$V_2 \times 10^{10}$ K^{-2}	$V_3 \times 10^6$ bar^{-1}	$V_4 \times 10^{12}$ bar^{-2}
bikitaite	−3365.2002(1)	163.01(1)	88.9(9)	435.41(1)	−36.085(1)	−79.585(1)	158.451(1)	15.145(1)	54.850(1)	−1.805(1)	5.112(1)
cookeite	−8512.200(1)	504.8(1)	196.2(1)	1152.84(1)	−95.454(1)	−198.69(1)	350.026(1)	26.452(1)	0.0(1)	−1582(1)	0.0(1)
eucryptite	−2147.00(1)	84.85(1)	47.97(2)	241.30(1)	−18.62(1)	−54.300(1)	113.018(1)	29.464(1)	88.633(1)	−0.791(1)	1.351(1)
petalite	−4867.10(1)	233.20(8)	128.4(2)	504.64(1)	−33.70(1)	−130.157(1)	222.130(1)	31.552(1)	200.00(1)	−2.22(1)	6.000(1)
quartz	−910.940(4)	41.84(4)	22.69(3)	80.01(6)	−2.403(6)	−35.467(6)	−49.157(6)	23.895(6)	0.0(6)	−2.434(6)	10.137(6)
spodumene	−3054.7384(4)	129.2856(4)	58.37(2)	329.08(1)	−23.65(1)	−79.585(1)	149.388(1)	23.118(1)	25.785 (1)	−0.86(1)	2.149(1)
zabuyelite	−1215.8704(4)	90.3744(4)	3.713(7)	866.992(5)	−221.036(5)	878.062(5)	−1268.38(5)				

Sources of thermodynamic data: (1) Vidal & Goffé (1991), (2) London (1984), (3) Fasshauer *et al.* (1998), (4) CRC Handbook of Chemistry and Physics (1991), (5) present study, (6) Berman (1988), (7) Janz *et al.* (1979), (8) Hemingway *et al.* (1984), (9) Vidal & Goffé (1989). All other data used in the calculations are taken from Berman (1988).

sions occur as either isolated blades or planar arrays of blades parallel to prominent {110} cleavage directions (Figs. 4a, c), or within healed fractures that cross-cut spodumene laths (Fig. 4b), indicating a secondary or pseudosecondary origin. Individual solid – liquid – vapor inclusions in fractures are elongate parallel to the *c* axis of the spodumene regardless of the orientation of the microcrack.

Populations of cogenetic inclusions invariably display a wide range of phase ratios (Fig. 4a). The measured percentage of vapor and solid phases *versus* total volume of an inclusion for coeval solid – liquid – vapor fluid inclusions is shown in Figures 5a and b. Several important features are revealed in these plots: 1) coeval inclusions contain between 0 and 80 vol.% solids, 2) inclusion size is directly proportional to the volume percent occupied by solid phases, 3) inclusion size is inversely proportional to the volume percent occupied by the vapor bubble at room temperature, and 4) there is a continuum between crystal-absent and crystal-rich (80% solid phases) inclusions within the same plane. These features can be attributed to extensive necking during and after the precipitation of the solid phases in the fluid inclusion. Vapor-rich segments in necked inclusions, and the wide range in temperatures of liquid–vapor homogenization (Fig. 6), suggest that in some cases necking continued even after nucleation of the vapor bubble. In some fluid inclusions, partial dissolution of zabuyelite was observed at temperatures above the temperature of liquid–vapor homogenization ($\mathrm{Th}_{\mathrm{L–V}}$), as indicated by rounding of the crystal. However, decrepitation of the inclusions invariably occurs at various temperatures above $\mathrm{Th}_{\mathrm{L–V}}$ but before dissolution of the zabuyelite. Roedder (1984) considered necking, resulting in diverse proportions of phases, to be one of the reasons why solid phases in some fluid inclusions do not dissolve.

In the course of extensive examination, no groups of inclusions were found to contain nearly identical proportions of phases. The continuum in phase proportions observed, and the relationship between inclusion size and the percentage of contained solid phases, suggest that most liquid–vapor fluid inclusions in spodumene were formed by necking of larger inclusions rather than by the simultaneous trapping of a separate low-density fluid. A similar model was proposed by Samson & Sinclair (1992) to explain variations in the phase proportions observed in quartz-hosted fluid inclusions in the Seagull batholith, Yukon Territory.

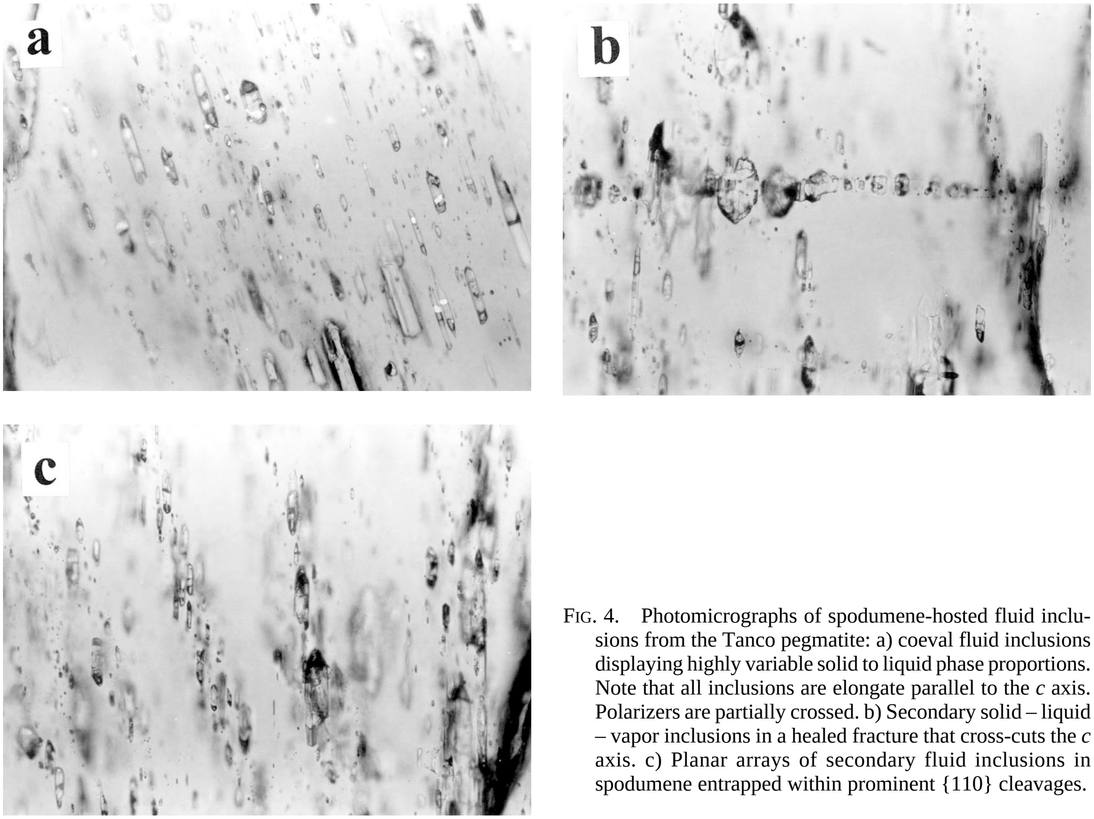

FIG. 4. Photomicrographs of spodumene-hosted fluid inclusions from the Tanco pegmatite: a) coeval fluid inclusions displaying highly variable solid to liquid phase proportions. Note that all inclusions are elongate parallel to the *c* axis. Polarizers are partially crossed. b) Secondary solid – liquid – vapor inclusions in a healed fracture that cross-cuts the *c* axis. c) Planar arrays of secondary fluid inclusions in spodumene entrapped within prominent {110} cleavages.

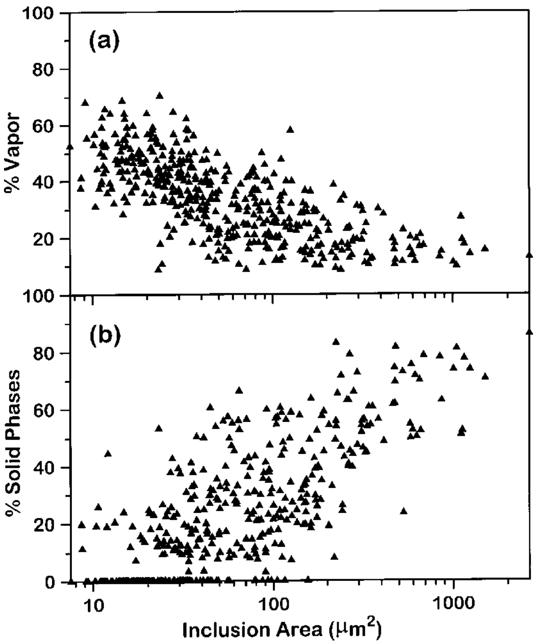

FIG. 5. Total area of a fluid inclusion *versus* a) percent area of vapor bubble and b) percent area occupied by solid phases, for 455 fluid inclusions for three different populations of coeval fluid inclusions.

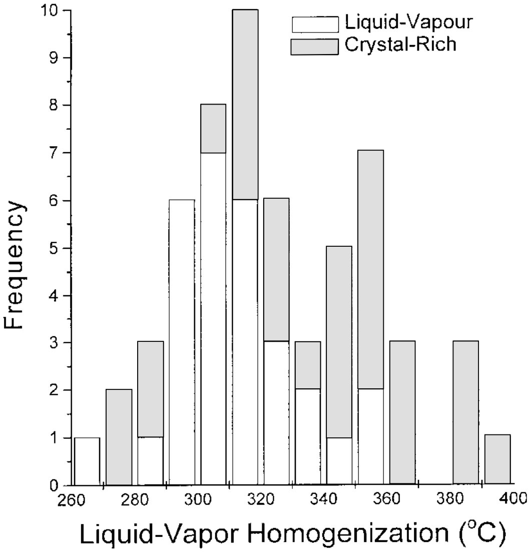

FIG. 6. Histogram showing the frequency of liquid–vapor homogenization temperature for liquid – vapor (unshaded) and solid – liquid – vapor (shaded) fluid inclusions in spodumene.

Composition of fluid inclusions

Laser Raman analyses of over 500 solid – liquid – vapor fluid inclusions show that 96% of the high-birefringence grains are zabuyelite. Table 2 shows that the vibrational frequencies for a reagent-grade lithium carbonate are essentially identical to those of a zabuyelite crystal extracted from a fluid inclusion. A Raman spectrum obtained from a zabuyelite crystal within a spodumene-hosted fluid inclusion is compared to a spectrum obtained from the inclusion-free spodumene host in Figure 3. No inclusions were found to contain diomignite (natural lithium tetraborate), including 30 inclusions in a spodumene wafer from the Smithsonian Institution (catalogue #164236) reported to contain the type samples of diomignite (London *et al.* 1987). In addition to zabuyelite, quartz is a very common mineral in the spodumene-hosted fluid inclusions. Only a few inclusions were found to contain other minerals that yielded Raman signals: these are cookeite, apatite, and three different unidentified minerals.

Many inclusions contain two and in some cases three zabuyelite crystals. The observed variations in interference colors of the zabuyelite crystals are due to differences in optical orientation and crystal size. Other high-birefringence phases include calcite and a second unidentified carbonate. Although sassolite (H_3BO_3) has been reported in quartz-hosted fluid inclusions from the wall zone at Tanco (R. Thomas, pers. commun., 2000), it was not detected in spodumene- or quartz-hosted inclusions in SQUI from the intermediate zones of the Tanco pegmatite.

A small percentage (<5%) of quartz-hosted fluid inclusions in SQUI contain solid phases. Raman analyses of these solids typically show the presence of muscovite and calcite. The solid–liquid phase ratios in the quartz-hosted fluid inclusions appear to be highly variable. Zabuyelite was found in only one quartz-hosted fluid inclusion near a grain boundary with spodumene.

Elemental analyses of individual fluid inclusions from the Tanco pegmatite by SEM–EDS, synchrotron X-ray fluorescence (SXRF) and laser-ablation ICP–MS systematically reveal the presence of C, Na, Cl, Cs and Br, with variable amounts of K, Ca, Rb, Mn, Fe and As. Li in the inclusions could not be reliably measured owing to the high concentrations of Li in the host spodumene. Most inclusions examined by SXRF and LA–ICP–MS contain only trace amounts of Cs. Essentially all of the Si and Al in the SXRF spectra are from the host spodumene. Examples of SXRF spectra from spodumene-hosted fluid inclusions that contain detectable concentrations of K, Ca, Cs and As are shown in Figure 7. Ga and Ge in the spectra are from the spodumene host, and Ar is contributed from the air in the path of the incident X-ray beam.

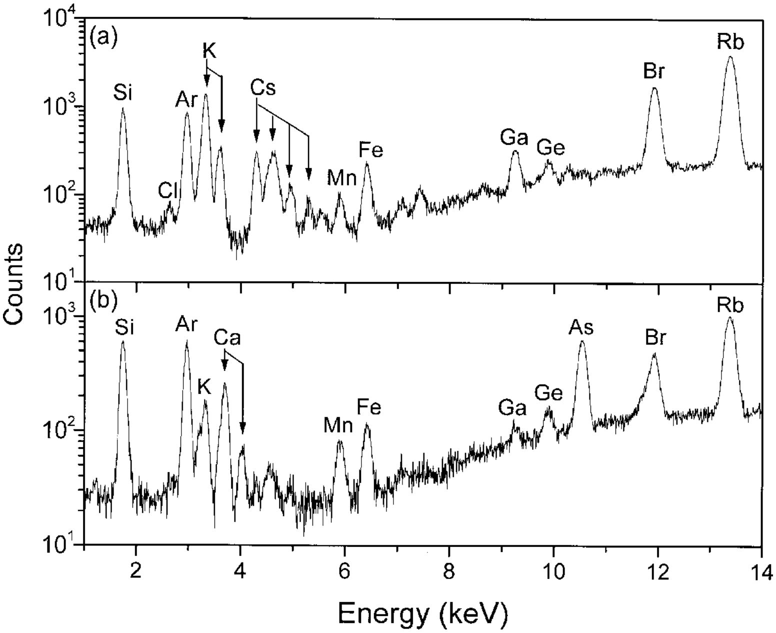

FIG. 7. Synchrotron X-ray-fluorescence spectra collected from two unopened solid – liquid – vapor inclusions (a, b) in spodumene from the Tanco pegmatite.

The spodumene- and quartz-hosted fluid inclusions in SQUI from the Tanco pegmatite contain essentially the same chemical constituents. The composition of quartz-hosted fluid inclusions in SQUI agrees with previously reported results of analyses of leachates from fluid inclusions in quartz from the core and intermediate zones of the Tanco pegmatite using ion chromatography (Channer & Spooner 1992). High concentrations of boron were not detected in spodumene- and quartz-hosted fluid inclusions in SQUI. This result is consistent with previous proton-induced gamma-ray emission (PIGE) analyses (Anderson *et al.* 1989, MacArthur *et al.* 1990), and ion-chromatography analysis of leachates from quartz (<1300 ppm B: Channer & Spooner 1992).

TABLE 5. AVERAGE PROPORTION OF PHASES IN FLUID INCLUSIONS WITHIN SELECTED REGIONS OF SPODUMENE CRYSTALS FROM THE TANCO PEGMATITE, MANITOBA

Sample	Vapor	Total solids	Liquid	N
T-SQUI-F	31.2 vol.%	26.3 vol.%	42.5 vol.%	182
T-SQUI-D	34.8	21.6	43.6	208
T-SQUI-G	45.2	15.6	39.2	63
Pooled results	34.8	22.7	42.6	453

In the case of spodumene-hosted fluid inclusions that are demonstrably modified after trapping, an estimate of the bulk composition of the original entrapped fluid should be based on an average composition obtained from a large number of cogenetic inclusions. We assume that the total volume of the measured inclusions is close to that of the original single inclusion that was necked down (Roedder 1984). The average proportion of liquid, vapor and solid phases by volume in three separate populations of spodumene-hosted fluid inclusions is given in Table 5. These data are used to calculate the bulk composition of the fluid on the supposition that quartz and zabuyelite occur in nearly equal proportions (Table 6). Aluminosilicates such as cesian analcime and cookeite occur sporadically (see Raman and SEM–EDS results above) and are therefore not included in the estimate. However, where different aluminosilicates are included in the calculations, there is very little change in the calculated bulk density of the fluid (*ca.* 1.1 to 1.2 g/cm^3). The mol.% CO_2 of the fluid estimated from phase proportions in spodumene-hosted inclusions (Table 6) is in broad agreement with microthermometric measurements of the CO_2 content in quartz-hosted fluid inclusions in intermediate zones of the Tanco pegmatite (Thomas & Spooner 1992). The Li_2O values given in Table 6 refer to the bulk composition of the inclusion, which is the product of spodumene–fluid interaction and thus does not exactly match the composition of the original carbonic fluid. The lithium concentrations are high relative to the fluid inclusions in quartz owing to the interaction with the spodumene host.

TABLE 6. BULK COMPOSITION OF FLUID INCLUSIONS AND DENSITY ESTIMATED FROM THREE DIFFERENT POPULATIONS OF SPODUMENE-HOSTED FLUID INCLUSIONS FROM THE TANCO PEGMATITE, MANITOBA

	T-SQUI-F	T-SQUI-D	T-SQUI-G
SiO_2 mol.%	13.18	10.93	8
Li_2O	8.54	7.08	5.18
H_2O	69.74	74.91	81.65
CO_2	8.54	7.08	5.18
ρ g/cm^3	1.17	1.1	1.04

Origin of the spodumene-hosted inclusions and the formation of zabuyelite

The results presented above indicate that spodumene in the Tanco, Kamativi and Bikita granitic pegmatites did not trap a silicate melt, but rather a comparatively low-density aqueous carbonic fluid, similar to that found in the quartz-hosted fluid inclusions in SQUI. We propose that the contrasting constitution of spodumene- and quartz-hosted fluid inclusions is due to the different physical properties of these host minerals and their disparate reactions with a carbonic fluid during and after trapping. The formation of solid phases in fluid inclusions as a result of reactions with the host minerals (unofficially referred to as "stepdaughter" minerals) has been reported previously. Andersen *et al.* (1984) described diopside-bearing fluid inclusions that contain carbonate and amphibole, formed by a back-reaction of the diopside host with the entrapped fluid. Similarly, Heinrich & Gottschalk (1995) showed that two single crystals of calcite and quartz in wollastonite-bearing fluid inclusions were formed after fluid entrapment through the reaction wollastonite + CO_2 = calcite + quartz. They also noted that fluid inclusions in the adjacent quartz, which trapped the same carbonic fluid, did not contain any solid phases. Although back reaction of the host with the CO_2 component of the fluid during retrogression is known in metamorphic rocks, inclusion-host reactions have not been fully considered in granitic pegmatite systems.

Subsolidus alteration of lithium aluminosilicate minerals has been investigated experimentally (*e.g.*, Lagache *et al.* 1995) and theoretically (Wood & Williams-Jones 1993). However, in spite of the fact that CO_2-bearing inclusions are common in rare-element pegmatites (Roedder 1984, 1992), no attempts have been made to date to study reactions involving an aqueous carbonic fluid and lithium aluminosilicates. In this study, therefore, some possible subsolidus zabuyelite-generating reactions were explored thermodynamically using the program PTAX (Berman 1991) in order to assess the feasibility of such reactions. The curves for three reactions in the systems $Li_2O–Al_2O_3–SiO_2–H_2O–CO_2$ and $Li_2O–Al_2O_3–SiO_2–K_2O–H_2O–CO_2$ are shown in Figure 8. Our analysis shows that many other zabuyelite-generating reactions, involving phases such as albite, eucryptite and petalite, are also possible and generally occur below 300°C.

The Tanco pegmatite-forming liquid is estimated to have crystallized at a pressure between 2.5 and 3.0 kbar (London 1986, Thomas *et al.* 1988). At these pressures, several different zabuyelite-generating reactions may occur at about 300°C, which is also the approximate pressure and temperature condition at which CO_2 effervescence occurs in fluids in the Tanco pegmatite (Channer *et al.* 1999). Although the late-stage fluid–rock reactions in rare-element pegmatite systems are considerably more complex than those modeled here, our thermodynamic analysis demonstrates that subsolidus zabuyelite-generating reactions involving spodumene and a carbonic fluid are indeed possible.

Trapping of the fluid inclusions

Entrapment of the carbonic fluid was followed by protracted necking over a wide range of temperatures, as indicated by textural evidence, variations in solid – liquid – vapor phase proportions, and by the variation in homogenization temperatures for coeval fluid inclusions (Fig. 6). Theoretical studies by Wood & Williams-Jones (1993) showed that fluids in equilibrium with

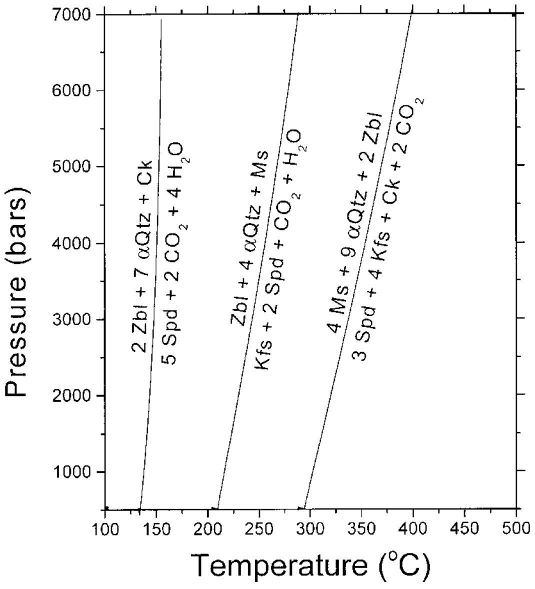

FIG. 8. Reaction curves for three possible zabuyelite-generating reactions involving spodumene (Spd), cookeite (Ck), K-feldspar (Kfs), H_2O and CO_2. Products include muscovite (Ms), alpha quartz (αQz), cookeite (Ck) and zabuyelite (Zbl).

typical subsolidus rare metal pegmatite assemblages will have high Li contents, and that Li concentrations in the aqueous fluid increase dramatically with decreasing temperature. This effect may thus contribute to higher concentrations of Li in the spodumene-hosted inclusions relative to that in quartz-hosted inclusions. Figure 9 is a schematic diagram depicting the stages of formation of secondary fluid inclusions in spodumene. The process begins with the incursion of a low-salinity, alkali-rich supercritical aqueous carbonic fluid into fractures and cleavages. This is followed by recrystallization of the host and precipitation of quartz and zabuyelite (± cookeite, cesian analcime and albite). Spodumene solubility appears to be governed by crystallographic orientation, which in this case is parallel to the *c* axis. The euhedral negative crystal-shape of most inclusions attests to the high solubility of spodumene in the fluid. Trapping and necking of the secondary fluid inclusions continued as the host spodumene cooled across the NaCl (5–8 wt.%)–H_2O–CO_2 solvus into the two-phase immiscibility region. Volume reduction of many spodumene-hosted inclusions is arrested by early-formed quartz and zabuyelite crystals, as indicated by the positive correlation between fluid-inclusion size and the volume percentage of solids in the inclusion (Fig. 5). Nucleation of the vapor bubble occurs after trapping of the solids, with many individual inclusions having two vapor bubbles separated by a solid phase.

Implications for the evolution of fluid phases associated with Li-rich granitic pegmatites

It is well known that postmagmatic recrystallization is common in mineralized granites and granitic pegmatites, and that the recognition of primary fluid inclusions formed during late-magmatic stages is complicated by overprinting of late generations of inclusions (Rankin & Alderton 1985). Previous investigators of quartz-hosted fluid inclusions in rare-element pegmatites reported the presence of fluids derived from both the cooling melt and external metamorphic fluids (*e.g.*, Thomas *et al.* 1988, 1990, London 1985, Whitworth & Rankin 1989). In the Tanco pegmatite, the low-salinity (2–7 equivalent wt.% NaCl), H_2O–CO_2-bearing fluids are inferred to have separated from an evolved magma (Thomas & Spooner 1992), but there is disagreement regarding the precise time in the internal evolution of the pegmatite that an aqueous fluid appeared (London 1990).

There is abundant petrographic evidence supporting secondary, or possibly pseudosecondary, entrapment of carbonic fluids in SQUI. We propose that the solid-bearing fluid inclusions in spodumene are the products of the reaction between the host spodumene and a trapped low-density carbonic fluid rather than an equilibrium assemblage that crystallized from a hydrous borosilicate melt (*i.e.,* primary melt inclusions: London 1986, 1990,

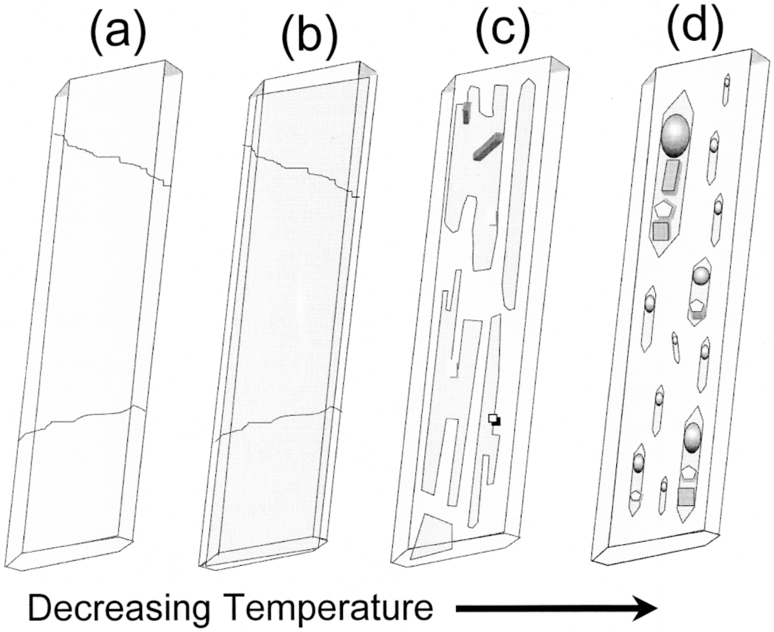

FIG. 9. Schematic diagram depicting the trapping and maturation of spodumene-hosted fluid inclusions. See text for explanation.

London *et al.* 1987). The common occurrence of zabuyelite in spodumene-hosted inclusions from many different pegmatites indicates that the zabuyelite-generating process is common to many Li-rich rare-element pegmatites and is probably a consequence of the exsolution of a magmatic volatile phase during the late stages of pegmatite crystallization and its reaction with early spodumene.

Data on fluid inclusions in spodumene from the Tanco pegmatite are often cited as evidence for extreme boron enrichment in granitic melts (*e.g.,* Dingwell *et al.* 1996, Fasshauer *et al.* 1998). The results presented here, however, show that the fluid entrapped in spodumene-hosted inclusions is not a boron-rich melt. The apparent absence of diomignite (even in the type samples) and the failure to detect significant concentrations of boron in the inclusions have important implications regarding models for the internal evolution of rare-element pegmatites. If, as we suggest, the solid – liquid – vapor inclusions in spodumene represent a trapped low-salinity carbonic fluid instead of a hydrous silicate melt, then previous *P*–*T* estimates of their entrapment (*i.e.,* 475°C and 2.75 kbar) based on fluid-inclusion isochores are invalid. An estimate of the P–T evolutionary path of the fluids represented by spodumene-hosted fluid inclusions must be constrained using isochores in the system $NaCl–H_2O–CO_2$ (Duan *et al.* 1995). In addition, the precise composition and physical properties of the melt from which the intermediate zones of the Tanco granitic pegmatite formed remain uncertain.

The exact timing of fluid entrapment in spodumene is not known, although Thomas *et al.* (1988) have shown that carbonic aqueous fluids were trapped by quartz over a wide temperature range (600–262°C) above and below the *ca.*7 wt.% $NaCl–H_2O–CO_2$ solvus. The proportions of H_2O and CO_2 in the fluid inclusions in SQUI are nearly uniform (London 1986); however, small variations in the proportion of H_2O and CO_2 observed among inclusions in the quartz are probably due to necking. Initial trapping thus probably occurred at temperatures above the $NaCl–H_2O–CO_2$ solvus (*i.e.,* > 300°C, assuming a pressure of 3 kbar).

Fluorine-, boron-, phosphorus-rich melt inclusions in quartz are known to occur in the stockscheider pegmatites of the Variscan Ehrenfriedersdorf complex, Germany (Thomas *et al.* 2000). At room temperature, these melt inclusions contain several different solids that may occupy 80% of the total volume of the inclusion. Similar crystal-rich inclusions occur sporadically in quartz from the Tanco pegmatite, but unlike the quartz-hosted inclusions from Ehrenfriedersdorf, the phase proportions appear to be highly variable. A more comprehensive study of the crystal-rich inclusions in quartz from Tanco may be needed to determine if the solid-rich inclusions are the products of a silicate melt or if the crystals are accidentally trapped solids.

CONCLUSIONS

In this communication, we have described a new zabuyelite-bearing paragenesis in spodumene-hosted fluid inclusions in rare-element granitic pegmatites. Reexamination of the petrography and composition of fluid inclusions in SQUI yields the following conclusions:

1) The majority of inclusions in spodumene are secondary, or possibly pseudosecondary, in origin.

2) The predominant solid phases in spodumene-hosted fluid inclusions from the Tanco pegmatite are quartz and zabuyelite.

3) Natural lithium tetraborate, diomignite, is not present in any of the fluid inclusions examined, including those in the type samples from the Tanco pegmatite.

4) Spodumene from the Tanco pegmatite did not trap a hydrous borosilicate melt, as previously suggested by London (1986) and London *et al.* (1987).

5) Most of the fluid inclusions in spodumene and in the coexisting quartz trapped a relatively low-density, alkali-rich carbonic fluid.

6) A carbonation reaction between the fluid and the spodumene host produced a quartz + zabuyelite assemblage with or without cookeite, cesian analcime and albite.

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REFERENCES

ANDERSEN, T., O'REILLY, S.Y. & GRIFFIN, W.L. (1984): The trapped fluid phase in upper mantle xenoliths from Victoria, Australia: implications for mantle metasomatism. *Contrib. Mineral. Petrol.* **88**, 72-85.

ANDERSON, A.J. & BODNAR, R.J. (1993): An adaptation of the spindle stage for geometric analysis of fluid inclusions. *Am. Mineral.* **78**, 657-664.

________, CLARK, A.H., HARRISON, F. & BODNAR, R.J. (1994): Zabuyelite (Li_2CO_3) in spodumene-bearing pegmatites. *Geol. Assoc. Can. – Mineral. Assoc. Can., Program Abstr.* **19**, A3.

________, ________, MA, XIN-PEI, PALMER, G.R., MACARTHUR, J.D. & ROEDDER, E. (1989): Proton-induced X-ray and gamma-ray emission analysis of unopened fluid inclusions. *Econ. Geol.* **84**, 924-939.

BAZAROV, L.S. (1975): Inclusions of "melt solutions" in minerals of rare-earth pegmatite. *Dokl. Acad. Sci. USSR, Earth Sci. Sect.* **215**, 102-105.

BERMAN, R.G. (1988): Internally-consistent thermodynamic data for minerals in the system Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2. *J. Petrol.* **29**, 445-522.

________ (1991): Thermobarometry using multi-equilibrium calculations: a new technique, with petrological applications. *Can. Mineral.* **29**, 833-855.

________ & BROWN, T.H. (1985): Heat capacity of minerals in the system Na_2O–K_2O–CaO–MgO–FeO–Fe_2O_3–Al_2O_3–SiO_2–TiO_2–H_2O–CO_2: representation, estimation and high temperature extrapolation. *Contrib. Mineral. Petrol.* **89**, 168-183.

BROOKER, M.H. & BATES, J.B. (1971): Raman and infrared spectral studies of anhydrous Li_2CO_3 and Na_2CO_3. *J. Chem. Phys.* **54**, 4788-4796.

CHANNER, D.M.DER., BRAY, C.J. & SPOONER, E.T.C. (1999): Integrated cation-anion/volatile fluid inclusion analysis by gas and ion chromatography; methodology and examples. *Chem. Geol.* **154**, 59- 82.

________ & SPOONER, E.T.C. (1992): Analysis of fluid inclusion leachates from quartz by ion chromatography. *Geochim. Cosmochim. Acta* **56**, 249-259.

CHAPLYGINA, N.M. & ITKINA, L.S. (1968): Double salt of lithium and sodium carbonates formed in aqueous solutions. *Russ. Inorg. Chem.* **13**, 943-946.

CHAROY, B., LHOTE, F., DUSAUSOY, Y. & NORONHA, F. (1992): The crystal chemistry of spodumene in some granitic aplite–pegmatite of northern Portugal. *Can. Mineral.* **30**, 639-651.

CHASE, M.W., CURNUTT, J.L., HU, A.T., PROPHET, H., SYVERUD, A.N. & WALKER, A.C. (1974): JANAF thermodynamic tables, 1974 supplement. *J. Phys. Chem. Ref. Data* **3**, 311-480.

CRC HANDBOOK OF CHEMISTRY AND PHYSICS (71th edition, D.R. Lide, ed.) (1991): CRC Press, Boca Raton, Florida.

DINGWELL, D.B., PICHAVANT, M. & HOLTZ, F. (1996): Experimental studies of boron in granitic melts. *In* Boron Mineralogy, Petrology and Geochemistry (E.S. Grew & L.M. Anovitz, eds.). *Rev. Mineral.* **33**, 331-385.

DORIA, A., CHAROY, B. & NORONHA, F. (1989): Fluid inclusion studies in spodumene-bearing aplite–pegmatite dykes of Covas de Barroso, northern Portugal. *ECROFI X* (*London*), 25 (abstr.).

DUAN, Z., MOELLER, N. & WEARE, J.H. (1995): Equation of state for the NaCl–H_2O–CO_2 system: prediction of phase equilibria and volumetric properties. *Geochim. Cosmochim. Acta* **59**, 2869-2882.

FASSHAUER, D.W., CHATTERJEE, N.D. & CEMIC, L. (1998): A thermodynamic analysis of the system $LiAlSiO_4$–$NaAlSiO_4$–Al_2O_3–SiO_2–H_2O based on new heat capacity, thermal expansion, and compressibility data for selected phases. *Contrib. Mineral. Petrol.* **133**, 186-198.

FERSMAN, A.E. (1940): *Pegmatites.* **I**. *Granitic Pegmatites*. Akad. Nauk SSSR, Moscow, Russia (in Russ.).

GATTER, I., PREINFALK, C. & MORTEANI, G. (1999): The fluid inclusions of pegmatites with lithium mineralization, of the Araçuaí pegmatite district (Eastern pegmatite province, Minas Gerais, Brazil). *Chem. Erde* **59**, 307-327.

GÜNTHER, D., JACKSON, S.E. & LONGERICH, H.P. (1999): Laser ablation and arc/spark solid sample introduction into inductively coupled plasma mass spectrometers. *Spectrochimica Acta* **54B**, 381-409.

HEINRICH, W. & GOTTSCHALK, M. (1995): Metamorphic reactions between fluid inclusions and mineral hosts. I. Progress of the reaction calcite + quartz = wollastonite + CO_2 in natural wollastonite-hosted fluid inclusions. *Contrib. Mineral. Petrol.* **122**, 51-61.

HEMINGWAY, B.S., ROBIE, R.A., KITTRICK, J.A., GREW, E.S., NELEN, J.A. & LONDON, D. (1984): The heat capacities of osumilite from 298.15 to 1000 K, the thermodynamic properties of two natural chlorites to 500 K, and the thermodynamic properties of petalite to 1800 K. *Am. Mineral.* **69**, 701-710.

JACKSON, S.E., LONGERICH, H.P., DUNNING, G.R. & FRYER B.J. (1992): The application of laser ablation microprobe – inductively coupled plasma – mass spectrometry (LAM–ICP–MS) to *in situ* trace element determinations in minerals. *Can. Mineral.* **30**, 1049-1064.

Janz, G.J., Allen, C.B., Bansal, N.P., Murphy, R.M. & Tompkins, R.P.T. (1979): Physical properties data compilations relevant to energy storage. II. Molten salts: data on single and multi-component salt systems. *U.S. Department of Commerce – National Bureau of Standards*, **NSRDS-NBS 61**, *Part* **II**.

________ & Lorenz, M.R. (1961): Molten carbonate electrolytes: physical properties, structure, and mechanism of electrical conductance *J. Electrochem. Soc.* **108**, 1052-1058.

Lagache, M., Dujon, S.C. & Sebastian, A. (1995): Assemblages of Li–Cs pegmatite minerals in equilibrium with a fluid from their primary crystallization until their hydrothermal alteration: an experimental study. *Mineral. Petrol.* **55**, 131-143.

Linke, W.F. (1965): *Solubilities of Inorganic and Metal-Organic Compounds II* (fourth ed.). American Chemical Society, Washington, D.C.

London, D. (1984): Experimental phase equilibria in the system $LiAlSiO_4$–SiO_2–H_2O: a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **69**, 995-1004.

________ (1985): Origin and significance of inclusions in quartz: a cautionary example from the Tanco pegmatite, Manitoba. *Econ. Geol.* **80**, 1988-1995.

________ (1986): Magmatic–hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase-equilibrium experiments. *Am. Mineral.* **71**, 376-395.

________ (1990): The application of experimental petrology to the genesis and crystallization of granitic pegmatites. *Can. Mineral.* **30**, 499-540.

________, Zolensky, M.E. & Roedder, E. (1987): Diomignite: natural $Li_2B_4O_7$ from the Tanco pegmatite, Bernic Lake, Manitoba. *Can. Mineral.* **25**, 173-180.

Loucks, R.R. (2000): Precise geothermometry on fluid inclusion populations that trapped mixtures of immiscible fluids. *Am. J. Sci.* **300**, 23-59.

MacArthur, J.D., Ma, Xin-Pei, Palmer, G.R., Anderson, A.J. & Clark, A.H. (1990): Below surface analysis of inclusions with PIXE and PIGE. *Nucl. Instrum. Meth.* **B45**, 322-326.

Makagon, V.M. (1973): Crystallization temperatures of lithium-bearing minerals in East Siberian rare-metal pegmatites. *Sibirskov Otdelenie Akad. Nauk SSSR* **81**, 133-138 (in Russ.; abstr. *Proc. COFFI* **7**, 133).

Mallard, E. (1892): Sur la forme cristalline du carbonate de lithine. *Bull. Soc. fr. Minéral.* **15**, 21-26.

Marshall, W.L., Loprest, F.L. & Secoy, C.H. (1958): The equilibrium $Li_2CO_3(s) + CO_2 + H_2O \rightleftharpoons 2\,Li^+ + 2HCO_3^-$ at high temperature and pressure. *J. Solution Chem.* **80**, 5646-5648.

Rankin, A.H. & Alderton, D.H.M. (1985): Fluids in granites from southwest England. In *High Heat Producing* (*HHP*) *Granites, Hydrothermal Circulation and Ore Genesis*. Institution of Mining and Metallurgy, London, U.K (287-299).

Rivers, M.L., Sutton, S.R. & Jones, K.W. (1991): Synchrotron X-ray fluorescence microscopy. *Synchrotron Radiation News* **4**, 23-26.

Roedder, E. (1984): Fluid Inclusions. *Rev. Mineral.* **12**.

________ (1992): Fluid inclusion evidence for immiscibility in magmatic differentiation. *Geochim. Cosmochim. Acta* **56**, 5-20.

Rossovskii, L.N., Makagon, V.M. & Kuz'mina, T.M. (1978): Characteristics of the formation of a kunzite deposit in Afghanistan. *Int. Geol. Rev.* **23**, 1312-1320.

Samson, I.M. & Sinclair, W.D. (1992): Magmatic hydrothermal fluids and the origin of quartz–tourmaline orbicules in the Seagull batholith, Yukon Territory. *Can. Mineral.* **30**, 937-954.

Sutton, S.R., Rivers, M.L., Bajt, S., Jones, K. & Smith, J.V. (1994): Synchrotron X-ray fluorescence microprobe – a microanalytical instrument for trace element studies in geochemistry, cosmochemistry, and the soil and environmental sciences. *Nucl. Instrum. Methods Phys. Res.* **A**. *Accelerators, Spectrometers, Detectors and Associated Equipment* **347**, 412-416.

Thomas, A.V., Bray, C.J. & Spooner, E.T.C. (1988): A discussion of the Jahns–Burnham proposal for the formation of zoned granitic pegmatites using solid–liquid–vapour inclusions from the Tanco pegmatite, S.E. Manitoba, Canada. *Trans. R. Soc. Edinburgh: Earth Sci.* **79**, 299-315.

________, Pasteris, J.D., Bray, C.J. & Spooner, E.T.C. (1990): H_2O–CH_4–NaCl–CO_2 inclusions from the footwall contact of the Tanco granitic pegmatite: estimates of internal pressure and composition from microthermometry, laser Raman spectroscopy, and gas chromatography. *Geochim. Cosmochim. Acta* **54**, 559-573.

________ & Spooner, E.T.C. (1992): The volatile geochemistry of magmatic H_2O–CO_2 fluid inclusions from the Tanco zoned granitic pegmatite, southeastern Manitoba, Canada. *Geochim. Cosmochim. Acta* **56**, 49-65.

Thomas, R. & Schmidt, W. (1986): First results of thermobarometric analysis of inclusions of mineral-forming media in minerals of pegmatites of the Republic of Mozambique and some remarks on methodological problems. *Freiberger Forschungshefte* **C402**, 31-48. (in German).

________, Webster, J.D. & Heinrich, W. (2000): Melt inclusions in pegmatite quartz: complete miscibility between silicate melts and hydrous fluids at low pressure. *Contrib. Mineral. Petrol.* **139**, 394-401.

VIDAL, O. & GOFFÉ, B. (1989): Etude expérimentale préliminaire de l'équilibre: bikitaïte = spodumène + eau. *C.R. Acad. Sci. Paris* **309**, 233-238.

________ & ________ (1991): Cookeite $LiAl_4(Si_3Al)O_{10}(OH)_8$: experimental study and thermodynamical analysis of its compatibility relations in the Li_2O–Al_2O_3–SiO_2–H_2O system. *Contrib. Mineral. Petrol.* **108**, 72-81.

WHITWORTH, M.P. & RANKIN, A.H. (1989): Evolution of fluid phases associated with lithium pegmatites from SE Ireland. *Mineral. Mag.* **53**, 271-284.

WOOD, S.A. & WILLIAMS-JONES, A.E. (1993): Theoretical studies of the alteration of spodumene, petalite, eucryptite and pollucite in granitic pegmatites: exchange reactions with alkali feldspars. *Contrib. Mineral. Petrol.* **114**, 255-263.

ZAGORSKY, V.YE., PROKOF'YEV, V.YU. & KUZ'MINA, T.M. (1994): Melt inclusions in spodumene and quartz from rare-metal pegmatites. *Dokl. Akad. Nauk SSSR*, **327**(8), 121-123 (in Russ.).

ZEMANN, J. (1957): Die Kristallstruktur von Li_2CO_3. *Acta Crystallogr.* **10**, 664-666.

ZHENG, MIANPING & LIU, WENGAO (1987): A new Li mineral – zabuyelite. *Acta Mineralogica Sinica* **7**, 221-226 (in Chinese).

ZOLENSKY, M.E. & BODNAR, R.J. (1982): Identification of fluid inclusions daughter minerals using Gandolfi X-ray techniques. *Am. Mineral.* **67**, 137-141.

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