

# Crustal melts below 400 °C

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## ABSTRACT

We propose that the internally zoned, Li-bearing Tin Mountain pegmatite in the Harney Peak granite-pegmatite system of the Black Hills, South Dakota, crystallized from fluid-rich, compositionally complex melts at ~400–350 °C. The low crystallization temperatures resulted from the combined fluxing effects of Li, B, P, H<sub>2</sub>O, and carbonate anions. The presence of hydrous silicate melts at temperatures of ~350 °C is revealed by microthermometric data on primary fluid inclusions cogenetic with crystallized-melt inclusions. Mineral assemblages of the crystallized-melt inclusions and chemistry of bulk-fluid leachates indicate that the melts and fluids contained significant amounts of Li and Na as carbonates and/or borates that acted as powerful fluxes. The low temperatures give a new perspective on the stability of silicate melts in the crust.

**Keywords:** pegmatite, solidus, lithium bearing, fluid inclusions, melt inclusions, carbonate ions.

## INTRODUCTION

Alkaline carbonates and borates are used for their fluxing properties in the manufacturing of glass, ceramics, and glazes, and in the digestion of rock samples. Li, Cs, Rb, P, and B can potentially depress the solidi of silicate liquids, as is thought to happen in granitic pegmatites (London et al., 1989; Thomas et al., 2000). But, at how low a temperature can granitic pegmatites crystallize?

In spite of more than a century of intensive research devoted to pegmatite petrogenesis, their crystallization temperatures are not well known. Numerous studies have addressed the effects of dissolved volatiles and fluxing species on liquidus and solidus temperatures, compositions of the haplogranite minima, and pegmatite magma properties (e.g., Wyllie and Tuttle, 1964; Stewart, 1978; Manning and Pichavant, 1985; Burnham and Nekvasil, 1986; Holtz et al., 1996; London, 1997). For example, experiments with LiF, LiCl, or LiOH have demonstrated significant lowering of solidus temperatures of haplogranites (e.g., Glyuk and Trufanova, 1977). However, to our knowledge, up to now there have been no experiments performed with the simultaneous addition of all relevant volatiles and fluxing components pertaining to a pegmatite system. Moreover, because the solubility of CO<sub>2</sub> in haplogranitic melts coexisting with H<sub>2</sub>O-CO<sub>2</sub> fluids is very low (Holloway and Blank, 1994), the effect of molten alkali carbonate components has not been investigated.

Microthermometry on fluid inclusions and homogenization experiments on cogenetic crystallized-melt inclusions can potentially reveal the pressure-temperature (*P-T*) conditions of crystallization. Heating experiments at 2

kbar pressure indicated reactions between crystalline phases and homogenization to a borosilicate glass and CO<sub>2</sub>-bearing fluid between 370 and 470 °C (London, 1986). Magmatic inclusions in quartz from the Tanco pegmatite revealed trapping temperatures ranging from ~720 °C to ~260 °C (Thomas et al., 1988). By using compositions of coexisting plagioclase and nonperthitic K-feldspar in a Li-bearing pegmatite-aplite layered dike, Morgan and London (1999) inferred crystallization between ~435 and 350 °C. In contrast, Anderson et al. (2001) suggested that lithium carbonate (zabuyelite) crystals within inclusions in the Tanco pegmatite and other Li-bearing pegmatites are products of subsolidus reactions between a secondary CO<sub>2</sub>-rich fluid and spodumene. Anderson et al. (2001), however, left open the possibility that primary crystal-rich inclusions in quartz may represent trapped silicate melts.

In this paper we use several lines of evidence to show that the Li-bearing Tin Mountain pegmatite, Black Hills, South Dakota, crystallized at temperatures below 400 °C from a hydrous silicate melt because of the fluxing effects of lithium carbonate and other melt species that dramatically depressed its solidus.

## LOCATION AND TECHNIQUES

The Tin Mountain pegmatite is located in the Precambrian core of the Black Hills of South Dakota, within the aureole of the 1715 Ma Harney Peak leucogranite (Norton and Redden, 1990). The pegmatites intruded a sequence of metapelites and metagraywackes at the culmination of the Trans-Hudson orogeny (Redden et al., 1990). The granite and pegmatites are not metamorphosed and show little signs of deformation.

The Tin Mountain pegmatite is a large, mineralogically and texturally zoned LCT-

type (Li-Cs-Ta; Černý, 1993) pegmatite. It is an ~200 × 20 × 30 m, L-shaped intrusion, consisting of a border zone, a wall zone, three intermediate zones, and a core (Staatz et al., 1963; Norton, 1994; Walker et al., 1986). It intruded quartz-mica schists and amphibolites previously metamorphosed to sillimanite grade.

Microthermometry was performed on two quartz samples of an equigranular, coarse-grained assemblage of quartz + cleavelandite + muscovite from the wall zone and three samples of massive quartz from the core (details in Sirbescu and Nabelek, 2003a). Solid phases in the inclusions were identified by their optical properties, crystal habits, X-ray energy spectra, and Raman spectra.

Chemical analyses were carried out on inclusions leached from 20 crushed samples. The leachates were analyzed by ion chromatography (IC) for anions and inductively coupled plasma-atomic emission spectroscopy (ICP) for cations. Leachate compositions are reported as ratios (Table DR1<sup>1</sup>). The leachates may have included water-soluble solids present in the inclusions. Cl<sup>-</sup>, F<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and SO<sub>4</sub><sup>2-</sup> were analyzed with a reproducibility of ±10%. CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were not determined. B, Ba, Ca, Fe, K, Li, Mg, Mn, Na, S, and Sr analysis by ICP has a reproducibility of <5%.

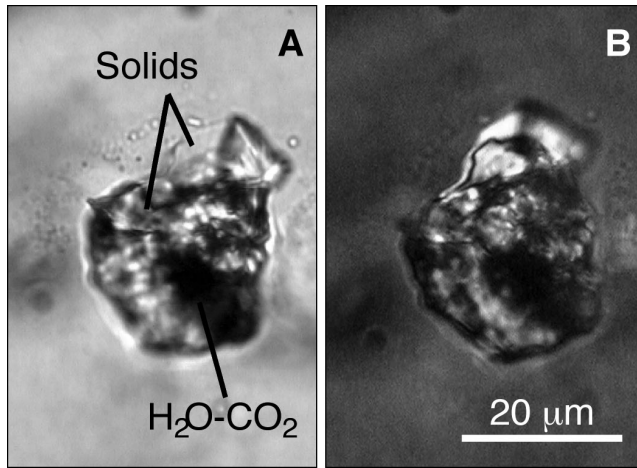
## INCLUSION PETROGRAPHY

Primary mixed H<sub>2</sub>O-CO<sub>2</sub> fluid inclusions coexist with primary crystal-rich inclusions in all Tin Mountain zones, although the latter account for <1% of the total primary inclusion assemblage. The crystal-rich inclusions are interpreted to represent a part of the complex silicate-rich melt from which the magmatic quartz crystallized. The fluid inclusions represent the fluid phases that exsolved during crystallization. The crystal-rich inclusions have volume ratios of crystals to fluid of >50% (Fig. 1). These multigrain, transparent to semiopaque inclusions are usually round (~10–50 μm) and are similar to crystallized-melt inclusions described in other granites and pegmatites worldwide (A. Thomas et al., 1988; Frezzotti, 1992; R. Thomas et al., 2000). Silicates muscovite ± kaolinite are pre-

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<sup>1</sup>GSA Data Repository item 2003098, Appendix 1, fluid inclusion leachate analyses, and Appendix 2, average microthermometric data for H<sub>2</sub>O-CO<sub>2</sub>-CH<sub>4</sub>-NaCl inclusions from Tin Mountain pegmatite, is available from Documents Secretary, GSA, P.O. Box 9140, Boulder CO 80301-9140, editing@geosociety.org or at www.geosociety.org/pubs/ft2003.htm.

**Figure 1. Crystallized-melt inclusion in quartz from core of Tin Mountain pegmatite. Inclusion contains assemblage of unidentified anisotropic grains and mixed CO<sub>2</sub>-H<sub>2</sub>O fluid. A: Plane-polarized light. B: Cross-polarized light. Note decrepitation halo of minute fluid inclusions around crystallized-melt inclusion.**



dominant in all crystallized-melt inclusions. Dawsonite—NaAl(CO<sub>3</sub>)(OH)<sub>2</sub>—is common in both crystallized-melt and fluid inclusions in quartz from the pegmatite core (Sirbescu and Nabelek, 2003b).

Primary fluid inclusions are H<sub>2</sub>O-CO<sub>2</sub> fluids of low salinities consisting of two or three fluid phases in variable proportions at room temperature and to 10 vol% of solids. These inclusions occur in three-dimensional, lattice-oriented arrays or have preferential orientations along crystal-growth zones. Two types occur in a given assemblage: type L (which homogenized to liquid upon heating) with a mean volume fraction of CO<sub>2</sub>/(H<sub>2</sub>O + CO<sub>2</sub>) of 0.24, and type V (which homogenized to vapor upon heating) with a mean ratio of 0.72 (Fig. 2). The primary H<sub>2</sub>O-CO<sub>2</sub> inclusions make up from 0 to 90% of the total fluid inclusions. Fluid from some primary inclusions was locally redistributed in decrepitation haloes (Fig. 1A). Furthermore, secondary aqueous and nearly pure CO<sub>2</sub> inclusions occur in trails that cut mineral growth zones and contacts. These are thought to represent magmatic fluid that fully unmixed at subsolidus conditions (Nabelek and Ternes, 1997). However, only samples that were dominated by primary fluid inclusions were analyzed for bulk chemistry by crush leaching.

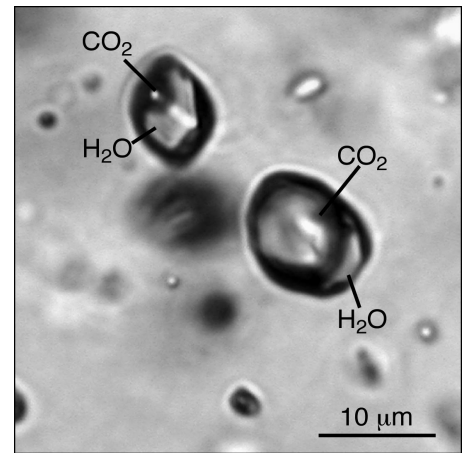
#### LINES OF EVIDENCE FOR LOW CRYSTALLIZATION TEMPERATURES

Microthermometric data on the L- and V-type fluid inclusions, the textural evidence for their simultaneous trapping, and the consistency of CO<sub>2</sub>-H<sub>2</sub>O-NaCl-CH<sub>4</sub> component partitioning between the two types (Sirbescu and Nabelek, 2003a) demonstrate coexistence of two immiscible fluids: a CO<sub>2</sub>-rich, low-density phase and an H<sub>2</sub>O-rich, high-density phase. The data (Table DR2; see footnote 1) define a solvus on a  $T_h$  vs.  $V$  plot (Fig. 3) as a projection of a  $P_h$ - $T_h$ - $V$  phase boundary, where  $T_h$  is the homogenization temperature,  $P_h$  is the implied homogenization pressure, and  $V$  is the

molar volume. Trapping along the liquid-vapor phase boundary implies that the  $T_h$  values are equal to the trapping temperatures, on average 340 °C (44 cogenetic inclusions, standard error of  $\pm 39$  °C). Because the liquid-vapor boundary is univariant in  $P$ - $T$  space, the trapping temperature defines the trapping pressure as  $2.7 \pm 0.3$  kbar. There are no significant differences between the  $P$  and  $T$  conditions at which the inclusions in the wall zone and the core were trapped in the quartz crystallizing from the magma.

To our knowledge, no tartan twinning occurs in K-feldspar in the Tin Mountain pegmatite (Staatz et al., 1963). The lack of such twinning is consistent with crystallization temperatures below  $\sim 450$ – $500$  °C, the minimum temperature of the monoclinic-to-triclinic inversion in K-feldspar (Brown and Parsons, 1989). We applied the ternary-feldspar thermometer of Elkins and Grove (1990) to compositions of coexisting Tin Mountain plagioclase and K-feldspar reported by Walker et al. (1986) and obtained exchange-equilibrium temperatures of  $\sim 350 \pm 57$  °C at a pressure of 2.7 kbar, in excellent agreement with the microthermometric data, although a late compositional reequilibration of the feldspars cannot be discarded. In addition, our preliminary data suggest that the K-feldspar is nonperthitic. Instead, it contains inclusions of euhedral plagioclase. This is consistent with a subsolvus, simultaneous crystallization of K-feldspar and plagioclase.

Quartz-feldspar-muscovite  $\delta^{18}O$  data for three samples reported by Walker et al. (1986) indicated equilibration temperatures between 580 and 500 °C. In the remaining 20 samples the minerals did not define an equilibrium relationship. The  $>500$  °C temperatures indicated by the isotopes may be only apparent, because rapidly crystallized minerals may preserve the isotopic composition of the melt and not completely equilibrate at the crystallization temperature. However, oxygen isotope ra-

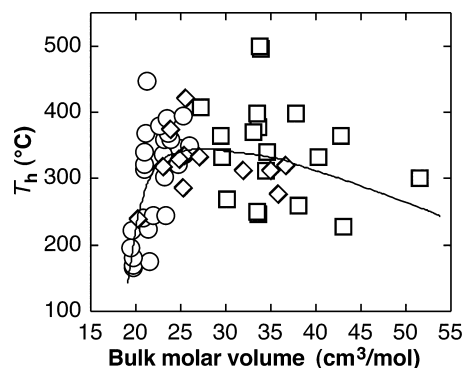


**Figure 2. Pair of cogenetic primary inclusions of types L (left) and V (right).**

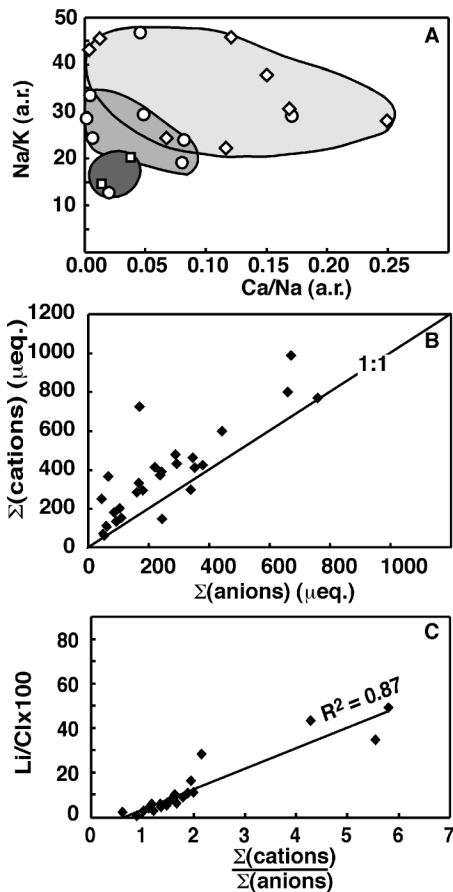
tios in coexisting quartz and K-feldspar in cores of several simple pegmatites in the Black Hills indicated temperatures of  $\sim 350$  °C (Nabelek et al., 1992).

#### FLUID CHEMISTRY

The Tin Mountain magmatic fluids are essentially binary CO<sub>2</sub>-(H<sub>2</sub>O-4.3 wt% NaCl<sub>eq</sub>) fluids. However, daughter minerals such as dawsonite, nahcolite, and tentatively identified sassolite (H<sub>3</sub>BO<sub>3</sub>) indicate high alkalinity and B concentrations in the fluid. The integrated ICP-IC analyses confirm high levels of Li and B and, less reliably, of P, Rb, and Cs (Table DR1; see footnote one). The Tin Mountain zones have variable Na/K atomic ratios (a.r.), mostly between 10 and 45 (Fig. 4A), with the highest values in the core. An aqueous fluid in equilibrium with a peraluminous leucogranitic melt at 800 °C (e.g., Gangotri Granite, High Himalaya, experiments of Scaillet et al., 1995) should have a Na/K a.r. of  $\sim 2$  and Ca/Na of  $\sim 0.01$  (distribution coefficients from Holland, 1972;  $m_{Cl} = 1$ ). The observed de-



**Figure 3. Plot of homogenization temperature  $T_h$  vs. bulk molar volume of CO<sub>2</sub>-(H<sub>2</sub>O-4.3 wt% NaCl<sub>eq</sub>) inclusions. Distribution and homogenization behavior of data points is consistent with trapping along solvus curve; squares—type V inclusions; circles—type L inclusions; diamonds—inclusions with critical behavior.**



**Figure 4. A: Major cation ratios in bulk-fluid leachates in Tin Mountain zones; a.r.—atomic ratios. Squares—wall zone; circles—undifferentiated intermediate zones; diamonds—core. B: Charge balance in bulk-fluid leachates; B as  $B(OH)_3$ . Departure from neutral solution is attributed to omission of carbonate ions from ion chromatography analysis. C: Plot of Li/Cl ratios vs. ratio between cations and anions; B as  $B(OH)_3$ . Regression line suggests that Li ligands in magmatic fluid were carbonate ions.**

departure of Na/K ratios in the Tin Mountain pegmatite from the calculated or experimentally determined equilibrium fluid + mineral  $\pm$  melt partitioning (Orville, 1963) is attributed to significant amounts of carbonate anions in the aqueous fluid, which prefer the lighter alkalis (Iiyama, 1965; Channer et al., 1999). The increase in the Na/K ratio toward the core may relate to the carbonate/bicarbonate content of the melt because inclusions in samples with the most frequent carbonate daughter minerals have the highest Na/K ratios.

We assume that the main species that control the pH of the leachates are carbonate/bicarbonate and B species, as weak acids. Concentrations of B in the leachate solutions are high [average a.r.  $B(OH)_4^-/Cl^-$  in 19 samples is 0.14, with the highest value of 0.67 occurring in one core sample]. We attribute the negative-charge deficit shown in Figure 4B mainly to the omission of carbonate/bicarbon-

ate ions from the integrated IC-ICP analysis. There is a good correlation between the Li/Cl ratios and the charge imbalance (Fig. 4C) that does not change significantly even if all B is assumed to be  $BO_3^{3-}$  instead of neutral boric acid  $B(OH)_3$ . There is also a very good correlation between Li and B values, suggesting that any Li- and B-containing fluids or minerals within quartz crystals are completely dissolved during crush leaching. A progressive enrichment of alkali carbonate  $\pm$  borate component in the melt from the wall zone toward the core, whether reflected by composition of the bulk fluid alone or together with soluble daughter minerals, suggests sequential crystallization of the pegmatite.

## DISCUSSION

We suggest that the fluid compositional trends reported in this paper and the macroscopic and cryptic mineral zoning of the Tin Mountain pegmatite (Spilde and Shearer, 1992) reflect sequential, disequilibrium crystallization (London et al., 1989) at a temperature below 400 °C. In addition to lowering the crystallization temperatures and solidi, fluxing elements lead to a decrease in viscosity and nucleation rates and a significant increase in the crystallization rate, as has been shown to occur when  $a_{H_2O}$  in magmas becomes high (Fenn, 1977). Rapid crystallization of the Tin Mountain melt is supported by the constancy of quartz crystallization temperatures in the wall zone and the core, by mineral zoning (Spilde and Shearer, 1992), and by the spherulitic shapes of micas and phosphates (Staatz et al., 1963).

The Tin Mountain pegmatite crystallized  $\sim 10$  m.y. after the consolidation of the main Harney Peak granite pluton (Krogstad and Walker, 1994). The granite was intruded at  $\sim 3.5$  kbar (Helms and Labotka, 1991), a pressure  $\sim 0.8$  kbar higher than for the Tin Mountain pegmatite. This translates to a reasonable unroofing rate of  $\sim 0.3$  mm/yr for this part of the Trans-Hudson orogen, consistent with numerical simulations (Nabelek et al., 2001). The estimated temperature of the country rock at the time of Tin Mountain melt intrusion was  $\sim 300$  °C. Because the temperature of the Tin Mountain pegmatite was only slightly higher, it could not impose a significant thermal contact aureole.

The Tin Mountain melt contained high concentrations of Li, Cs, Rb, B, P, and  $H_2O$ . Thomas et al. (2000) showed the existence of similar silicate melts with at least 30 wt%  $SiO_2$  and  $<45$  wt%  $H_2O$  at 500 °C and 1 kbar, in rehomogenized crystallized-melt inclusions from a central Erzgebirge pegmatite, Germany. Together with our results, this study indicates that highly fluxed silicate melts can exist in the crust at temperatures far below the normal granite solidus, overlapping with temperatures

characteristic of hydrothermal processes, low-grade metamorphism, and high-temperature diagenesis. The volatile-rich melts have densities and viscosities comparable to an aqueous fluid (Thomas et al., 2000), and thus are more mobile than the regular silicate melts.

The Tin Mountain crystallized-melt inclusions texturally resemble colloidal silica inclusions ( $>90\%$   $SiO_2$ ) produced in the system  $K_2O-CO_2-H_2O-SiO_2$  at  $T > 300$  °C and  $P = 1$  kbar (Wilkinson et al., 1996) and described in greisen topaz (Williamson et al., 1997). The “silicothermal” fluid (Wilkinson et al., 1996) coexisted immiscibly with a  $KHCO_3-CO_2-H_2O$  fluid, suggesting that the alkali carbonate may have enhanced the  $H_2O-SiO_2$  coupling in the K-Si-rich fluid, although the exact formation mechanism and the structure of the silica-rich phase was not explained.

The controversial  $CO_2$ -promoted melting of crustal rocks was proven unfounded (Clemens, 1993; Clemens et al., 1997). However, recent infrared spectroscopic studies of  $CO_2$  speciation in aluminosilicate melts support our contention that carbonate anions are significant species in certain depolymerized melts, and therefore may contribute to lowering their crystallization temperatures. Nowak et al. (2003) showed that carbonate content of Fe-free dacite glasses increased with decreasing temperature, from 1330 to 500 °C. Taylor (1990) observed dawsonite-like infrared peaks in glass, indicating that  $CO_2$  can dissolve as a Na-Al carbonate. Although Taylor (1990) used silica-undersaturated compositions, the occurrence of dawsonite in the Tin Mountain crystallized-melt inclusions indicates that the melt contained dissolved alkali carbonates.

Whether formed through immiscibility from a parent leucogranitic melt (Thomas et al., 2000) or through local, partial melting of fluxed country rocks, the extremely mobile hydrous silicate melts of low densities and viscosities may extract incompatible elements from percolated rocks (Thomas et al., 2000) at relatively low temperatures. Therefore, they may play an effective role in mass transfer and crustal differentiation processes, leading to the occurrence of migmatites, various quartz-bearing veins, and, ultimately, to pegmatites. Further investigations of the low-temperature fluxed melts may lead to a better understanding of controversial features of some rare-element pegmatite fields currently unexplained by classic fractional-crystallization models linking pegmatites to a parental granite (e.g., Černý, 1993), such as their extreme compositional diversity and lack of geochemical zoning around the central pluton.

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