Dawsonite: An inclusion mineral in quartz from the Tin Mountain pegmatite, Black Hills, South Dakota

MONA-LIZA C. SIRBESCU1,* AND PETER I. NABELEK2

1Department of Geology, Central Michigan University, Mt. Pleasant, Michigan 48859, U.S.A.
2Department of Geological Sciences, University of Missouri–Columbia, Columbia, Missouri 65211, U.S.A.

ABSTRACT

Dawsonite —NaAl(CO₃)(OH)₂—was identified in primary fluid inclusions in quartz from the Li-rich Tin Mountain pegmatite, Black Hills, South Dakota, by petrography, SEM-EDS analysis, and Raman spectroscopy. This is the first report of dawsonite as an inclusion mineral in a pegmatite. The presence of dawsonite in the inclusions is evidence for the existence of carbonate ions in the complex pegmatite melt and/or exsolved magmatic fluid. The lack of dawsonite as a macroscopic mineral is attributed to its high solubility in the late pegmatite fluids and to the small fraction of carbonate ions in the melt. However, its common occurrence, along with other carbonate and borate minerals in fluid inclusions, suggests that carbonate and borate complexes play an important role in petrogenesis of pegmatites.

INTRODUCTION

Dawsonite, NaAl(CO₃)(OH)₂, named in 1874 after J.W. Dawson (1820–1899), a Canadian geologist, is usually a low-temperature, hydrothermal, diagenetic or authigenic mineral that forms by decomposition of aluminum silicates in the presence of carbonate/bicarbonate-rich solutions. The mineral is of some interest as a potential source of Al and in the pharmaceutical industry as an antacid. The structure of dawsonite is orthorhombic-disphenoidal (space group Imam), consisting of distorted AlO₄(OH)₄ and NaO₄(OH)₂ octahedra and CO₃ groups (Corazza et al. 1977). Vibration-frequency modes of infrared and Raman spectra were reported by Serna et al. (1985). Dawsonite typically occurs in colorless to white rosettes or spherules and Raman spectra were reported by Serna et al. (1985). Dawsonite occurs in: (1) hydrothermal products of weathering of igneous rocks; (2) sedimentary rocks derived from volcanics or affected by CO₂-rich ± alkaline, thermal solutions; and (3) a wide variety of sedimentary rocks with no direct relationship with igneous rocks (summary in Stankevich and Batalin 1976; Corazza et al. 1977; Baker et al. 1995). Dawsonite is affiliated with various types of magmatism, including alkaline (i.e., Monterregian alkaline intrusions, Canada), felsic (ryholitic ignimbrites, Bolzano, Italy), mafic (basalts, Sollingen, Germany), and ultramafic (chromian dawsonite, serpentinitite, Franciscan Complex, California; Dunning 2000).

Coveney and Kelly (1971, XRD study) and Metzger et al. (1977, SEM-EDS study) described dawsonite as an abundant daughter product in fluid inclusions in gold-quartz veins of the Oriental mine, Alleghany district, California, and interpreted it as either an equilibrium phase in the system sodic plagioclase–quartz–sodium bicarbonate-brine, or a metastable phase in the same system.

Dawsonite was synthesized from sodium carbonate/bicarbonate solutions in Al-rich environments at room temperature (Chesworth 1971; Furmakova 1981 and references therein). Optimum conditions of autoclave synthesis were: T = 175–200 °C, P CO₂ = 1.035 bars, and a high Na/Al atomic ratio (~43, Jackson et al. 1972). At atmospheric pressure, dawsonite dissolves incongruently in water to produce gibbsite (Furmakova 1981) and decomposes thermally at ~300 °C to release CO₂ (Huggins and Green 1973). The thermodynamic data for synthetic dawsonite and parameters of decomposition reactions up to 400 °C, at atmospheric pressure, were tabulated by Ferrante et al. (1976). To our knowledge, there are no published studies concerning dawsonite stability at elevated pressures. We identified dawsonite during a petrographic and SEM-EDS survey of fluid and crystallized melt inclusions in the Harney Peak Granite (HPG) and associated pegmatites in the Black Hills. Its presence as an inclusion mineral within fluid inclusions in quartz from the Tin Mountain (TM) pegmatite was confirmed by laser Raman microprobe spectroscopy (LRMS).

OCCURRENCE

The TM pegmatite is an extensively studied, zoned, Li-rich pegmatite, located ~12 km southwest of the main pluton of the 1,715 Ma HPG, near the outer boundary of the pegmatite aureole (Norton and Redden 1990). It consists of a continuous, 1 to 10 m thick wall zone (albite-quartz-mica) with a very thin outer border zone, and four discontinuous, inner zones that are vertically stacked rather than concentric. The succession of zones, from top to bottom, is: 1st intermediate zone (perthite-quartz-
albite–muscovite), 2nd intermediate zone (perthite ~90% = quartz–albite), and 3rd intermediate zone (albite–quartz–spodumene). The core (quartz–spodumene–muscovite) is sandwiched between the 2nd and 3rd zones. A small fracture-filling unit that has the same mineral assemblage as the core cuts through the intermediate and wall zones. Locally, the spodumene crystals are rimmed by a replacement assemblage of lepidolite ± cookeite ± cleavelandite + quartz (Walker et al. 1986). Tourmaline and zircon are rare accessories. At least 35 other minerals have been found in trace amounts: Li, Fe, and Mn phosphates; U, Pb–U, or Ca–U oxides, silicates, or phosphates; Cu sulfides, etc. (Broughton 1972; Campbell and Roberts 1985). Trace amounts of carbonates azurite, malachite, smithsonite, and auralchalcite appear together with Cu sulfides and sphalerite in vugs from large montebrasite crystals. Fine crystals of calcite were found sparingly with cleavelandite and cassiterite in a fracture filling (Smith and Roberts 1964).

Dawsonite was identified in two, clear to cloudy-gray quartz samples that are part of the massive core, and are in an assemblage with coarse ~0.1–2 m long spodumene crystals, and rounded to subhedral, ~0.5 m ambygloi–montebrasite crystals. Several crystal inclusions with similar optical properties (but not confirmed by LRMS) were found in nine other quartz samples from the wall zone, the 1st intermediate zone, and the core. Dawsonite occurs in both fluid inclusions and crystallized melt inclusions, in assemblages with mica, Ca sulfate, smithsonite, and sphalerite in vugs from large montebrasite crystals. Fine crystals of calcite were found sparingly with cleavelandite and cassiterite in a fracture filling (Smith and Roberts 1964).

Dawsonite appears to be associated mostly with the primary CO2–rich inclusions (Fig. 1a) or with a complex melt that formed crystal-rich inclusions with <20% CO2–H2O fluid (Fig. 1b). The primary character of inclusions that contain the birefringent crystals is not always clear. However, secondary re-distribution of fluid, if any, appears to have occurred only along short trails (typically <100 μm) or in <30 μm decrепitation aureoles around large inclusions. Thus, the system appears to have remained closed at the scale of the pegmatitic quartz crystals (tens of centimeters).

Dawsonite crystals are short prismatic (Fig. 1a), rhombic or pseudocubic (Figs. 1b, and 2a–b) rather than hair-like, which is its typical appearance in inclusions in hydrothermal quartz (Coveney and Kelly 1971). Crystal size ranges from ~3 to 50 μm. In cross-polarized light, crystals larger than ~3 μm show bright interference colors (Figs. 1a–b, and 2a). Colored interference rings are typical of larger crystals. In plane-polarized light, there is an obvious variation in the refractive index, consistent with the high birefringence of 0.127.

The Raman vibrational frequencies of two inclusion crystals are virtually identical to our dawsonite reference material (Fig. 3). The excellent match between these spectra and those collected by Serna et al. (1985) on synthetic dawsonite further confirms that the inclusion mineral has the structure of dawsonite (Table 1). In addition, the EDS spectra of the inclusion mineral and of the dawsonite reference material are very similar (Fig. 4). Spectra of several other crystals had the same Na:Al peak ratio, within 10%, and did not contain other elements heavier than 5%. The concentration of carbonate ions was inferred from charge-balance calculations.

The inclusion systematics and microthermometric results were reported in detail by Sirbescu and Nabelek (2003), thus only a brief summary is given here. The average composition of the magmatic fluids falls within the CO2–(H2O–4.3 wt% NaCl) binary. The fluid inclusions are intimately associated with crystal-rich inclusions interpreted to be crystallized melt. The melt inclusions consist of at least 50% solids with the remaining volume occupied by CO2 or H2O–CO2 fluid. The primary character of the H2O–CO2 inclusions was established from their distribution in three-dimensional, lattice-oriented arrays, and, in some cases, preferential orientation along crystal growth zones. In contrast, late, secondary inclusions were distinguished by their occurrence along distinctive healed fractures, generally crossing crystal grain boundaries.

There are two populations of primary fluid inclusions of contrasting CO2/(CO2 + H2O) volume ratios (at 25 °C) and homogenization behavior showing evidence of trapping under conditions of immiscibility between an H2O-rich phase and a CO2-rich phase. The two populations pass the three main criteria of fluid immiscibility listed by Ramboz et al. (1982): (1) occurrence in the same inclusion assemblage; (2) the low-density inclusions have an average CO2/(CO2 + H2O) = 0.72 ± 0.1 and homogenize to the vapor phase, whereas the high-density inclusions have an average CO2/(CO2 + H2O) = 0.24 ± 0.1 and homogenize to the liquid phase; and (3) the homogenization temperatures of 340 ± 40 °C (N = 46) and calculated homogenization pressures of 2.7 ± 0.8 kbar overlap for the two populations of primary inclusions. Trapping under conditions of immiscibility implies that the homogenization temperature equals the trapping temperature. The unusual depression of the pegmatite solidus to ~340 °C is due to the combined effect of various fluxes, including the Na and Li carbonates (see Sirbescu and Nabelek 2003).
than F, except for small amounts of Si, probably contributed by the host quartz. The bulk fluids extracted from TM quartz samples in which dawsonite was identified are complex Na, Cl, bicarbonate solutions with significant concentrations of boric acid [B(OH)$_4$/$\text{Cl}^-$ ionic ratios of 0.05 to 0.44], Li (Li/Cl ratios of 0.11 to 0.49), and other alkaline metals (crush-leach analysis of quartz; Sirbescu 2002). Of twenty TM samples analyzed, sample 131-4c has the highest concentration of carbonate ions (ratio of carbonate/Cl$^-$ = 4.4; the average ratio in TM samples is 1.0), which correlates with the highest frequency of strongly birefringent daughter minerals inferred to be dawsonite. Because the mineral has a high solubility in water, we expect that at least some of the dawsonite crystals dissolved into the leach solution. Values of the atomic ratio of Na/K of samples 131-4b and 131-4c are 24.0 and 45.2, respectively. These values are indeed significantly higher than experimental and calculated fluids in equilibrium with similar granitic systems (Orville 1963; Hemley 1968; Scaillet et al. 1995). The elevated values can be attributed to the large concentrations of carbonate anions in the aqueous fluid, as Na complexes preferentially over K with carbonate anions (Iiyama 1965). This inference is consistent with results of IC analysis of leachate solution, which indicated high concentrations of carbonate ions in the leachates.

**FIGURE 1.** Dawsonite in quartz (no. 131-4b) from the core of Tin Mountain pegmatite. (a) Dawsonite (Raman spectrum in Fig. 3) in a primary CO$_2$-rich inclusion. (b) Dawsonite (unconfirmed) in a crystallized melt inclusion with several unidentified solids and ~5% CO$_2$-H$_2$O fluid. Left = plane-polarized light; right = cross-polarized light.

**FIGURE 2.** Dawsonite in a decrepitated primary inclusion in quartz sample (no. 131-4c). The inclusion also contains muscovite and contained ~15% CO$_2$-H$_2$O fluid prior to opening. (a) Cross-polarized light and (b) Back-scattered electron image. The back-scattered image is slightly enlarged and rotated.

**DISCUSSION**

The irregular distribution of dawsonite within the primary inclusion assemblage and its protruding appearance in some inclusions suggests that it formed as a primary solid, accidentally trapped by the exsolving fluid, rather than a daughter mineral, precipitated from the inclusion fluid. If the dawsonite is of primary origin, it coexisted with the immiscible fluids and melt during growth of the host crystal at $T$ of ~340 °C and $P$ of ~2.7 kbar (Sirbescu and Nabelek 2003). Although dawsonite solubility at elevated pressures is unknown, it is conceivable that high alkalinity and $P_{\text{CO}_2}$ promote high activity of dawsonite component in the pegmatitic melt. Unmixing of a fluid into H$_2$O-rich and CO$_2$-rich phases and a reduction of partial $P_{\text{CO}_2}$ are known to reduce carbonate solubility to precipitate carbonates. Dawsonite crystals did not dissolve during heating of inclusions up to ~430 °C (Coveney and Kelly 1971; this study). This finding suggests that dawsonite crystallization was promoted by fluid immiscibility instead of decreasing temperature.

Whether an accidentally trapped or a daughter mineral, dawsonite was found in primary inclusion assemblages trapped at $T$ of ~340 °C and $P$ of ~2.7 kbar (Sirbescu and Nabelek 2003). Therefore, a low-temperature origin, for instance, interaction of a percolating, bicarbonate-containing groundwater with albite or other Al minerals, can be dismissed. Thus, the occur-
rence of dawsonite in quartz must reflect the primary fluid chemistry. In the bulk primary inclusions, carbonate, bicarbonate, and borate ions are the essential non-conservative anions (Sirbescu 2002). Thus, these species define the total alkalinity of the TM magmatic fluid.

Carbonate and borate minerals (borosilicates excluded) are typically not found in peraluminous pegmatites and leucogranites. The main B-bearing mineral in the TM pegmatite is tourmaline, which occurs only in minor amounts, confined to a hydrothermal vein-filling from the core. Tourmaline also occurs in the surrounding schist. However, carbonates and borates can be abundant in Li-rich pegmatites as primary inclusion minerals. Dawsonite (this study) and sassolite (H₂BO₃; Peretyazhko et al. 2000 and references therein; Thomas 2002; this study, as yet not confirmed) were found as widespread primary or daughter minerals in magmatic quartz. Therefore, these minerals represent important species in the pegmatite melts, where they acted as fluxes in lowering the temperature of crystallization (Sirbescu 2002). Among other inclusion minerals identified in pegmatites are nahcolite = NaHCO₃, borax = Na₂B₂O₅(OH)₄·8H₂O, teepleite = Na₂B(OH)₄Cl, and avogadrite = (K,Cs)BF₄ (Russian literature cited in Roedder 1984).

Zabuyelite (Li₂CO₃; Anderson et al. 2001) included in spo-

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* Spectrum of host quartz crystal was subtracted.
† Sample from Eklutna Tunnel, Anchorage, AK.
‡ From Serna et al. (1985).

**FIGURE 3.** (a) Raman spectrum of inclusion dawsonite shown in Figure 1a. (b) Raman spectrum of dawsonite reference material.

**FIGURE 4.** (a) The X-ray EDS spectrum of inclusion dawsonite shown in Figure 2. (b) The EDS spectrum of reference dawsonite.
alkaline species in the metamorphic-granite-pegmatite system. Maline in the TM pegmatite are consistent with the presence of granite-derived fluids. Instability of tourmaline in the high-alkaline metapelitic rocks, under the influence of alkali-rich, tourmaline-related perhaps to their origin as partial melts in carbon-peraluminous pegmatites, or an ab initio compositional signature related perhaps to their origin as partial melts in carbonaceous metapelitic rocks, under the influence of alkali-rich, granite-derived fluids. Instability of tourmaline in the high-grade metamorphic aureole of the HPG and the scarcity of tourmaline in the TM pegmatite are consistent with the presence of alkaline species in the metamorphic-granite-pegmatite system (cf., Morgan VI and London 1989; Wilke et al. 2002).

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REFERENCES CITED


Thomas, A.W., Bray, C.J., and Spooner, E.T.C. (1988) A discussion of the Jahns-Dumene or other pegmatitic minerals, quartz is not susceptible to reaction with an inclusion fluid at subsolidus conditions; and (2) the massive quartz samples containing dawsonite appear to have remained closed to secondary fluid flow.

Primary inclusions in the HPG and its pegmatites revealed that CO2 was abundant in the magmatic fluid (Nabelek and Ternes 1997; Sirbescu and Nabelek 2003). Fluid inclusion leachates extracted from TM quartz have the highest Na/K ratios when compared with other simple and complex pegmatites in the HPG aureole (Sirbescu and Nabelek 2000). The Na/K ratio progressively increased from the wall zone toward the core, together with increasing Li, B, carbonate ions, and large-ion lithophile elements (Sirbescu 2002), with maximum values in dawsonite-bearing samples. The high alkalinity of complex pegmatitic melts and their exolved fluids appears to be either a normal trend in the evolution of some Li-rich peraluminous pegmatites, or an ab initio compositional signature related perhaps to their origin as partial melts in carbonaceous metapelitic rocks, under the influence of alkali-rich, granite-derived fluids. Instability of tourmaline in the high-grade metamorphic aureole of the HPG and the scarcity of tourmaline in the TM pegmatite are consistent with the presence of alkaline species in the metamorphic-granite-pegmatite system (cf., Morgan VI and London 1989; Wilke et al. 2002).

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