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VOLATILE EVOLUTION IN ARCHEAN RARE-ELEMENT GRANITIC PEGMATITES: EVIDENCE FROM THE HYDROGEN ISOTOPIC COMPOSITION OF CHANNEL H_2O IN BERYL

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ABSTRACT

The channel H_2O in beryl constitutes a large reservoir of molecular water; concentrations attain 2.4 wt.%. Stepwise heating experiments, carried out *in vacuo*, permitted the differential extraction of both the channel H_2O and water from other minor sources (*e.g.*, fluid inclusions) for quantification and hydrogen isotope analysis. Beryl is a ubiquitous primary mineral in the two groups of Late Archean granitic pegmatites that occur in the Dryden area, in Ontario, and the hydrogen isotope composition of its channel H_2O has a range of *ca.* 25‰. Igneous fractionation trends in the rare-element granitic pegmatites of the Mavis Lake group, the focus of this study, are described by: (1) systematic changes in the mineral assemblage of the pegmatites with increasing distance from the parent granite (beryl to spodumene - beryl - tantalite), (2) decreasing K/Rb ratio in blocky K-feldspar that coexists with beryl (K/Rb_{Kfs} = 59 to 16), (3) increasing concentrations of channel H_2O in beryl (1.76 to 2.25 wt.%), and (4) increasing δD values in beryl (-78 to -53‰). As there is no compelling field or petrographic evidence for vapor saturation during the bulk of pegmatite crystallization, these trends are interpreted to have resulted from crystallization at vapor-undersaturated conditions, with the composition of the channel H_2O in the beryl approximating that of dissolved magmatic H_2O. Hydrogen isotope fractionations between muscovite and the channel H_2O in coexisting beryl from the Taylor Beryl No. 2 ($\Delta_{Ms-H_2O} = -21$‰) and Fairservice Property No. 1 ($\Delta_{Ms-H_2O} = -19$‰) pegmatites are analytically indistinguishable, and yield temperatures of crystallization in the range 530–430°C, which agree well with those based on phase-equilibrium studies. As such, the existence of molecular H_2O, trapped in channels in beryl during the late stages of pegmatite crystallization, may facilitate the detailed study of volatile evolution in a wide range of Archean and younger granitic pegmatite systems.

Keywords: pegmatite, beryl, channel H_2O, magmatic volatiles, hydrogen isotopes, Dryden, Ontario.

SOMMAIRE

Les canaux dans la structure du béryl forment un réservoir important d'eau moléculaire. Les concentrations d'eau peuvent atteindre 2.4% en poids. Il est possible de libérer cette eau, ainsi que l'eau de sources moins importantes, celle des inclusions fluides par exemple, par chauffage par étapes sous vide, afin de mesurer les quantités d'eau et la géochimie isotopique de l'hydrogène. Le béryl est un minéral primaire répandu dans deux groupes de pegmatites granitiques archéennes de la région de Dryden, en Ontario. L'eau piégée dans les canaux a une composition isotopique de l'hydrogène qui s'étale sur environ 25‰. L'évolution des pegmatites granitiques à éléments rares du groupe du lac Mavis, sur lesquelles nous nous sommes attardés, se voit par: (1) des changements systématiques des assemblages de minéraux selon la distance du pluton granitique qui serait la source des magmas évolués (béryl → spodumène - béryl - tantalite), (2) une diminution dans la valeur du rapport K/Rb, de 59 à 16, dans les cristaux trappus de feldspath potassique en coexistance avec le béryl, (3) une augmentation de la teneur en eau des canaux du béryl, de 1.76 à 2.25% (en poids), et (4) une augmentation de la valeur de δD de cette eau, de -78 à -53‰. Nous ne voyons aucun signe convainquant sur le terrain ou dans les lames minces qu'il y a eu saturation du magma en phase aqueuse au cours de sa cristallisation. Nous pensons donc que le magma a évolué sous conditions de sous-saturation en eau, et que la composition isotopique de l'eau dans les canaux du béryl représenterait celle de l'eau en solution dans le magma. Le degré de fractionnement de l'hydrogène entre muscovite et l'eau des canaux dans les pegmatites dites Taylor Beryl No. 2 ($\Delta_{Ms-H_2O} = -21$‰) et Fairservice Property No. 1 ($\Delta_{Ms-H_2O} = -19$‰) sont identiques, aux erreurs analytiques associées près, et indiquent une température de cristallisation dans l'intervalle 530–430°C, ce qui concorde bien avec les études expérimentales pertinentes. L'occlusion de l'eau moléculaire dans les canaux du béryl au cours des stades ultimes de cristallisation faciliterait donc l'étude détaillée de l'évolution de la phase volatile dans les pegmatites granitiques d'âge archéen ou plus récent.

(Traduit par la Rédaction)

Mots-clés: pegmatite granitique, béryl, eau des canaux, phase volatile magmatique, isotopes d'hydrogène, Dryden, Ontario.

INTRODUCTION

Beryl is most commonly found in vugs in granite and granitic pegmatite; it also occurs in massive form in pegmatites, and is occasionally found in metamorphic rocks. The dominant feature of its structure are the hexagonal rings of six linked Si–O tetrahedra, which are stacked one above another, thus producing a series of open channels aligned parallel to the **c** axis of the mineral (Deer *et al.* 1986). In this respect, the structure of beryl is similar to that of cordierite, $(Mg,Fe^{2+})_2Al_4Si_5O_{18}$ (Gibbs 1966). The hollow channels in the two minerals are large enough to permit the incorporation of nonessential molecules of volatiles such as H_2O and CO_2, and inert gases such as He and Ar.

Early studies of volatiles in beryl identified the occurrence of helium (Strutt 1908, Rayleigh 1933), and argon (Aldrich & Nier 1948), in great excess over that which can be accounted for by radioactive decay. As well as the inert gases, Damon & Kulp (1958) measured the abundances of H_2O, CO_2, and N_2 released at high temperature (>700°C) from a variety of beryl specimens of different ages (Late Archean to Upper Paleozoic). In all cases, their study, like the earlier ones, documented significant excess helium and argon. In addition, they described an important age-dependence, first alluded to by Lord Rayleigh (1933): the proportion of the inert gases (released from the channels) increases, but the proportions of H_2O, CO_2, and N_2 remain essentially constant, with increasing age of the sample.

Three basic hypotheses were proposed by Damon & Kulp (1958) to explain the "excess" inert gases in beryl: (1) He and Ar are created within the crystal structure by radioactive decay or nuclear reactions, (2) the concentration of the inert gases in the mineral increases with time by diffusion into the structure from the surroundings, and (3) the "excess" He and Ar were entrained by the mineral at the time of its formation. They determined that the last hypothesis is the only reasonable one, and concluded that "... *this excess inert gas must represent a sample of the magmatic gases in the immediate environment of the forming crystal*" (1958, p. 433), and that "*Minerals such as beryl and cordierite provide a most effective method for sampling the volatiles which are present in the environment during the process of regional metamorphism and pegmatite formation*" (1958, p. 454). The experimental techniques used by Damon & Kulp are very similar to those used in this study; their findings encouraged us to believe that the study of the channel constituents in beryl from granitic pegmatites of all ages will assist in providing a more complete record of the nature of volatile evolution in such felsic magmatic systems as a function of geological time.

ASPECTS OF BERYL MINERALOGY

Although normally regarded as $Be_3Al_2Si_6O_{18}$, beryl usually contains, in addition to H_2O and inert gases, other nonessential channel constituents such as alkalis: the total alkali content (ΣR_2O) may rise to around 5 to 7 wt.% in igneous beryl (Deer *et al.* 1986), and may exceed 14 wt.% in certain varieties of hydrothermal beryl (Evans & Mrose 1967). As well as Na and Li, the larger alkali ions K and Cs are found, but Rb is less common.

Wood & Nassau (1968) recognized the existence, at room temperature, of two types of H_2O within the channels of beryl. The type-I water molecule is oriented in the hollow channels with its C_2 axis of symmetry perpendicular to the *c* axis of the beryl. This orientation is documented even in synthetic beryl known to be free of alkali. The type-II water molecule is rotated 90° by the action of a nearby alkali ion on the dipole and lies with its C_2 axis of symmetry parallel to the *c* axis. Wood & Nassau proposed that type-I H_2O occurs where there are no alkali ions in the adjacent 2b positions, and that type-II H_2O exists where there are, with the result that the contents of type-II H_2O and alkali ions are positively correlated (*cf.* Bakakin & Belov 1962). The type-I H_2O is thus unbonded, whereas the type-II H_2O is coordinated to channel cations (Wood & Nassau 1968), with most likely two H_2O molecules being bonded with each Na^+ ion (Hawthorne & Černý 1977, Sherriff *et al.* 1991) located at the 2b site in the channel.

In a study of the high-temperature behavior of H_2O and CO_2 in beryl and cordierite, Aines & Rossman (1984a) determined that above 400°C, H_2O that is structurally bound in the channels begins to partition into an unbound state with the characteristics of a gas. The process is fully reversible and involves both types of H_2O (*i.e.*, the ratio of type-I to type-II H_2O is the same before and after heating). At high temperatures, the gas-like H_2O molecules are thus not bound and can assume any orientation in the channel, although they are still confined to certain sections of the structural channel until dehydration begins. Dehydration occurs after most of the H_2O is in this unbound state and channel cations are no longer coordinated by the type-II H_2O molecules, at temperatures of around 700°C for cordierite and 800°C for beryl. These cations (*e.g.*, Na^+) can then move to the wall of the channel or be expelled from the channel, opening the channel for dehydration.

The conclusions of the research discussed above suggest to us that the H_2O released from the structural channels of beryl ($T > 800$°C, *in vacuo*) represents the original water of formation, which may be characterized by its D/H ratio. The nature and magnitude of hydrogen isotope fractionation that is attendant upon the entrapment of H_2O in the structural channels in beryl remain unclear. However, the findings of Aines & Rossman (1984a), which suggest that at high temperatures (>400°C), the gas-like water molecules are not bound, but merely confined to the channel voids, lead us to believe that fractionation, if any, is minimal under these conditions. Accordingly, we have measured the δD of channel H_2O released from beryl (T >800°C) to investigate the nature of the water present during its crystallization. In addition, assuming that the beryl grew in isotopic equilibrium with the pegmatitic melt, the $\delta^{18}O$ of the mineral will reflect the $^{18}O/^{16}O$ of the melt and the temperature of crystallization. We therefore also measured the $\delta^{18}O$ of silicate framework oxygen in the beryl (*i.e.,* oxygen in the beryl residues after stepwise heating) to complement the δD data on the channel H_2O, and to look for possible systematic variations.

Of the very limited number of minerals that are known to contain water in the molecular form, beryl is the most common and widely distributed mineral that occurs in granites (Hall & Walsh 1971, Bazarov 1974, Kinnaird *et al.* 1985) and granitic pegmatites (Norton *et al.* 1958, Mulligan 1965, Černý 1975, Gallagher 1975, Černý & Simpson 1977, Jahns & Ewing 1977). The use of channel H_2O in beryl from such occurrences for the measurement of the hydrogen isotopic composition of magmatic water not only obviates the need for an independent measurement of temperature, but also reduces significantly any possibility of contamination intrinsic in the analysis of inclusion fluids (*cf.* Roedder 1984 for a comprehensive review of this topic), which are typically present in multiple generations and in concentrations less than 0.1 wt.%.

In addition to providing a new method for the elucidation of volatile evolution in rare-element granitic pegmatites and other felsic magmatic systems, the approach adopted here could herald more widespread applications, most notably because it provides an opportunity to determine the hydrogen isotopic composition of Archean magmatic water. It is very important to establish whether there has been a secular variation in the D/H ratio of the hydrosphere over geological time. There is therefore great interest in the hydrogen isotopic composition of the various terrestrial aqueous reservoirs during the Precambrian. The occurrence of beryl in granitic pegmatites in rocks as old as the Late Archean may thus provide an unsurpassed means of examining the nature of the magmatic aqueous reservoir over the last 3 billion years.

REGIONAL GEOLOGICAL SETTING

Granite-related mineralization is regionally scattered throughout the boundary zone between the Winnipeg River Subprovince to the north and the Wabigoon Subprovince to the south (Fig. 1). This 15–40 by 250 km zone, recently defined by Beakhouse (1989) as the Sioux Lookout Terrane, is characterized by: (a) inverted stratigraphy and stacking of allochthonous metavolcanic and metasedimentary rocks that range in age from 2733 ± 1 to 2703 ± 2 Ma (Davis *et al.* 1988, Davis 1990, Blackburn *et al.* 1991), (b) a wide range in metamorphic grade, (c) zones of metasedimentary migmatite, (d) plutons consisting of strongly peraluminous, two-mica granite of Late Archean age (2681 ± 20 Ma; Krogh *et al.* 1976), distributed over a distance of 150 km, and (e) a distinctive metallogeny featuring the widespread development of lithophile-element-enriched mineral occurrences, which, in addition to rare-element pegmatites (*n.b.:* the terms and definitions relating to granitic pegmatites used in this study follow those of Černý 1990), include granite-related deposits of Mo, Sn, W, Th, and U (Breaks & Janes 1991).

Rare-element-enriched granitic pegmatites in the Dryden area of northwestern Ontario were first described by Mulligan (1965), who termed their concentration the "Dryden Pegmatite Field". More recent accounts have divided the pegmatite field into two areally distinct clusters of pegmatite bodies, the Mavis Lake and Gullwing Lake - Tot Lake groups, situated about 10 km apart (Breaks 1989, Breaks & Janes 1991, Breaks & Moore 1992). The genesis of the Mavis Lake Group pegmatites, which form the focus of this study, was linked to the emplacement of the strongly peraluminous, cordierite-bearing Ghost Lake Batholith (Breaks 1989), which is the largest of the two-mica plutons situated within the boundary zone between the Winnipeg River and Wabigoon subprovinces. The petrographically and chemically zoned Ghost Lake Batholith comprises a late tectonic, comagmatic plutonic complex (with eight internal units) emplaced discordantly to regional metamorphic zones.

The main study-area (*i.e.,* where the Mavis Lake Group of pegmatites is exposed) comprises an apical zone in the eastern lobe of the Ghost Lake Batholith (Fig. 2) dominated by units of pegmatitic granite classified according to Černý & Meintzer (1988): pegmatitic leucogranite, fine-grained leucogranite, potassic pegmatite, and layered aplite; the area also includes the adjacent pegmatite aureole, which reveals systematic zoning in rare-

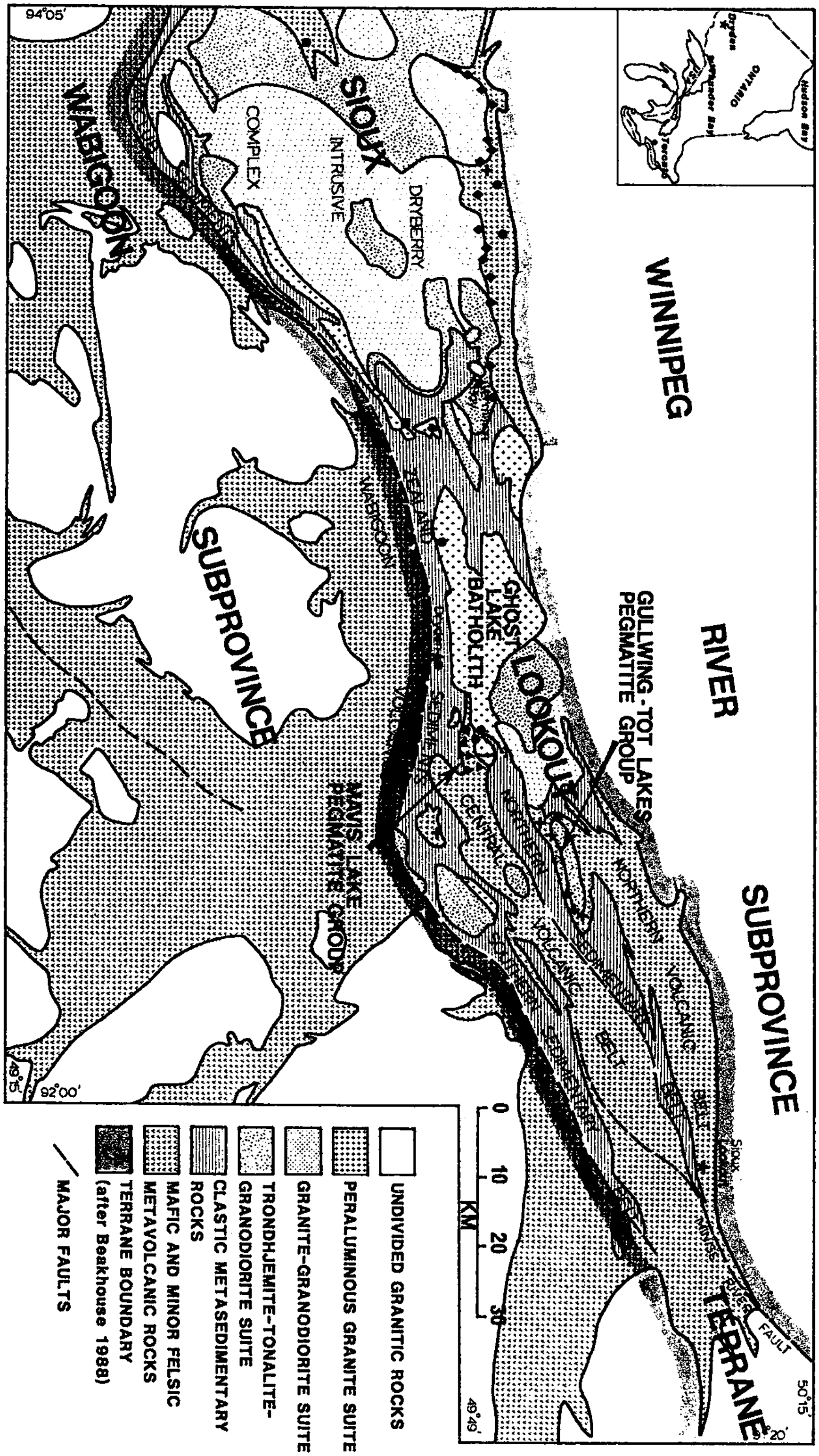

FIG. 1. General geology of part of the Sioux Lookout Terrane showing the location of the Mavis Lake and Gullwing Lake–Tot Lake pegmatite groups (after Breaks & Janes 1991).

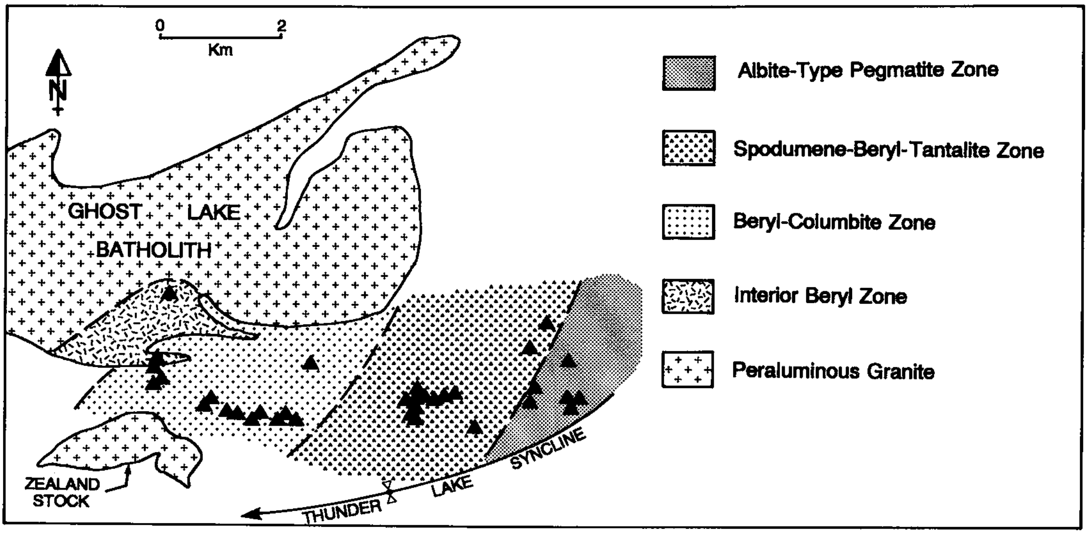

FIG. 2. Geology and distribution of zones of granitic pegmatites in the Mavis Lake pegmatite group (after Breaks & Janes 1991). The filled triangles represent individual rare-element pegmatites.

element minerals and an increase in albite-rich replacement-related features with increasing distance from the contact of the batholith (Fig. 2, Table 1).

TABLE 1. PETROLOGICAL AND GEOCHEMICAL FEATURES OF BERYL-BEARING OCCURRENCES FROM THE GHOST LAKE BATHOLITH AND MAVIS LAKE PEGMATITE GROUP

Occurrence and sample description	Lithology, structure, and geochemical association	Primary mineral assemblage	Extent of late-stage replacement zones and wall-rock alteration
	Interior Beryl Zone		
Dryden Airport occurrence, DA1-2 & DA1-3: primary, lime-green beryl.	Unzoned, internal, potassic pegmatite. Intrusive into leucogranite; B-(Be).	Kfs-Ms-Tur-Ab-Qtz-Grt-(Brl).	No evidence of Ab replacement.
	Beryl-columbite Zone		
Contact Beryl occurrence, RED-2G: primary, light blue beryl in albitite dyke.	Albitite dykes cut exocontact greisen vein system at S.E. contact of GLB. Be-B-F-Li-(Sn-Rb).	Brl-Tur-Ab-Qtz-(Cst-Grt).	Exogreisen vein system cuts metavolcanic rocks and is cut by Ab-Tur-Qtz dykes which locally contain Brl in vugs. Dykes can be traced to pegmatitic granite of GLB.
Taylor Beryl occurrence, RED-4A: primary, white to very light green beryl.	Unzoned, external, pegmatites proximal to GLB. Intrusive into metamorphosed ultramafic rocks; B-Be-(Sn-Nb>Ta).	Brl-Ms-Kfs-Qtz-Tur-Ab-(Clb-Grt-Ap).	Sporadic local zones (4x10cm) of Ab replacement in pegmatite dike. Metasomatic selvedge (10cm) of Phl-Tur-Hlm in wall-rocks along S.E. contact of dike.
	Spodumene-beryl-tantalite Zone		
Fairservice Property, North Zone, FS1-1, FS1-2 & FS2-1: primary, blue to white beryl in core zone.	Crudely zoned, external pegmatites 4.6 km from S.E. contact of GLB. Qtz-rich core zone has abundant green Spd. Intrusive into mafic metavolcanic rocks; Li-Be-Ta>Nb-B-(Sn-Rb).	Brl-Ms-Ab-Spd-Kfs-Qtz-(Ap-Grt-Tur-Clb).	Variable amounts (10%-60%) of Ab replacement in pegmatite dike. Holmquistite masses and Tur porphyroblasts occur in metavolcanic rocks adjacent to contact of dyke where Ab replacement occurs.

Note. Data are from Breaks (1989) with the sampling occurrences being listed in order of increasing distance eastward from the Ghost Lake Batholith (GLB). Accessory minerals and subordinate elements placed in parentheses. Mineral abbreviations after Kretz (1983), with the addition of Hlm = holmquistite, and Clb = columbite-tantalite.

PETROLOGY OF THE RARE-ELEMENT GRANITIC PEGMATITES

The rare-element-enriched granitic pegmatites have been the subject of a recent study by Breaks; comprehensive accounts of their geological setting, petrographic and geochemical characteristics, and petrogenesis are contained in Breaks (1989) and Breaks & Moore (1992). Features of rare-element mineralization in the Dryden Pegmatite Field pertinent to this study are summarized in Table 1.

Mavis Lake Pegmatite Group

The Mavis Lake Group consists of a 0.8–1.5 by 8 km, east-trending concentration of pegmatites, albitites, and related exomorphic features, which includes internal pegmatites of the parent Ghost Lake Batholith (Fig. 2). The group exhibits a classic regional zonation, involving systematic changes in the mineral assemblage of the pegmatites with distance from the parent granite (Cameron *et al.* 1949, Heinrich 1953), which compares closely with that observed in the Kivu region of Zaire (Varlamoff 1972). The following zones have been delineated (Breaks 1989): interior beryl, beryl–columbite, spodumene - beryl - tantalite, and albite-type pegmatites.

The *interior beryl zone* occupies a 1.5 by 3.5 km area of pegmatitic granites within the eastern part of the Ghost Lake Batholith (Fig. 2) and is defined by the occurrence of sporadic, primary, green beryl in dykes and masses of potassic pegmatite. In the adjacent mafic metavolcanic country-rocks, the *beryl-columbite zone* marks the first division of the exocontact. This latter type of rare-element mineralization is contained in muscovite–tourmaline-bearing potassic pegmatites, as exemplified by the Taylor No. 1 and 2 Pegmatites (Table 1).

Spodumene occurs within the pegmatites of the *spodumene - beryl - tantalite zone*. These rare-element granitic pegmatites of the "albite-spodumene type" (Černý 1989) initially appear about 4.6 km east of the chemically most evolved pegmatitic granites of the Ghost Lake Batholith (Fig. 2). Twelve spodumene-bearing pegmatites, which vary in size from 3 by 15 m to 15 by 280 m, are known in this zone of the Mavis Lake Group. Most of the pegmatites are lensoidal bodies with moderate to steep dips, that strike parallel to the foliation in the host mafic metavolcanic rocks. Internal zoning, although normally indistinct, is evident in the Fairservice No. 1 Pegmatite, where it is marked by the occurrence of three gradational zones of increasing quartz content: an outer zone of spodumene-bearing potassic pegmatite, a zone of spodumene–quartz-rich pegmatite, and a quartz-rich core zone.

The most distal zone of the Mavis Lake Pegmatite Group is defined by the occurrence of albite-rich pegmatites considered to be of the "albite type" of Černý (1989). These pegmatites comprise thin (<1 m) sheets rich in albite, which also contain sporadic, fine-grained aggregates of muscovite–albite after primary spodumene and tantalite, white beryl, and rare green tourmaline (Breaks 1989).

Exomorphic alteration-haloes, characterized by tourmaline, holmquistite, and biotite, are a feature of the rare-element pegmatites of the Mavis Lake Group, with the exception of those of the interior beryl zone (Fig. 2). Typically, they comprise narrow (<20 cm), discontinuous contact-aureoles or occur as networks of thin, interconnecting veins in the host mafic and ultramafic rocks within 1 or 2 m of the pegmatite contact. They are particularly common around the spodumene pegmatites of the Fairservice Property (Table 1) in the spodumene - beryl - tantalite zone (Fig. 2).

Gullwing Lake - Tot Lake Pegmatite Group

Pegmatites of this group define an elongate, 0.8-2.2 by 15 km, ENE-trending cluster (Fig. 3). The host rocks are dominated by highly deformed, amphibolitic, mafic metavolcanic rocks, which envelop the Lateral Lake Stock. In addition to the differences in the structural setting of the two pegmatite groups, the Gullwing Lake - Tot Lake group also is distinct in several other respects: (1) the absence of a well-defined regional zonation, (2) a greater diversity in metal association, (3) the presence of a complex pegmatite of the "spodumene subtype" (Černý 1989), (4) the absence of a well-developed, boron-rich exomorphic halo, and (5) the absence of a clearly defined parental granite (Breaks 1989, Breaks & Janes 1991).

The Gullwing Lake and Tot Lake pegmatites are unique in the Dryden Field in that they contain pollucite, a mineralogical indicator of extreme fractionation (*cf.* Černý & Meintzer 1988).

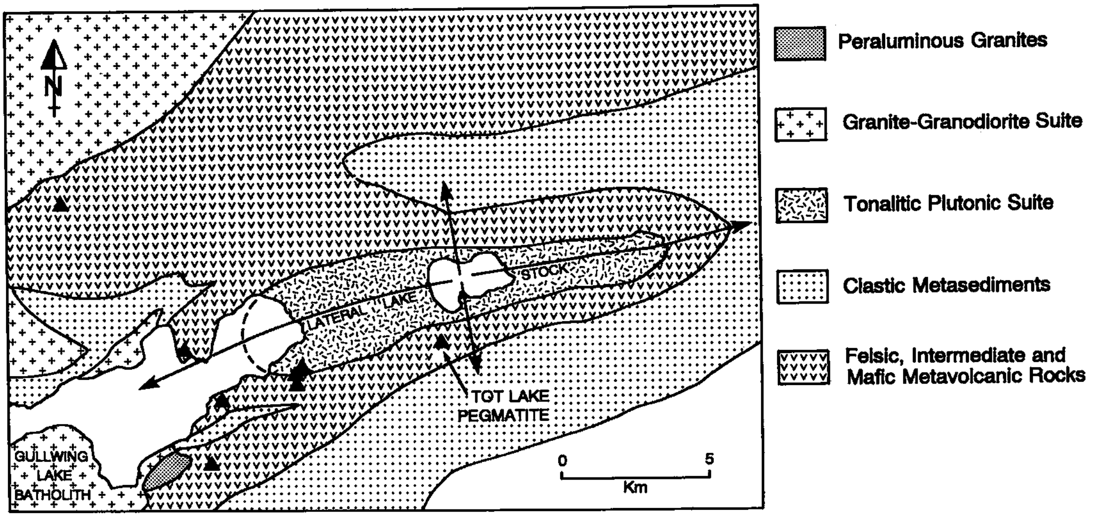

FIG. 3. Geology and distribution of granitic pegmatites in the Gullwing Lake - Tot Lake pegmatite group (after Breaks & Janes 1991). The filled triangles represent individual rare-element pegmatites.

SAMPLE DESCRIPTIONS AND METHODS

Beryl was collected from four representative occurrences in the study area (Table 1). Primary beryl is found in: (1) pegmatites from the interior beryl (*e.g.*, Dryden Airport occurrence), beryl–columbite (*e.g.*, Taylor Beryl occurrence), and spodumene - beryl - tantalite (*e.g.*, Fairservice Property) zones of the Mavis Lake Group (Fig. 2), and (2) late-stage rare-metal albitites (*e.g.*, Contact Beryl occurrence). A specimen of primary beryl also was collected from the spodumene-bearing Tot Lake pegmatite (Fig. 3), of the adjacent Gullwing Lake - Tot Lake group, for the purpose of comparison. In each location, care was taken to select only euhedral crystals of beryl that occur well away from zones of albite replacement and that are entirely free of any evidence of alteration. Mineral separates were made using conventional procedures (heavy liquids, Frantz isodynamic magnetic separator), followed by several episodes of hand-picking under a binocular microscope, grinding in an agate mortar and pestle, and washing with an organic solvent (reagent-grade acetone), strong acids, and then repeatedly in distilled–deionized water in an ultrasonic cleaner. X-ray-diffraction patterns of the beryl concentrates show them to be extremely pure (>98%), with quartz as the only detectable impurity.

The general procedures for stepwise heating have been described previously (Fallick *et al.* 1987, Fallick & Barros 1987). However, because of the somewhat unique design of each series of stepwise heating experiments, some additional comments are warranted. Initially, a preliminary two-step experiment was carried out on an aliquot of beryl sample (specifically FS1-2, Table 2) in order to: (1) ascertain whether any of the channel fluid (released in this preliminary experiment at T > 700°C) or the fluid from other sources (*e.g.*, fluid inclusions, released at T < 700°C) contain a detectable amount of CO_2 or CH_4; although CH_4 typically represents only a very minor component of the fluid in fluid inclusions from felsic igneous rocks, the magnitude of the hydrogen isotope fractionation between CH_4 and H_2O is large enough (*ca.* 120‰ at 400°C, Richet *et al.* 1977) to warrant that care be taken to detect the gas; and (2) monitor the fluid-release behavior during a stepwise heating experiment of extended duration. Because the release systematics of H_2O and other gases can vary quite markedly, particularly for the fluid released from fluid inclusions and other sources (T<700 to 800°C), a preliminary experiment of this type can facilitate the selection of the appropriate temperature-intervals for subsequent multiple-step experiments.

TABLE 2. SUMMARY OF STEPWISE DEGASSING EXPERIMENTS OF BERYL: HYDROGEN ISOTOPE COMPOSITIONS AND WATER CONTENTS

Temperature interval (°C)	DA1-2/DAGP (chips, 150.6 mg)	DA1-3/DAGP (chips, 156.3 mg)	RED-4A/TBGP (1 crystal, 74.6 mg)	FS1-1/FSGP (chips, 188.7 mg)
130°-350°		-44‰ (0.16%)		-86‰ (0.03%)
350°-600°	-83‰ (0.16%)	-27‰ (0.13%)	-115‰ (0.15%)	-57‰ (0.08%)
600°-800°	-134‰ (0.10%)	-85‰ (0.16%)		-124‰ (0.04%)
800°-1400°	-78‰ (1.76%)	-65‰ (1.89%)	-59‰ (1.98%)	-53‰ (2.07%)
	(H_2O^+=2.02%)	(H_2O^+=2.34%)	(H_2O^+=2.13%)	(H_2O^+=2.22%)

Temperature interval (°C)	FS1-2/FSGP (chips, 142.6 mg)	FS2-1/FSGP (chips, 152.3 mg)	RED-2G/GLBAD (chips, 150.6 mg)	RED-10A/TLGP (chips, 146.7 mg)
130°-350°		-131‰ (0.04%)		
350°-600°	-102‰[1] (0.16%)	-112‰ (0.06%)	-82‰ (0.10%)	-164‰ (0.07%)
600°-800°		-149‰ (0.04%)	-104‰ (0.07%)	na (0.05%)
800°-1400°	-53‰[2] (2.39%)	-53‰ (2.25%)	-55‰ (1.80%)	-60‰ (1.60%)
	(H_2O^+=2.55%)	(H_2O^+=2.39%)	(H_2O^+=1.97%)	(H_2O^+=1.72%)

Note. [1]Temperature interval = 130°-700°C; [2]temperature interval = 700°C-1400°C; na = not analyzed/insufficient gas for analysis. Abbreviations are DA = Dryden Airport occurrence, FS = Fairservice Property, TB = Taylor Beryl occurrence, TL = Tot Lake, GP = granite pegmatite, and AD = albitite dyke. The numbers in parentheses following the hydrogen isotopic compositions are water concentrations in weight percent for a particular temperature interval, and the total water content (H_2O^+) for each experiment is shown at the foot of each column. All isotopic values in per mil relative to SMOW.

Accordingly, an expanded vacuum-extraction line that included a circuit with a Cu_2O/Cu furnace (*cf.* Kyser & O'Neil 1984) was used for this preliminary two-step experiment, which had a duration of more than 8 hours. The results of this preliminary experiment, together with those of two subsequent multiple-step heating experiments on separate aliquots of the same beryl crystal (FS1-1 and FS2-1, Table 2) are presented in Figure 4. These data serve to illustrate the degree of internal consistency that can be achieved for replicate samples of a single specimen of beryl under carefully prepared experimental conditions.

In the procedure used for the extraction of hydrogen in the stepwise heating experiments, the blank is less than 1 μmole H_2 which, for an average sample of 150 mg (Table 2), corresponds to 7 X 10^{-3} μmole mg^{-1} or 1 X 10^{-2} wt.%. In combination with the use of a VG 602 gas-source mass spectrometer equipped with an inlet system adapted to a small-volume sample, such a blank permits the characterization of the hydrogen isotope composition of very small amounts of H_2 (*ca.* 5 μmoles) released over temperature intervals of as little as 100°C (*cf.* Fallick & Barros 1987).

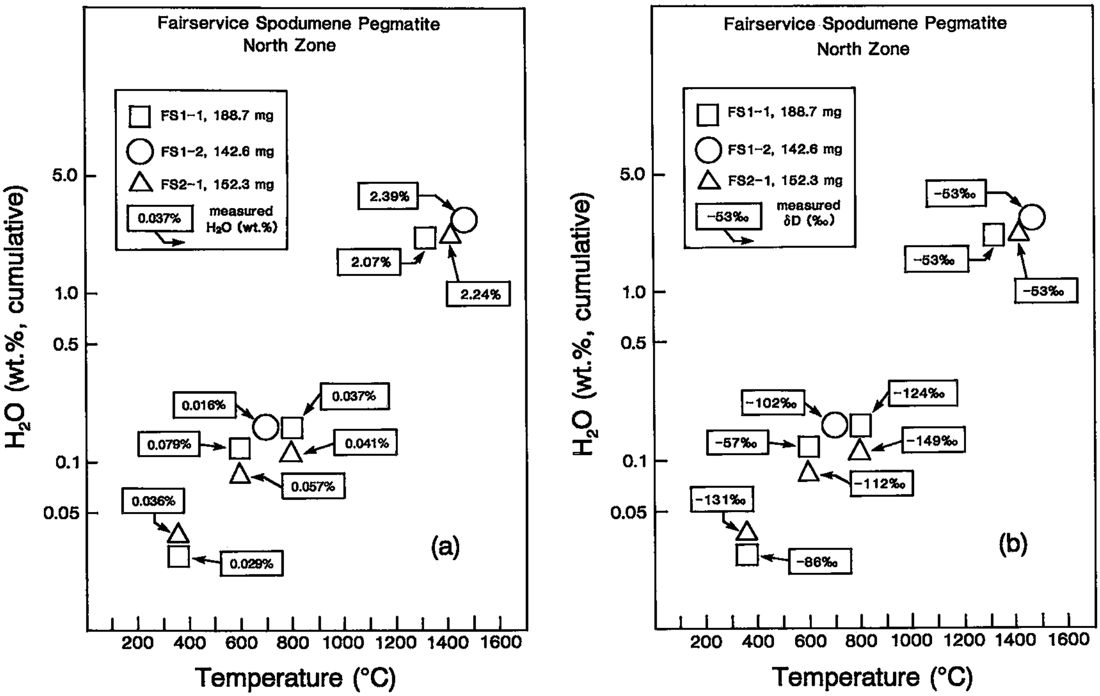

FIG. 4. Plots of the cumulative amount of H_2O^+ released from beryl *versus* (a) the concentration, and (b) the δD value of H_2O in each increment of the stepwise heating experiment. Data are from a series of three different experiments carried out on aliquots of a single, primary beryl crystal from the Fairservice Property Pegmatite No. 1.

The extraction of framework oxygen from the beryl residues (individually stored in a vacuum desiccator after the completion of each of the stepwise heating experiments) for isotopic analysis utilized standard techniques with either BrF_5 (Clayton & Mayeda 1963) or ClF_3 (Borthwick & Harmon 1982) as the reagent. All of the isotopic ratios are reported, in ‰ relative to the Standard Mean Ocean Water (SMOW) reference standard (*cf.* O'Neil 1986, for a recent compilation of data for standards). For NBS 28, we find $\delta^{18}O = 9.6‰$, and for NBS 30, $\delta D = -65‰$. Replicate analyses of pure, isotopically homogeneous material suggest an analytical precision (1σ) of around 0.2‰ for $\delta^{18}O$, 2.0‰ for δD, and 0.02 wt.% for H_2O.

RESULTS AND INTERPRETATION

The results of the stepwise heating experiments on euhedral, primary beryl from granitic pegmatites of three different zones of the Mavis Lake Pegmatite Group and a related rare-metal albitite at the Contact Beryl occurrence are given in Table 2. Comparative data for beryl from the adjacent Tot Lake pegmatite also are included in Table 2. The concentrations and δD values of H_2O released from beryl over different intervals of temperature are discussed in terms of the temperature of release (*e.g.*, H_2O released between 130° and 800°C is identified by $T_{REL} < 800°C$), and the total water content of beryl (*i.e.*, $T_{REL} > 130°C$) is identified as H_2O^+. In addition to the field relationships, petrological indicators of igneous fractionation in granitic pegmatites, *e.g.*, decreasing K/Rb ratio in blocky K-feldspar (K/Rb_{Kfs}) (Černý 1990), have been used to examine variations in the concentration of channel H_2O ($T_{REL} > 800°C$) and its hydrogen isotopic composition in the primary beryl. The temperatures of crystallization were calculated with the hydrogen isotope fractionation for muscovite–H_2O of Suzuoki & Epstein (1976, equation #1, p. 1234), and coexisting muscovite and beryl (channel H_2O); the calculations assume that the hydrogen isotope fractionation accompanying the entrapment of H_2O in the structural channels in beryl at high temperatures (T >400°C; see above) is negligible.

Release systematics of H_2O in beryl

An examination of the data in Table 2 yields several features of note. Firstly, it is readily apparent that a "clean" separation of fractions released is achieved (Fig. 5), with typically less than 0.16 wt.% H_2O given off below 800°C, and more than 1.60 wt.% H_2O above 800°C (also see Fig. 2 in Fallick & Barros 1987). Secondly, the reproducibility of determinations of channel H_2O (T_{REL} > 800°C) for subsamples (Fig. 4) of a single crystal of beryl is excellent, given the analytical precision. These findings are consistent with the observations of Aines & Rossman (1984a) and the conclusions of Polupanova *et al.* (1985) on the thermal stability of beryl, and also with the results of the study of Brown & Mills (1986, p. 547) who, in an investigation of alkali-rich beryl from the Harding pegmatite, recorded that "*heat treatment at 800°C for 72 hours had little effect on the occupancies of channel sites*", and that "*little dehydration occurred because the large alkali ions effectively plug the channels*". Our interpretation of the H_2O released at a T greater than 800°C, that it is contained in the crystallographic channels of the mineral, is thus consistent with the results of investigations of the crystal chemistry of the mineral.

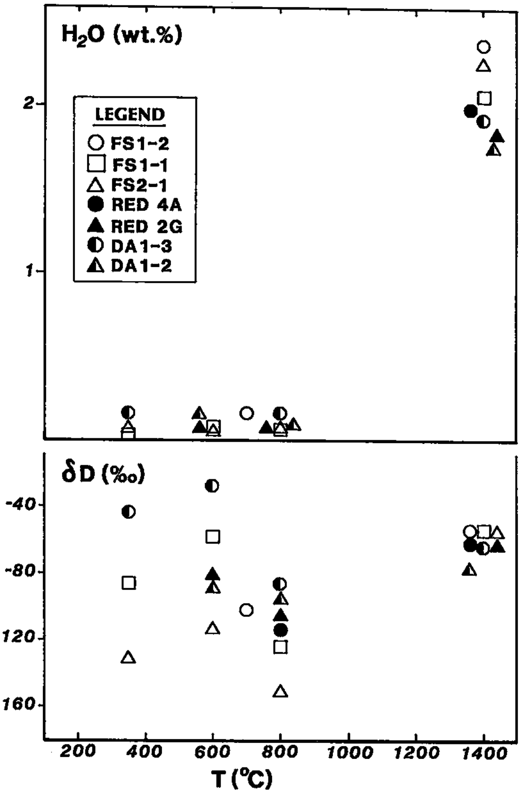

FIG. 5. The variation with release temperature of: (a) water yield (H_2O^+, wt.%), and (b) hydrogen isotope composition (δD, ‰), for different specimens of primary beryl from the Mavis Lake pegmatite group (*note:* the data for the Tot Lake pegmatite are not plotted). The isotopic compositions are relative to SMOW.

Water contents of beryl

The total water content (H_2O^+) of the samples of primary beryl range from 1.72 to 2.55 wt.% (Table 2). Such values are quite typical of those of beryl from granitic pegmatites (*e.g.*, 1.20 < H_2O^+ < 2.28 wt.%: Deer *et al.* 1986), and from granites and related hydrothermal rocks (*e.g.*, 1.78 < H_2O^+ < 1.95 wt.%: Hall & Walsh 1971). Channel H_2O (T_{REL} > 800°C), with concentrations ranging from 1.60 to 2.39 wt.%, typically constitutes greater than 90% of the total water in the mineral (Table 2). Two other features of the data are worthy of note. First, the concentration of channel H_2O (T_{REL} > 800°C) in beryl from the Mavis Lake Group of pegmatites (Fig. 2) increases regularly from the interior beryl zone (Dryden Airport occurrence, 1.76–1.89 wt.%), to the beryl–columbite zone (Taylor Beryl occurrence, 1.98 wt.%), to the spodumene – beryl – tantalite zone (Fairservice Property, 2.07–2.25 wt.%). Second, the concentration of channel H_2O in beryl from the most highly fractionated, spodumene-bearing pegmatite in each of the Mavis Lake Group (*i.e.*, Fairservice Property, 2.07–2.25 wt.%) and Gullwing Lake - Tot Lake Group (*i.e.*, Tot Lake pegmatite, 1.60 wt.%), is quite different (Table 2).

Analyses of the alkali contents of primary beryl in the granitic pegmatites of the Mavis Lake Group (Ucakuwun 1981, Breaks 1989) show increasing levels of enrichment in Na in the Dryden Airport, Taylor Beryl, and Fairservice Property pegmatites, respectively, with beryl from the last occurrence containing an average of 1.22 wt.% Na_2O (Table 52 in Breaks 1989). Such an enrichment in the concentration of Na in beryl is indicative of the presence of increased numbers of Na^+ in the 2b site in the structural channels of the mineral, and provides a mechanism for the incorporation of higher concentrations of channel H_2O (T_{REL} > 800°C) in the form of the type-II molecule (*cf.* Hawthorne & Černý 1977). In addition to its correlation with content of channel H_2O, the higher abundance of Na in beryl from the most fractionated granitic pegmatite of the Mavis Lake Group (*i.e.*, Fairservice Property, Pegmatite No. 1) is also compatible with: (1) an increased level of igneous fractionation (recorded by very low K/Rb ratios in blocky K-feldspar) in the host pegmatite, and (2) in a more general way, the trends of alkali enrichment recorded in other beryl-bearing pegmatites (*e.g.*, Greer Lake, Manitoba: Černý & Turnock 1975).

In this context, a comparison with a specimen of pink beryl from one of the primary, spodumene-bearing units of the Tot Lake pegmatite of the adjacent Gullwing Lake - Tot Lake Group (Fig. 3) also is of interest. The Tot Lake pegmatite is a zoned rare-element pegmatite of the "complex spodumene subtype" (Černý 1989). It is mineralogically and chemically the most fractionated ($7.9 < K/Rb_{Kfs} < 10.3$; Breaks 1989) of any of the pegmatites in the Dryden Field, and is unique in the area in containing pollucite. The δD value of channel H_2O in the Tot Lake beryl specimen (RED–10A) is similar to those of the most fractionated pegmatites in the Mavis Lake Group; however, its concentration is much lower (Table 2). Although the Tot Lake specimen has an almost equal content of Na to that of beryl in the highly fractionated Fairservice Property Pegmatite No. 1 of the Mavis Lake Group, by comparison it is highly enriched in Cs (1.06–2.13 wt.% Cs_2O; Table 52 in Breaks 1989). Cs^+ ions occupy the 2a site in the structural channels in beryl, where they are surrounded by vacancies at the neighboring 2b sites (Hawthorne & Černý 1977, Sherriff *et al.* 1991). The presence of increased numbers of Cs^+ ions in the channels will thus produce a significant decrease in the number of channel sites available to type-II H_2O, and a lower concentration of channel H_2O (types I and II combined) will result, as is the case of sample RED–10A from the Tot Lake pegmatite, which has a concentration of channel H_2O of only 1.60 wt.% (Table 2).

Hydrogen isotope compositions of the channel H_2O

The δD of channel H_2O ($T_{REL} > 800°C$) in primary beryl from granitic pegmatites in the Mavis Lake Group has a relatively restricted range of values, from −78 to −53‰ (Table 2), if compared to H_2O derived from other sites (*e.g.*, fluid inclusions) in the mineral ($T_{REL} < 800°C$; Fig. 5). The latter has a much broader spread of δD values, from −149 to −27‰ and generally lower values (Table 2).

The lowest δD values (−78 to −65‰) for channel H_2O ($T_{REL} > 800°C$) occur in beryl in potassic pegmatite from the Dryden Airport occurrence (Table 1), which is located in the interior beryl zone of the eastern lobe of the Ghost Lake Batholith (Fig. 2). Potassic pegmatite (unit GLB–7 of the Ghost Lake Batholith; Breaks 1989) can form pods gradational from its leucogranite host (unit GLB–5) or narrow, discrete dykes intrusive into the same host. Both types of potassic pegmatite are characterized by well-formed, partial to complete blocky crystals of microcline ($K/Rb_{Kfs} = 59$; Breaks 1989), which commonly project into local quartz-rich segregations. Coarse, euhedral accessories comprise muscovite, tourmaline, and rare lime-green beryl up to 8.5 by 3 cm (Table 1). Potassic pegmatite is notable in being the only internal unit of the Ghost Lake Batholith that contains beryl and columbite-tantalite, and is interpreted by Breaks (1989) to correlate with the rare-element granitic pegmatites of the Mavis Lake Group that occur in the adjacent country-rocks (Fig. 2).

The highest δD values (−53‰) for channel H_2O ($T_{REL} > 800°C$) occur in primary beryl from the core zone of granitic pegmatite in the North Zone of the Fairservice Property (Table 1). The Fairservice Pegmatite No. 1, which is situated in the spodumene – beryl – tantalite zone of the Mavis Lake Group, intrudes mafic metavolcanic rocks approximately 4.6 km east of the contact of the Ghost Lake Batholith (Fig. 2). Pegmatite No. 1 exhibits a crude internal zonation, with a quartz-rich core. The latter contains aggregates and single crystals of blocky microcline ($K/Rb_{Kfs} = 16$; Breaks 1989), spodumene, muscovite, albite, primary and secondary beryl, tourmaline, apatite, and garnet immersed in a massive quartz matrix (Table 1). A characteristic feature of parts of the core zone is the presence of spodumene megacrysts, up to 8 by 4 cm, partly to completely replaced around their rim by fine-grained albite. Associated with the albite-rich replacement zones, which contain partly altered spodumene, is secondary, white subhedral beryl that contrasts with the euhedral, primary beryl (up to 7 by 2 cm) that is disseminated throughout the core zone (Table 1).

Pegmatite Dyke No. 2 of the Taylor Beryl occurrence (Table 1), which is situated in the beryl–columbite zone of the Mavis Lake Group, is located within 1 km of the eastern contact of the Ghost Lake Batholith and occupies an intermediate position between the Dryden Airport and Fairservice Property granitic pegmatites (Fig. 2). Pink, subhedral, blocky K-feldspar ($K/Rb_{Kfs} = 36$; Breaks 1989) occurs together with quartz, muscovite, albite, tourmaline, beryl, and apatite in Pegmatite Dyke No. 2 at the Taylor Beryl occurrence. Channel H_2O ($T_{REL} > 800°C$) from the primary, euhedral beryl has a δD value of −59‰ (Table 2).

The hydrogen isotope composition of the channel H_2O ($T_{REL} > 800°C$) in primary beryl from the granitic pegmatites of the Mavis Lake Group thus varies systematically in terms of: (1) the position of the host pegmatite with respect to the

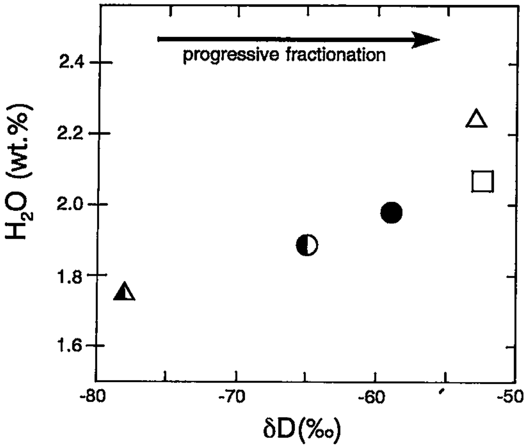

FIG. 6. Plot of δD (‰) *versus* the concentration of H_2O (wt.%) for channel H_2O (T_{REL} > 800°C) in beryl from primary units of the granitic pegmatites of the Mavis Lake Group. The arrow denotes the trend of igneous fractionation as defined by decreasing K/Rb ratio in blocky K-feldspar coexisting with beryl. The isotopic compositions are relative to SMOW.

parent Ghost Lake Batholith (Fig. 2), (2) the K/Rb ratio of the blocky K-feldspar that coexists with beryl, and (3) the concentration of channel H_2O (Fig. 6), relationships that indicate that both the concentration and δD value of H_2O dissolved in the felsic melt, and trapped in the channels of beryl during its crystallization, increased as igneous fractionation progressed. It is now known with some certainty that all but a small proportion of H_2O in alkali aluminosilicate melts at high pressure dissolves as molecular H_2O (D. London, pers. comm.). As there is no compelling field or petrographic evidence for the existence of a separate aqueous vapor phase during the bulk of pegmatite crystallization in the Mavis Lake Group, the increase in both the concentration and δD value of channel H_2O in beryl thus likely reflects changes in the felsic melt at vapor-undersaturated conditions (*cf.* the model for the internal differentiation of rare-element pegmatites: London 1990).

Unlike the occurrences of beryl in granitic pegmatite discussed above, the albitite dyke that was sampled at the Contact Beryl occurrence (Table 1) comprises one of a group of texturally homogeneous dykes of aplite composed of albite, beryl, tourmaline, and quartz and accessory minerals such as cassiterite and molybdenite. The dykes, which intrude mafic metavolcanic rocks immediately adjacent to the contact with the Ghost Lake Batholith, are interpreted to represent the very last stage of pegmatite crystallization at this locality (Breaks & Janes 1991). In terms of both their texture and composition, the dykes resemble the "rare-metal albitites" described by London (1987). Although the beryl specimen from the albitite dyke (sample RED-2G) has a δD value for channel H_2O (-55‰) that is very similar to that of the most fractionated Fairservice spodumene pegmatite of the Mavis Lake Group (Table 2), the concentration of channel H_2O is low (1.80 wt.%) for such a fractionated igneous host. However, unlike the comagmatic pegmatites, the albitite dykes at the Contact Beryl occurrence display a variety of textural evidence (*e.g.*, miarolitic cavities partly filled with beryl) for the former presence of an exsolved aqueous fluid, and this may provide an explanation for the low concentration of channel H_2O in primary beryl from this locality.

Crystallization temperatures for muscovite, which typically occurs together with beryl in primary units of the rare-element granitic pegmatites of the Mavis Lake Group, have been calculated using the hydrogen isotope fractionation of Suzuoki & Epstein (1976, p. 1234, Eq. #1). Muscovite-beryl (channel H_2O) pairs yield the following temperatures of crystallization: 470 ± 40°C ($\Delta_{Ms\text{-}H_2O} = -21‰$) for the quartz - K-feldspar - albite - muscovite - beryl - tourmaline-bearing unit of Pegmatite Dyke No. 2 at the Taylor Beryl occurrence, where the δD of channel H_2O in the beryl is -59‰ and 490 ± 40°C ($\Delta_{Ms\text{-}H_2O} = -19‰$) for the quartz - K-feldspar - albite - muscovite - beryl - tourmaline - spodumene-bearing unit in the core of the Fairservice Property Pegmatite Dyke No. 1, where the δD of channel H_2O in the beryl is -53‰. The errors associated with these determinations of temperature are the aggregate errors, and include both the uncertainties associated with the experimentally determined fractionation factor of hydrogen isotopes for muscovite-H_2O (Suzuoki & Epstein 1976) and those related directly to the stepwise heating procedure used in our experiments. Their magnitude is such that the temperatures of crystallization calculated for the Taylor Beryl and Fairservice Property pegmatites are indistinguishable within the limits of analytical uncertainty.

In his studies of rare-element pegmatites, of both the miarolitic and massive types, London (1986a, b) provided comprehensive evidence for crystallization temperatures in the range 475–425°C for spodumene-(beryl-tourmaline)-bearing assemblages. Our determinations of temperature for the Taylor Beryl and Fairservice Property granitic pegmatites, which indicate crystallization temperatures in the range 530–430°C, provide support not only for the results of London's studies, but also for the integrity of the data for the hydrogen isotope composition of the channel H_2O in beryl.

Hydrogen isotope compositions of H_2O from other locations in the structure

The isotopic composition and abundance of hydrogen in increments of H_2O released at a number of temperature intervals below 800°C also were determined as a routine part of each stepwise heating experiment (Table 2). The concentrations of this "non-channel" H_2O released between 130 and 800°C range from 0.12 to 0.45 wt.% (Table 2). Estimates of the abundance of inclusion fluids in minerals from a wide variety of geological settings suggest that the total fluid content (mostly H_2O) is typically around 0.1 wt.%, and that samples with more than 0.1 wt.% are relatively rare (Roedder 1984, Chapter 5). Consequently, although H_2O from fluid inclusions may represent the dominant component (>50%) of the non-channel H_2O in beryl from granitic pegmatites, minor amounts of H_2O from other locations (*e.g.*, isolated molecules; Aines & Rossman 1984b) also may be present. With few exceptions, the increments of non-channel H_2O have δD values that are significantly lower than those of the channel H_2O in the same crystal, regardless of the release temperature of the increment (Fig. 7). The small volumes of gas available from the non-channel increments (experimental yields of H_2 varied from 6.3 to 39.1 μmoles) for isotopic analysis could have been susceptible to contamination. However, we find no correlation between the yields of H_2 and the δD values to support such an interpretation; moreover, the results of the replicate analyses performed on subsamples of a single crystal from the Fairservice Property pegmatite (Fig. 4) indicate that the increments of non-channel H_2O released in the separate stepwise heating experiments have δD values that are internally consistent.

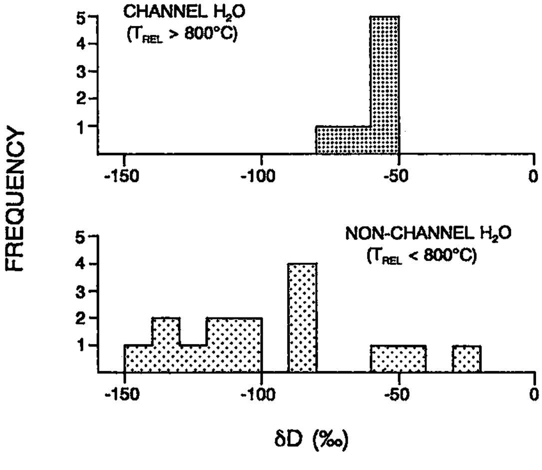

FIG. 7. Histogram plots of the frequency distribution of: (a) δD of channel H_2O (T_{REL} > 800°C), and (b) δD of non-channel H_2O (T_{REL} < 800°C) in beryl from primary units of the granitic pegmatites of the Mavis Lake Group. Isotopic compositions are relative to SMOW.

Therefore, disregarding the specifics of its location, an examination of the hydrogen isotope composition of non-channel H_2O released below 800°C indicates that the H_2O has a wide range of δD values, most of which are significantly lower than those of the corresponding channel H_2O (Fig. 7). Consequently, conditions of formation distinct from those of the channel H_2O must be considered. Processes such as "boiling", or exchange with H-rich (but D-poor) organic molecules (*cf.* Sheppard 1986) can result in H_2O with a significantly lower δD. Alternatively, the low δD values may reflect a component of meteoric H_2O to the non-channel H_2O (*cf.* Taylor 1974). The concept of boiling or unmixing of fluid as the process responsible for the variation in the hydrogen isotopic composition of the non-channel H_2O is the most appealing of these alternatives because it is consistent with London's (1990) model. After the crystallization and chemical fractionation of the bulk of the felsic melt, at vapor-undersaturated conditions, the separation of a homogeneous aqueous fluid at near-solidus temperatures is followed by a decrease in P and T, which results in unmixing of H_2O- and CO_2-rich fluids (London 1990), with highly variable δD values.

Oxygen isotope compositions of beryl

The oxygen isotope composition of the framework oxygen in the samples of primary beryl was determined using the residues of the stepwise heating experiments (Table 3). The measured $\delta^{18}O$ values range from 10.0 to 10.5‰. Although an experimentally determined fractionation factor for beryl–H_2O does not exist, it is possible to obtain a first-order estimate for the value of such a fractionation by the use of the increment method

TABLE 3. OXYGEN ISOTOPE COMPOSITIONS OF BERYL RESIDUES

	DA1-2 DAGP	RED-4A TBGP	FS1-1 FSGP	FS1-2 FSGP	FS2-1 FSGP	RED-2G GLBAD	RED-10A TLGP
$\delta^{18}O$ (‰)	10.3		10.1	10.5	10.2	10.0	10.3

Note. Abbreviations are: DA = Dryden Airport occurrence, FS = Fairservice Property, TB = Taylor Beryl occurrence, TL = Tot Lake, GP = granite pegmatite, and AD = albitite dyke. All isotopic values are in per mil relative to SMOW.

of Schüetze (1980). This method has been improved and extended by Richter & Hoernes (1988), who showed that mineral–H_2O fractionations calculated by this method are generally consistent with the experimentally determined calibrations (where available). Application of this technique gives the following fractionation equation (Gawen Jenkin, pers. comm.):

$$1000\ln\alpha_{\mathrm{Brl-H_2O(250-500)}} = 1.579(10^6/T^2 - 0.645(10^3/T) - 2.522$$

which yields a value of 10.9‰ for the H_2O (melt) in equilibrium with beryl in the core zone of the rare-element granitic pegmatite on the Fairservice Property.

DISCUSSION

The generally accepted model for the petrogenesis of granitic pegmatites during the 1970s and 1980s involved pegmatite crystallization from volatile-saturated melts, in the presence of a coexisting aqueous fluid phase (Burnham 1979, Jahns 1982, Burnham & Nekvasil 1986). Recent studies using Macusani rhyolitic glass (London *et al.* 1988, 1989, London 1990), which is an excellent approximation to the bulk composition of peraluminous, Li-rich pegmatites such as those of the Dryden Field, however, have failed to produce many of the key features of rare-element pegmatites in H_2O-oversaturated experiments; yet, somewhat paradoxically, they have succeeded in replicating most aspects of pegmatite geology, including fractionation trends, mineral textures, and internal zonation, at vapor-undersaturated conditions.

Clear evidence of the action of an exsolved aqueous fluid in granitic pegmatites of the Mavis Lake Group is limited to the sporadic occurrence of narrow, fracture-controlled, B- and Li-rich alteration haloes in mafic and ultramafic wallrocks immediately adjacent to the pegmatites (*e.g.*, Taylor Beryl and Fairservice Property occurrences; Table 1); in addition, small areas of albite replacement within the pegmatites (Table 1) also may have resulted from interaction with a magmatic aqueous fluid. However, there is no compelling field or petrographic evidence to support the presence of a separate aqueous fluid phase during the bulk of pegmatite crystallization in the Mavis Lake Group, most particularly with regard to the primary, beryl-bearing units that form the focus of this study. Instead, the correlation of both the concentration and δD value of channel H_2O in primary beryl with a variety of petrological indicators of igneous fractionation in pegmatites of the Mavis Lake Group (Fig. 6) is consistent with London's (1990) model of vapor-absent crystallization for a rare-element-enriched felsic melt, with the increases in both the concentration and δD value of the channel H_2O in beryl recording an increase in the activity of H_2O and a shift to higher δD values in the melt, with increasing igneous fractionation at vapor-undersaturated conditions.

Although the magnitude of the hydrogen isotope fractionation attendant upon entrapment of H_2O molecules in the structural channels in beryl at high temperatures (>400°C) remains uncertain, we contend that the isotopic composition of the channel H_2O in primary beryl in pegmatites of the Mavis Lake Group closely resembles that of the water dissolved in the pegmatite-forming melt. In addition, we believe that the large reservoir of molecular water trapped in the structural channels in beryl is, of all of the naturally occurring sites in minerals that contain volatiles such as H_2O and CO_2, the one least likely to have been substantially affected, subsequent to entrainment, by processes such as diffusion (of H_2) or contamination. Thus, regardless of whether the primary beryl in the granitic pegmatites of the Dryden Field grew at vapor-undersaturated conditions or in the presence of a separate aqueous magmatic fluid, the H_2O trapped in the channels is likely to provide the closest approximation to the composition of the magmatic H_2O (dissolved or exsolved) present in the evolving pegmatitic system.

Up to the present, the only igneous materials that have been recognized as being suitable for the direct analysis of retained magmatic volatiles (*i.e.*, dissolved magmatic H_2O) are young, bubble-free glass or obsidian (Taylor *et al.* 1983). For the vast majority of older, holocrystalline igneous rocks, however, the hydrogen isotope composition of dissolved magmatic H_2O has been calculated indirectly from the isotopic composition of fresh igneous rock (or mineral), by applying the mineral–H_2O isotopic fractionation factors at temperatures of about 700 to 1200°C (Taylor 1974). Occasionally, more direct methods, such as the analysis of fluid inclusions in minerals from granitic pegmatites (Taylor *et al.* 1979), have been utilized. Values of δD for magmatic H_2O in the range of −30 to −90‰ are typical (Sheppard 1986, Taylor 1986).

Although the distinction between the dissolved or exsolved nature of magmatic H_2O is a problem that is intrinsic to all investigations of the fluid component of holocrystalline igneous rocks, regardless of their age, it is clear that this problem is exacerbated by the minute amounts of fluid available for analysis in individual populations of fluid inclusions, and the consequent likelihood of contamination (Roedder 1984). Whereas the exact mechanism of incorporation of H_2O in the structure of beryl still awaits experimental elucidation, the presence of large amounts of channel H_2O (*ca.* 2 wt.%), trapped at high temperature, might well provide a means for the characterization of magmatic H_2O, both in its dissolved and exsolved form, that is: (1) much less susceptible to the problems of contamination associated with other direct methods of analysis, and (2) applicable to igneous rocks of a wide variety of ages, from the Late Archean to the present.

CONCLUSIONS

(1) The stepwise heating technique permitted the differential extraction of both the channel H_2O, and H_2O from other minor sources (*e.g.*, fluid inclusions) in beryl from the granitic pegmatites of the Dryden Field (*i.e.*, Mavis Lake and Gullwing Lake - Tot Lake groups) for quantification and hydrogen isotope analysis. In all of the stepwise heating experiments, a "clean" separation of channel H_2O ($T_{REL} > 800°C$) and non-channel H_2O ($T_{REL} < 800°C$) was achieved. Channel H_2O in primary beryl from the Dryden Field typically constitutes greater than 90% of the total water content of the mineral.

(2) The concentration and isotopic composition of the channel H_2O in primary beryl from internal units of rare-element granitic pegmatites of the Mavis Lake Group vary systematically with respect to: (a) the zonal distribution of the pegmatites relative to the parent Ghost Lake Batholith, and (b) well-established petrological indicators of igneous fractionation *e.g.*, K/Rb ratio of blocky K-feldspar. Concentrations and δD values of the channel H_2O are: interior beryl zone, Dryden Airport occurrence ($K/Rb_{Kfs} = 59$), 1.76 to 1.89 wt.%, -78 to -65‰; beryl-columbite zone, Taylor Beryl occurrence ($K/Rb_{Kfs} = 36$), 1.98 wt.%, -59‰; spodumene - beryl - tantalite zone, Fairservice Property ($K/Rb_{Kfs} = 16$), 2.07 to 2.25 wt.%, -53‰. As there is no compelling field or petrographic evidence to support the presence of a separate aqueous fluid during the bulk of crystallization of the granitic pegmatite in the Mavis Lake Group, the trend of increasing concentration of H_2O in the channels and increasing δD values in primary beryl is interpreted to record an increase in the activity of H_2O and a shift to higher δD values in the felsic melt with increasing igneous fractionation at vapor-undersaturated conditions.

(3) Hydrogen isotope fractionations between coexisting muscovite and beryl (channel H_2O) yield crystallization temperatures of 470 ± 40°C for beryl - muscovite - K-feldspar - quartz - tourmaline - albite pegmatite of the Taylor Beryl Pegmatite No. 2, and 490 ± 40°C for beryl - muscovite - spodumene - tourmaline pegmatite of the No. 1 pegmatite on the Fairservice Property. This range in temperature, from 530 to 430°C, is in good agreement with that based on fields of stability of lithium aluminosilicates and fluid-inclusion studies of rare-element granitic pegmatites (London 1986a, 1990).

(4) The experimental methodology used in this study offers the potential for the direct comparison of channel H_2O in beryl, whose composition is interpreted to closely approximate that of dissolved magmatic H_2O, in pegmatites from a wide variety of ages (Late Archean to the present) and tectonic settings, and also a means by which secular variation in the terrestrial magmatic aqueous reservoir over the last 3 billion years may be documented.

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