Evidence of a water-rich silica gel state during the formation of a simple pegmatite

R. Thomas[1],* and P. Davidson[2]

[1] German Research Centre for Geosciences GFZ, Telegrafenberg D320, Potsdam, Brandenburg D-14473, Germany
[2] ARC Centre of Excellence in Ore Deposits, University of Tasmania, Tasmania, Australia

ABSTRACT

This study reports the discovery of inclusions, which are inferred to represent trapped primary silicate gels, in simple pegmatites genetically connected to the Precambrian Rønne granite of Bornholm Island, Denmark. These inclusions are randomly associated with more typical melt and alkali-carbonate-rich and bicarbonate-rich fluid inclusions. Their relationship to the latter and to the formation of the pegmatite bodies is discussed. The silicate gel inclusions become increasingly common towards the quartz cores of the pegmatites, and are considered to demonstrate increasing water and alkali carbonate concentrations in the pegmatite-forming liquid, and an accompanying tendency for sol/gel formation. This discovery may have important implications for the formation of the quartz cores of pegmatites. The possible origin of the alkali-carbonate concentrations in pegmatite-forming fluids is also briefly discussed.

Introduction

Previous studies have noted that there is a compositional gap between silicate melts with H_2O concentrations of <10 wt.% and hydro-thermal fluids with H_2O concentrations >90 wt.%. Experimental work (Veksler and Thomas, 2002; Smirnov *et al*., 2012) suggests that this compositional space is represented by a continuum of water- and silica-rich phases ranging from very volatile-rich melts, through hydro-colloid suspensions, to very dense hydrothermal fluids. The importance of such colloidal systems is being increasingly recognized. They occur in two basic forms: sols are colloidal systems in which solid particles with dimensions from ~1 nm to 1 μm are dispersed in a liquid medium; and gels are systems in which the colloidal particles form a coherent cross-linked structure that is inter-penetrated by a liquid (Frondel, 1962 and references therein; Large, 1969; Dörfler, 2002). In this paper we discuss hydro-colloids, which are defined as colloidal systems in which the colloid particles, principally SiO_2, are dispersed in water.

With the exception of suggestions by Merritt (1923), Brotzen (1959), Taylor (2005, 2006) and Williamson *et al*. (2002), the possibility that hydrogel might be a transport medium in the formation of pegmatites has been essentially ignored. However, the transport of the silicate component as a hydrogel can be extremely efficient (Dörfler, 2002). The occurrence of gels and sols as important mineral-forming media in nature is well established, as for example in low temperature processes in dispersed clays. However, the recent observation that truly colloidal systems can survive without coagulation in inclusions for more than 100 Ma is surprising (Prokofiev *et al*., 2008).

Hydrothermal diamond anvil cell (HDAC) experiments (Veksler and Thomas, 2002;

Thomas *et al.*, 2006, 2011*b*) have shown that a silicate-gel state can occur in water-rich synthetic fluid systems similar in composition to the primary melt inclusions with type-B characteristics (water-rich peralkaline melts) found in many pegmatites, at relatively high temperatures of 450ºC (Thomas *et al.*, 2011*b*: fig 9g). These experiments also show that phase changes, for example coagulation, can be very abrupt over small temperature ranges (see also Large, 1969). Given the experimental evidence for the existence of silica gels and volatile-rich silicate melt inclusions in graphic pegmatites we can reasonably assume that both may coexist at temperatures at or above 600ºC.

Recently, Smirnov *et al.* (2012) published a study which addressed an intermediate composition, with approximately equimolar H_2O and SiO_2. They showed that at Na_2O concentrations >2 wt.% a water- and a silica-rich phase, referred to as a hydrosilicate liquid (HSL), with colloidal properties, developed from water- and alkali-rich silicate melts at ~600ºC and remained relatively stable to low temperatures. The quantity of HSL produced was proportional to the Na_2O concentration, and was unaffected by either NaCl or HF contents. The HSL was shown to be capable of dissolving high but unquantified amounts of Ta, and by inference may be important in the transport of other elements.

In recent years there has been a revival of the idea that pegmatites can be formed via crystallization from hydrous silicate gels (e.g. Wilkinson *et al.*, 1996; Williamson *et al.*, 2002). One contentious problem in pegmatite genesis is the common presence of massive almost monomineralic quartz cores, which indicates the deposition of very large amounts of SiO_2 with almost no other solid phases. If the typical solubility of quartz in hydrothermal solutions is used to explain the presence of this quartz, a mass balance problem emerges, as a very large amount of water is required to produce the deposit. This is inconsistent with the generally limited evidence for hydrothermal fluid flow through, or out of, most pegmatites. Brotzen (1959) discussed water-rich silica gel as a possible medium for SiO_2 transport in answer to this problem. Although there are difficulties with models that propose gels as the principal mechanism for pegmatite formation, the sol/gel state may provide an alternative explanation for some specific aspects of pegmatite development. Thomas and Davidson (2008) suggested that a gel

state as the final melt stage after everything else has crystallized is indeed a possibility, and this suggestion is supported by the recent observation of the presence of well crystallized topaz, apatite and other minerals preserved in blue chalcedony from the Otjozaharun pegmatite near Otjiwarongo, Namibia (Thomas *et al.*, 2012).

As a working hypothesis, Brotzen (1959) considered the gel state as important for the development of giant crystals in the core-margin association, although at the time, direct experimental evidence was lacking. The recently observed alkali-rich fluid or melt inclusions in quartz support this hypothesis, as the formation of a silica gel is favoured in strongly alkaline fluids (Large, 1969).

Silica gels can be highly effective ion-exchange media which can produce extreme enrichment of some trace elements. For example, the occurrence of the mineral hafnon adjacent to the quartz core of the Naipa and Muiane pegmatites in Mozambique (Correia Neves and Lopes Nunes, 1974) requires a very effective process of selective element enrichment to produce the 'inverse' elemental arrangement required to form hafnon, in which Hf is the main element and Zr is present only in traces.

From experiments and observations on natural inclusions in minerals, the rheological properties of the gels vary from more viscous or elastic liquids to those with quasi-solid characteristics. The transitions between a fluid and a quasi-solid material depend among other variables on the water content, temperature and the time-dependent change in viscosity during flow (thixotropic behaviour) (Dörfler, 2002).

Although experimental evidence shows that water-rich silica gel phases can occur, their existence and abundance in nature remains controversial. As they are structurally disordered they tend to alter over time into ordered silica or aluminosilicate minerals, or to more stable disordered aqueous solutions. Even if they are trapped as inclusions within stable phases their survival is not guaranteed. The research described here is a continuation of the study of the Rønne pegmatites presented by Thomas *et al.* (2011*b*). We describe the occurrence of inclusions in quartz and feldspar from samples representative of the quartz core of the pegmatite, which have trapped a silicate hydrogel phase. These inclusions resemble the fluid inclusions found in low temperature chalcedony or agate amygdales by Khakimov (1968) and Prokofiev *et al.* (2008).

Figure 1 is a schematic diagram of typical inclusions in geodes in chalcedony veins, which resemble the inclusions we describe from the quartz of the Rønne pegmatite. We also discuss the post-trapping processes that have brought these inclusions to their current state, and the possible significance of silicate hydrogel phases in the origin and evolution of pegmatites.

Sample description

The host rock: the Rønne granodiorite

The Rønne granodiorite at the Klippeløkkene quarry is the most mafic of all the Bornholm granitoids. It is a massive, medium-grained, melanocratic and deformation-free rock containing (vol.%): potassium feldspar (29%); plagioclase (30%); quartz (21%); hornblende (10%); biotite (5%); and minor amounts of titanium-rich magnetite; titanite; calcite (found during the present Raman study); apatite; and zircon (5%) (Noe-Nygaard, 1963, Zariņš and Johannson, 2009). Pyroxenes of the enstatite–ferrosilite series and diopside are locally present. The anorthite contents of the cores and rims of the plagioclase are 35−40 mol. % and 15−20 mol.%, respectively. Fresh well preserved potassium feldspar contains about 5000 ppm Ba (Noe-Nygaard, 1963). The rock contains at least two types of zircon: short prismatic crystals with an aspect ratio between about 1.3 and 2.5; and younger, highly elongated prismatic crystals with aspect ratios between about 25 and 50. Emeleusite, $Na_4Li_2Fe_2^{3+}Si_{12}O_{30}$, occurs as a rare

accessory phase as 40×80 μm crystals. The fresh Rønne granites are characterized by feldspars which contain numerous calcite crystals, up to 1000 μm in size, with no evidence for a secondary origin. This implies that the primary granite-forming magmas were carbonate-bearing.

The best age estimate for the Rønne granodiorite is 1459±4 Ma by U−Pb geochronology (Zariņš and Johannson, 2009). This agrees (within error) with the concordia age of 1456±5 Ma reported by Waight *et al*. (2012). The presence of pyroxene relics indicates relatively dry crystallization conditions, and is also consistent with the lowest water content of melt inclusions in quartz of all Bornholm granitoids (3.2 wt.%), and the extrapolated high solidus temperature of 742ºC (Thomas, 1994). According to data reported by Noe-Nygaard (1963) the rock has an aluminium saturation index (ASI) of 0.838, and in the pegmatite contact zone the granite has a CO_2 content of 0.59 wt.%, corresponding to a carbonate concentration of 0.76 wt.%. Away from the pegmatites the granite is carbonate-free, or carbonate is below the detection limit.

The Rønne pegmatites

The granodiorite from Rønne contains abundant sub-horizontal and swarms of subparallel vertical dilatational pegmatite veins with near parallel walls and thicknesses varying from centimetres to more than a metre; they are rarely less than 10 m long (Micheelsen, 1960; Jøgart, 2001). The very fresh flesh-coloured pegmatite is a simple abyssal
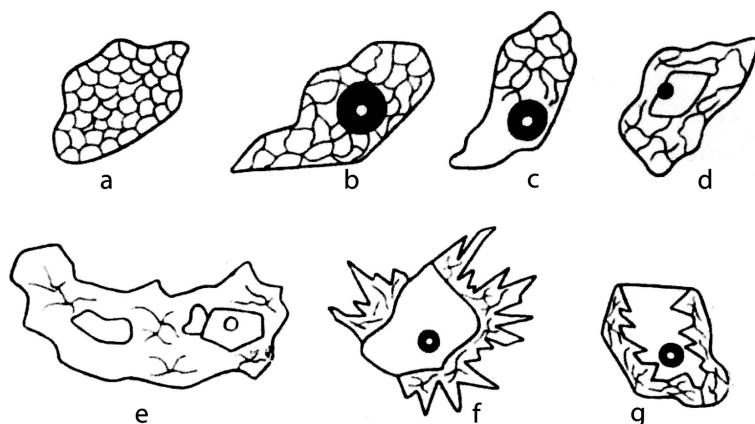

FIG. 1. Genetic types of inclusions in geodes of chalcedony-quartz veins modified from a sketch in Khakimov (1968). The inclusions *a* and *b* represent true colloid inclusions, *c* and *d* mixed colloid-water inclusions and in inclusions *e*, *f* and *g* there are larger volumes of aqueous solutions.

quartz-feldspar pegmatite with a conspicuous graphic texture and only minor amounts of mica (Fig. 2). The microcline perthite is graphically intergrown with quartz and contains 50−300 ppm Ba. None of the Rønne pegmatites contain miarolitic cavities.

The Rønne pegmatites are zoned, typically having sharp contacts between the country rock and a fine-grained graphic-textured zone (between A and B in Fig. 2a). This zone is primarily graphic-textured flesh-coloured microcline perthite, and also contains irregular pale patches of albite (An_8−An_{10}) and minor yellowish hyalophane [$(K,Ba)Al(Si,Al)_3O_8$] (Fig. 2a). The transition from the relatively fine-grained outer zone to the core-margin zone (between B and the central quartz aggregates of Fig. 2a) is marked by a significant increase in grain size, producing a
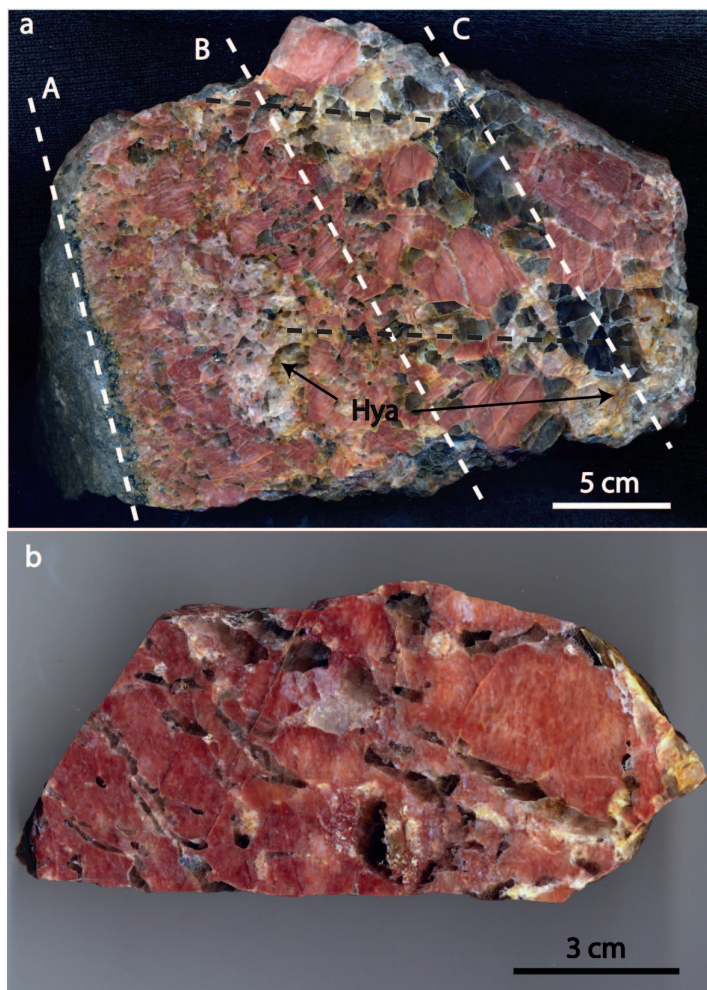

FIG. 2. (a) A section of a sub-horizontal pegmatite vein from the Rønne granite, Bornholm Island, Denmark. The line A indicates the footwall contact of the pegmatite with the granite; graphic granite is present between A and B; and C is the centre of the vein with large smoky quartz crystals in a compact quartz core. The irregular pale area between A and B contains albite and hyalophane [$(K,Ba)Al(Si,Al)_3O_8$] (Hya, arrowed). The horizontal dotted black lines show the axes of the channels of finer-grained material starting in the graphic zone and ending in the quartz core. (b) A polished specimen from the graphic granite zone containing flesh-coloured microcline and small isolated smoky quartz rods.

coarse pegmatitic texture. In addition to the graphic texture the large K-feldspar crystal aggregates are commonly rimmed by quartz borders up to 3 mm wide (Fig. 2b). The grain size of the near-black smoky quartz increases from $<1 \times 10$ mm at the pegmatite rim, to more than 5×4 cm in the centre of the pegmatite vein (line C in Fig. 2a), which is distinguished by large smoky quartz aggregates. Although these aggregates are not continuous, because of the generally small size of the veins, they can be considered to represent a discontinuous quartz core. Figure 2a shows the graphic zone, a diffuse zone containing mainly albite. A channel-like connection to the large smoky quartz aggregates in the centre of the vein starts in this zone and is arranged in a repetitive pattern. Rutile, apatite, zircon and

calcite, graphite, magnetite, ilmenite, pyrite and chalcopyrite occur as accessory phases. Christensen and Zimmerman (2004) have also described relatively large (up to $2 \times 2 \times 5$ cm) prismatic crystals of allanite-(Ce).

In a thick section the graphic granite is seen to contain graphite aggregates, in some cases up to 5×1 mm in size, covering ~1.5% of the surface and extending throughout the whole sample (Fig. 3b). Raman spectrometry revealed a peak-area graphite crystallinity index, R2, of 0.062. According to Beyssac et al. (2002), this value is equivalent to a crystallization temperature of ~700ºC. Together with our determinations (Thomas et al., 2011b), this indicates a range of 700 to 550ºC for the main stages of pegmatite formation. Quartz and some feldspars are
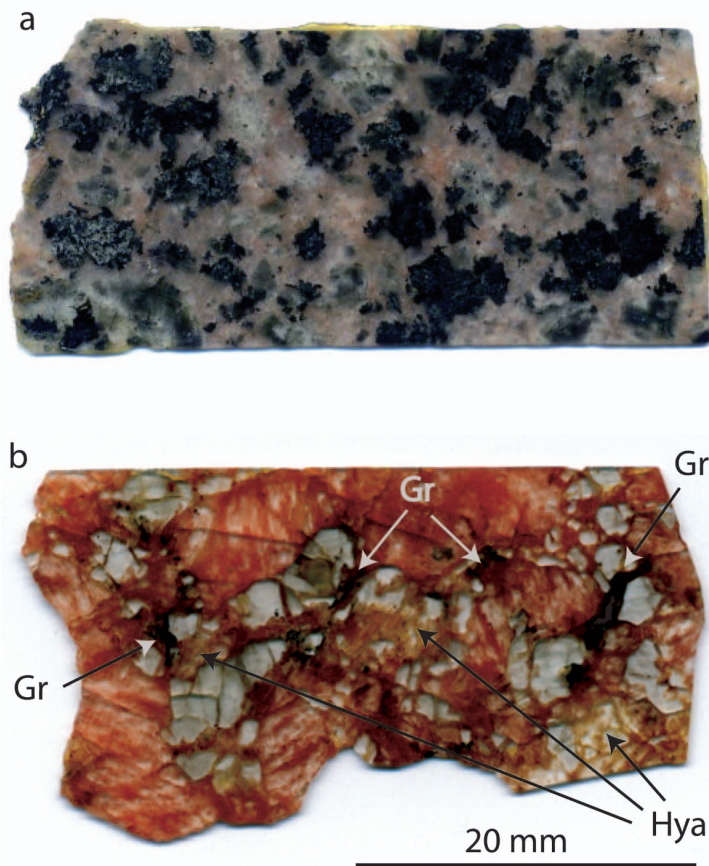

FIG. 3. Thick sections of (a) the Rønne granite and (b) pegmatite, containing mainly feldspars and quartz. The black patches in (b) are graphite (Gr) aggregates. Hya = hyalophane.

characterized by different inclusion types including rare silicate melt inclusions; nahcolite-rich and other carbonate/bicarbonate-bearing fluid inclusions (Thomas et al., 2011b); and 'gel-like' inclusions, which are described below. Some quartz crystals contain all of the described primary inclusion types at a density of up to about 1.4×10^7 per cm^3 (Thomas et al., 2011b).

Micro-Raman spectroscopy

During petrographic study of double-polished 500 µm thick sections from the Rønne pegmatite, many nahcolite-rich fluid inclusions were found in the quartz, at grain boundaries between different minerals, and as isolated inclusions in all of the main phases. As the identification of the very small carbonate and bicarbonate daughter mineral phases is difficult by optical microscopy we have used high-resolution micro-Raman spectroscopy for their characterization.

Raman spectra were recorded using a Jobin-Yvon LabRam HR800 spectrometer (grating: 1800 lines/mm), coupled to an Olympus optical micro-scope with a long-working-distance LMPlanFl $100 \times /0.80$ objective. We used the 514 and 488 nm excitation lines of a coherent Ar^+ Innova 70C laser, operating at a power of 300 mW (corresponding to ~14 mW at the sample), with a spectral resolution of $\leqslant 0.6$ cm^{-1}. Each unpolar-ized spectrum was constructed from six acquisi-tions of 10 s each. The spectra were collected at a laboratory temperature of 20ºC using a Peltier-cooled CCD detector; the positions of the Raman bands were corrected using the principal plasma lines of the argon laser as a reference. The divergence between the published and measured positions of the plasma lines is no greater than 0.6 cm^{-1}. If the inclusion geometry was suitable, the percentage volume occupied was estimated.

The main Raman bands for typical carbonates and bicarbonates in fluid and melt inclusions are listed in table 1 of Thomas et al. (2011a,b). For nahcolite (NaHCO$_3$); zabuyelite (Li$_2$CO$_3$); and calcite (CaCO$_3$) the diagnostic bands centred at 1045 cm^{-1}; 95 and 1090 cm^{-1}; and 1085 cm^{-1}, respectively.

Results

Description and characteristics of gel inclusions in the Rønne pegmatite

The term 'gel inclusion' is used here to describe inclusions which consist mainly of microcrystal-line quartz grains with minor amounts of other phases (Fe-oxides/hydroxides, carbonates). We propose that these formed by post-trapping accretive crystallization from the original gel state during declining $P-T$ conditions. As the sol or gel state is thermodynamically unstable, more stable polymorphs (e.g. β-quartz, cristobalite and mogánite) form over time by syneresis and phase transformation.

Gel inclusions resemble fluid inclusions, they commonly contain a small shrinkage vapour bubble (Figs 1 and 4), but unlike fluid inclusions contain a large volume (~50 to 100 vol.%) of solid material. This occurs principally as a fine-grained granular filling of micrometre-sized (0.5 to 1.5 µm) grains, primarily quartz, which forms regular grains and accretions of such grains merged into irregular clusters. These inclusions typically contain small but variable quantities of feldspar, more rarely FeOOH, and possible cristobalite. The remainder of the inclusion is filled with an alkali-carbonate-bearing aqueous solution, and commonly contains a vapour bubble. In a few larger inclusions, daughter crystals with sizes >5 µm (quartz, feldspar, calcite) occur; probably resulting from to post-trapping accretive crystallization and Ostwald ripening.

The inclusions typically range from ~10 µm to more than 100 µm across, and are rarely more than 500 µm. They are characterized by a prominent pseudo-granular texture (Fig. 4a−f). Near the bubbles and commonly at the phase boundaries with the host quartz or feldspar there are irregular patchy areas with aqueous solutions.

Small but significant numbers of calcite and nahcolite crystals in the inclusions indicate the presence of carbonate in the originally pegmatite-forming liquid. However, there are striking differences between such inclusions in quartz and feldspar host crystals. Nahcolite is the dominant carbonate phase in quartz, whereas calcite is the dominant carbonate phase in feldspar, probably because of reaction with calcium in the feldspar. In feldspars, the inclusions are commonly crystallographically-oriented (Fig. 5a−c) and very flat, making Raman spectroscopic studies difficult.

Quartz from the graphic zone contains flat former gel inclusions, characterized by quartz aggregates suspended in an aqueous solution with a slightly different orientation to the surrounding quartz (Fig. 6). It is commonly the case that the inclusion can only be seen as a result of this 'disorientation'. There is a clear difference in the
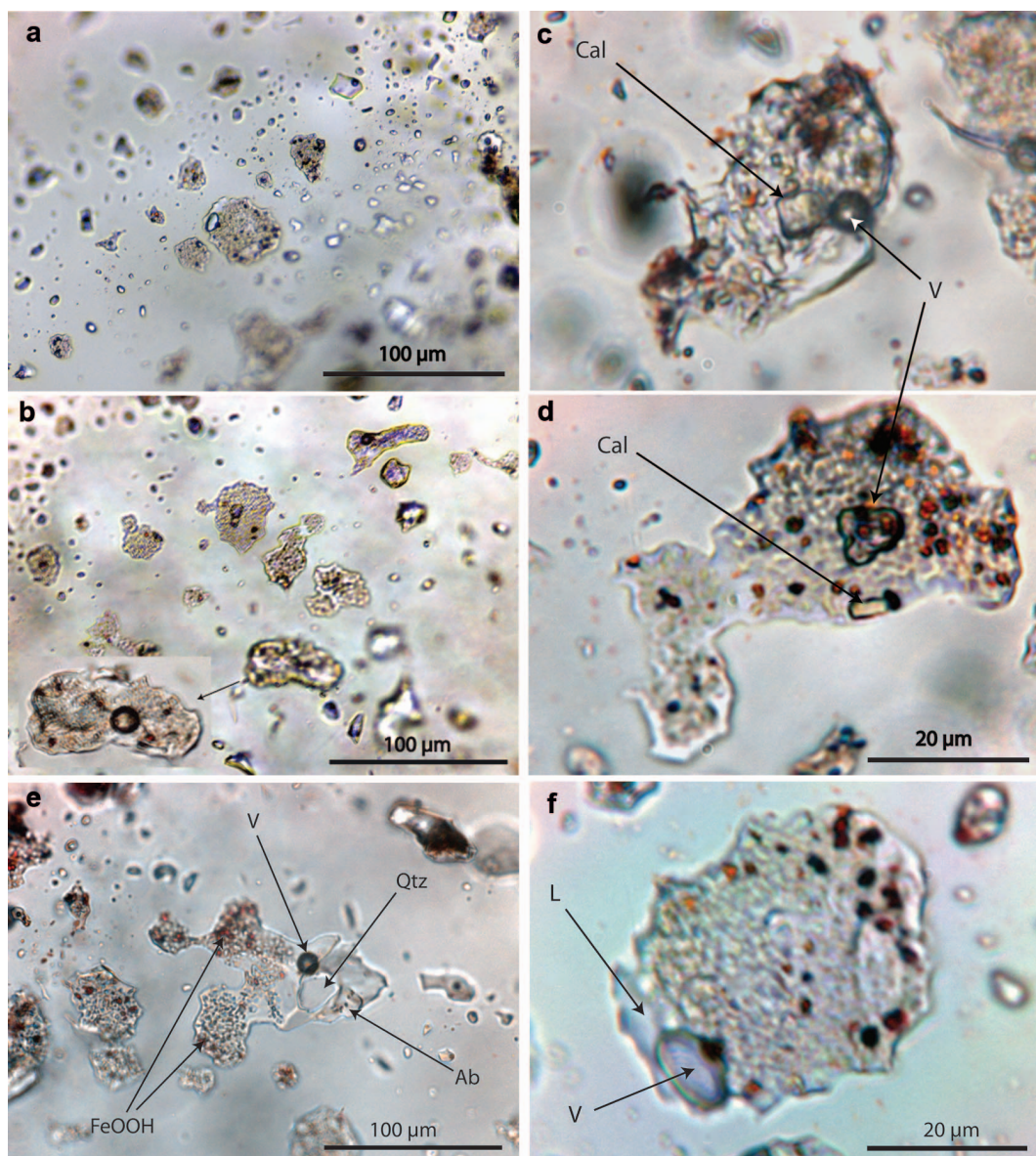
FIG. 4. Typical gel inclusions (*a*−*e*) in quartz from the Rønne pegmatite from the quartz core. (*c,d*) Larger crystals of calcite with granular quartz and dark FeOOH. The inclusion in the centre of (*e*) contains a larger quartz crystal. (*f*) A former gel inclusion in which the grain boundaries are indistinct and appear to merge. Abbreviations are as follows: Ab, albite; Cal, calcite; FeOOH, goethite; V, vapour; L, aqueous solution.

Raman spectra of the quartz that has crystallized from a melt or solution and the quartz that has crystallized from the gel state (Fig. 7).

Preliminary Raman spectrometry on gel inclusions shows that the SiO_2-dominated phases contain significant amounts of molecular water, as indicated by a broad and near-symmetrical Raman band at ~3440 cm^{-1}. From the integrated intensity an approximate estimation of the water concentration of 12.4±0.7 wt.% was calculated
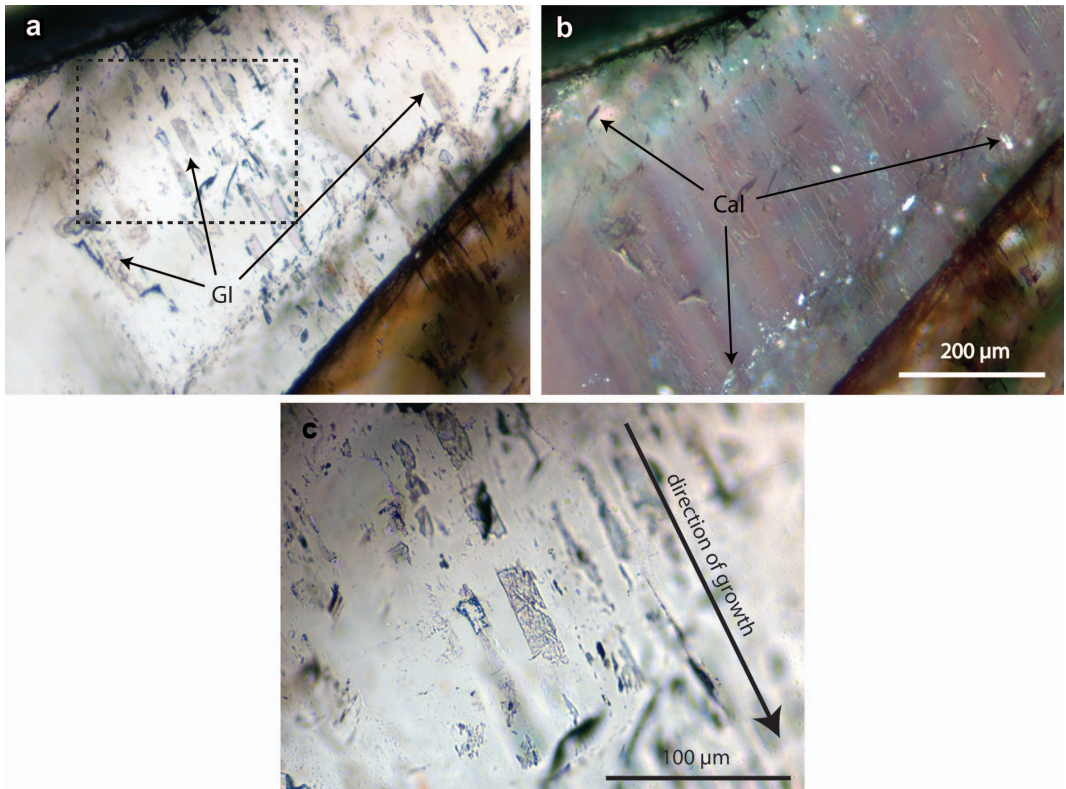
FIG. 5. Gel inclusions in plagioclase from the Rønne pegmatite (*a*) in plane polarized light, and (*b*) between crossed polarizers, showing the calcite (Cal) crystals perpendicular to the growth direction. (*c*) A higher magnification image of the area outlined in (*a*), showing the oriented arrangement of the inclusions.
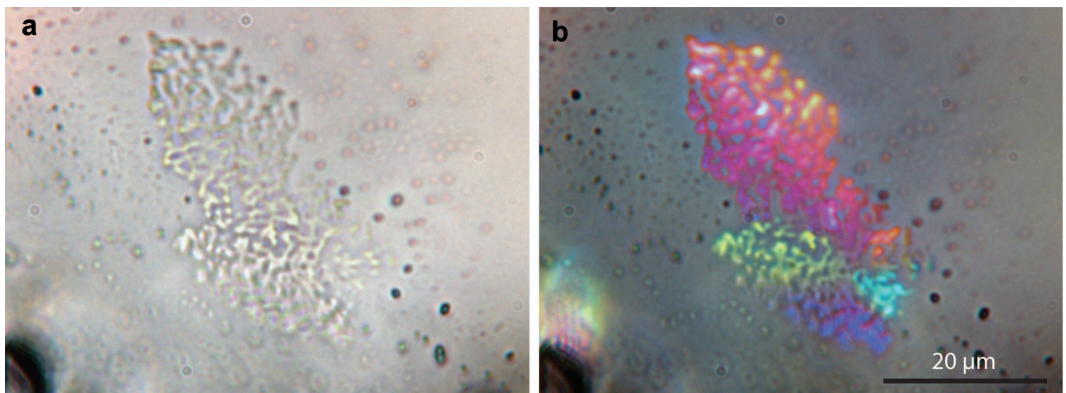

FIG. 6. Inclusion quartz which is interpreted as having formed as a result of crystallization of the gel within crystalline host quartz (*a*) in transmitted light, (*b*) between crossed polarizers. Note the small difference in interference colours produced by the wedge-like orientation of the quartz particles in the inclusion.

from 13 determinations. This value is very high in comparison to the estimated water content of igneous, hydrothermal and metamorphic quartz (Müller and Koch-Müller, 2009; Thomas *et al.*, 2008, 2009); natural quartz mostly has values less than 300 ppm. The ratio between sample and standard integral intensity (8.06 wt.% H_2O) is 1.54 (Thomas *et al.*, 2008). An added Raman
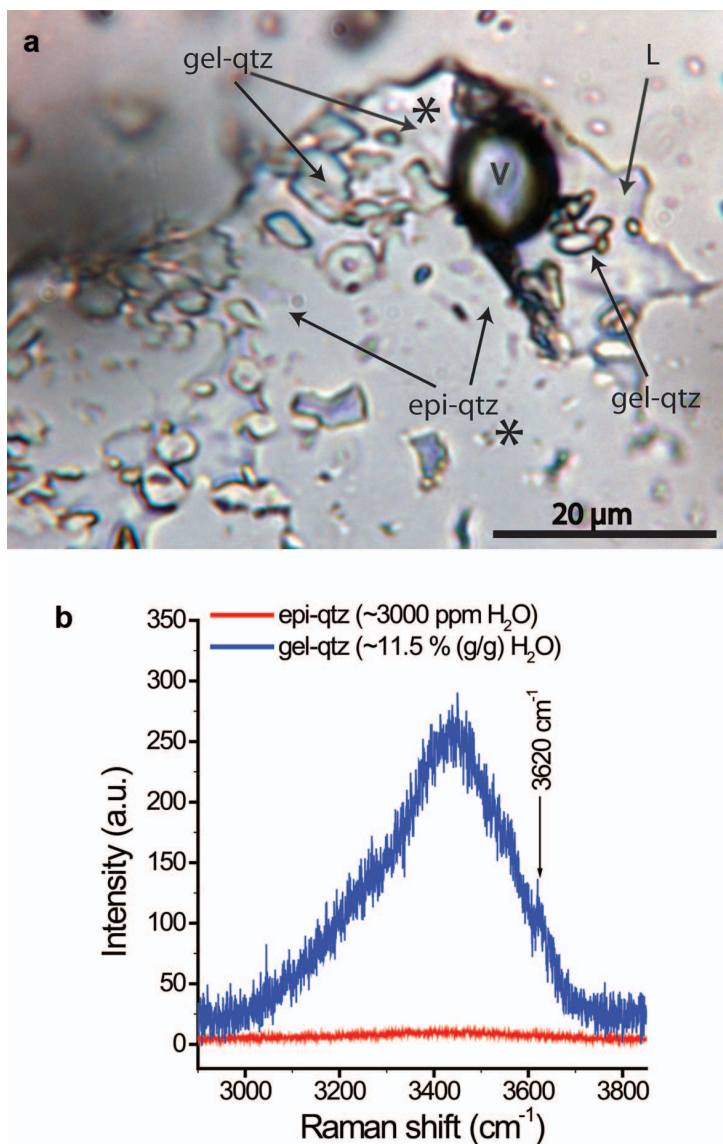

FIG. 7. (*a*) A large gel inclusion showing more advanced maturation, with some silica converted to euhedral quartz crystals which epitaxially overgrow the host quartz. Abbreviations are as follows: L, aqueous solution; V, vapour; and gel-qtz, newly formed quartz [single euhedral daughter crystals and some partially connected by epitaxial growth to the host quartz (epi-qtz)]. (*b*) Raman spectra in the high-wavenumber range of the host quartz (epi-qtz) with about 3000 ppm H_2O and former gel quartz (gel-qtz) containing about 11.5 wt.% H_2O. The weak band at 3620 cm^{-1} corresponds to small amounts of NaOH in the gel quartz (according to Walrafen and Douglas, 2006). The stars show the measuring positions.

band at 3625 cm^{-1} suggests that NaOH is present in significant amounts (Walrafen and Douglas, 2006). A typical total water content for whole inclusions is not given, as the values vary from inclusion to inclusion within a wide range (shown schematically in Fig. 1). The Raman spectrum of the post-trapping gel-quartz differs from that of the crystalline host quartz in the presence of a single and strong band at 1081 cm^{-1} and a very weak band at 1156 cm^{-1}. The crystalline host quartz has two weak bands at 1064 and 1080 cm^{-1} and a stronger band at 1158 cm^{-1} in this spectral range. Furthermore, the Raman spectrum of some post-trapping silica includes a distinct band at 502 cm^{-1}, corresponding to the monoclinic silica polymorph mogánite (Kingma and Hemley, 1994), which is a typical component of silica formed in alkaline fluids (Götze et al., 1998). These Raman data are preliminary and further studies are being conducted. The Raman study of the very small silica aggregates in the former gel inclusions in quartz is rendered difficult by the overwhelming intensity of the host spectra. Better spectra can be obtained from inclusions in other minerals, such as beryl or topaz (Thomas and Davidson, 2008).

During heating on a microscope heating stage, the vapour bubble, if present, disappears, generally at moderate temperatures (100−250ºC). The quartz and possible cristobalite grains show no changes during heating. Due to the very high quartz content of this inclusion type, melting to a glass does not occur in a realistic temperature range (<750ºC), i.e. typical for the trapping temperatures of the melt inclusions. Nonetheless, we interpret these as crystals which have formed in a colloid by ageing of a primary gel (Large, 1969). The gel inclusions have been irreversibly altered in this process.

In the former gel inclusions the concentration of alkali carbonates is at least an order of magnitude less than in the nahcolite- and zabuyelite-bearing fluid or melt inclusions (Thomas et al., 2011b). This implies that the process of sol/gel formation is connected with an effective separation of colloidal SiO$_2$ from the alkali ions, which is further amplified by the crystallization of albite.

Discussion and interpretation

If water-rich silica gel is present in pegmatitic systems, direct evidence of its existence should be preserved in pegmatites as inclusions. Recrystallization processes can irreversibly alter such inclusions. Silica-rich hydrocolloids can be irreversibly altered as the temperature falls, into more stable phases such as quartz, and they may also be affected by the destruction of the gel network stabilizers and flocculation by destabilizing of colloidal dispersions. Presumably such processes would also eliminate the gel inclusions in the high temperature stages of pegmatite evolution. However, gel-like inclusions have been found in some quartz, K-feldspar and plagioclase crystals. The identification of this type of inclusions is difficult (Fig. 4a−e), but we have identified large numbers of such inclusions in the quartz cores of several pegmatites worldwide (Thomas et al., 2012).

We infer a magmatic origin for the alkali-carbonate-rich inclusions, including the gel inclusions, on the basis of the following observations: (1) the dissolution of large amounts of nahcolite in water and CO$_2$-rich solutions is only possible at high temperatures; (2) nahcolite- or carbonate-rich rocks are absent in the neighbourhood of the granites and pegmatites; (3) there are no plausible mechanisms for the strong enrichment of alkali carbonates at low temperatures; (4) the corrosion of feldspars by an alkali carbonate- and SiO$_2$-rich melt or solution implies high temperature reactions; (5) the coexistence of three types of inclusions (silicate-melt inclusions, nahcolite-SiO$_2$-rich inclusions (Fig. 8a), nahcolite-rich CO$_2$ inclusions) is a clearly magmatic phenomenon; (6) the progressive enrichment of Li as Li$_2$CO$_3$ (zabuyelite) together with NaHCO$_3$ (Fig. 8b) during the pegmatite evolution from the outer rim towards the quartz core is a clear indication of a process connected with pegmatite formation.

Stable isotope studies are required to prove conclusively whether such fluids are directly genetically connected to the granitic host, or have a deeper source. However such studies would not be simple because of the small mass of the inclusion systems.

The presence of inclusions with extremely high concentrations of nahcolite in quartz, and of calcite as inclusions in plagioclase might be related to the same source. According to Thomas et al. (2011b) the formation of nahcolite from an alkali carbonate-rich aluminosilicate melt can be represented by the following reaction:
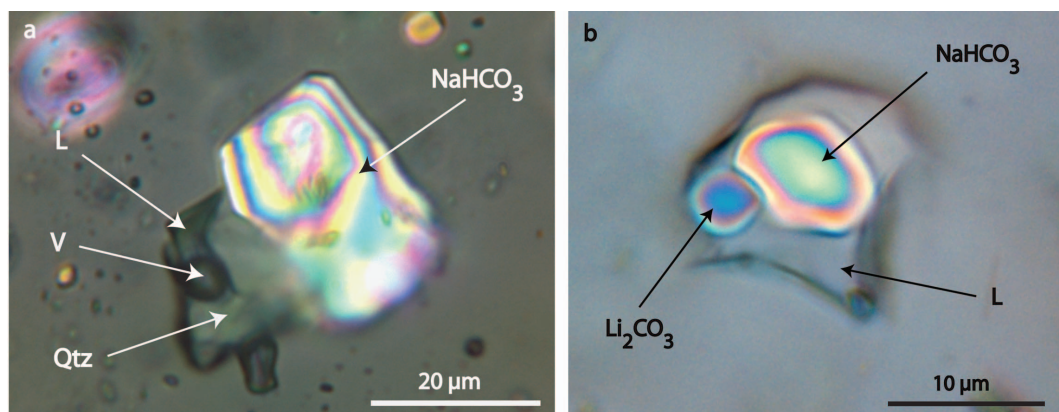
Carbonate-rich silicate melt fraction →
$$Na_2Si_2O_5 + 2CO_2 + H_2O \rightarrow 2NaHCO_3 + SiO_2 \quad (1)$$
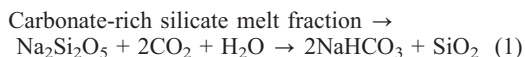
FIG. 8. Typical carbonate-rich inclusions in quartz of the Rønne pegmatite. (*a*) Early stage inclusion trapped in the graphic granite zone containing nahcolite, quartz and an aqueous solution with a vapour bubble. (*b*) Late stage trapped inclusion in the transition zone between graphic granite and the quartz core. Abbreviations are as follows: L, aqueous solution; V, vapour bubble; Qtz, quartz; $NaHCO_3$, nahcolite; Li_2CO_3, zabuyelite.

The Na_2CO_3 in the solution reacts with plagioclase according to the simplified equation:

$$CaAl_2Si_2O_8 + Na_2CO_3 + 4SiO_2 \rightarrow$$
$$2NaAlSi_3O_8 + CaCO_3. \qquad (2)$$
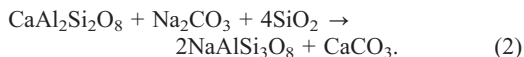
The SiO_2 and albite components, respectively, may then crystallize on the inclusion wall producing even more apparently nahcolite- or calcite-rich inclusions, in some cases containing up to 60% nahcolite (Thomas *et al.*, 2011*b*; Thomas and Davidson, 2012*b*). Such high carbonate concentrations in inclusions in a granite−pegmatite system would previously have been considered unusual, as such high values have only been described from carbonatites (Rankin and Le Bas, 1974*a*,*b*).

Hydrothermal diamond anvil cell (HDAC) experiments (Thomas *et al.*, 2011*b*) show that at temperatures >500ºC, Na_2CO_3-rich aqueous solutions are very reactive and can dissolve considerable amounts of SiO_2. These experiments have also shown the formation of a gel-like state with a relatively high packing density over a limited temperature interval (~448ºC) (Fig. 9*a*). During HDAC experiments in the system quartz−sodium disilicate−nahcolite−water, a metastable suspension-like hydrated melt phase (Fig. 9*b*) formed suddenly at 630ºC during cooling from a primary water-rich melt system at 650ºC (Veksler *et al.*, 2002; Veksler and Thomas, 2002).

In addition to gel inclusions trapped at high temperature there are also some unusual inclu-

sions in plagioclase crystals with a high OH^- contents. From Raman spectroscopy these correspond to an equivalent of 4.8±1.3 wt.% H_2O (Thomas *et al.*, 2008).

The reactivity of the peralkaline fluid can be determined from the reaction rims of newly-formed quartz at the contact with the feldspars, decorated by many small calcite crystals and nahcolite-rich fluid inclusions in the same quartz and feldspars (Fig. 10). The fluid inclusions in quartz contain mainly nahcolite, and all of the bright areas in plagioclase (Fig. 10) are crystals of calcite concentrated at the boundary zone between quartz and plagioclase. Rare fluid inclusions in plagioclase contain nahcolite and calcite daughter crystals. In the early stage of pegmatite formation the alkali concentration increases to very high values promoting the formation of hydrocolloids of silica.

In large quartz crystals from the centre of the pegmatite veins we found a greater number of inclusions, mainly containing small quartz grains which are similar to the gel inclusions in tourmaline (var. achroite) from Malkhan/ Transbaikalia (Thomas and Davidson, 2008) and to gel inclusions in the agate amygdales and veins described by Khakimov (1968). This suggests that the crystallization of achroitic tourmaline and quartz at a late stage of the pegmatite formation occurs from an alkaline water- and SiO_2-rich fluid, probably from a silica sol system. However, we have also found such gel inclusions in the
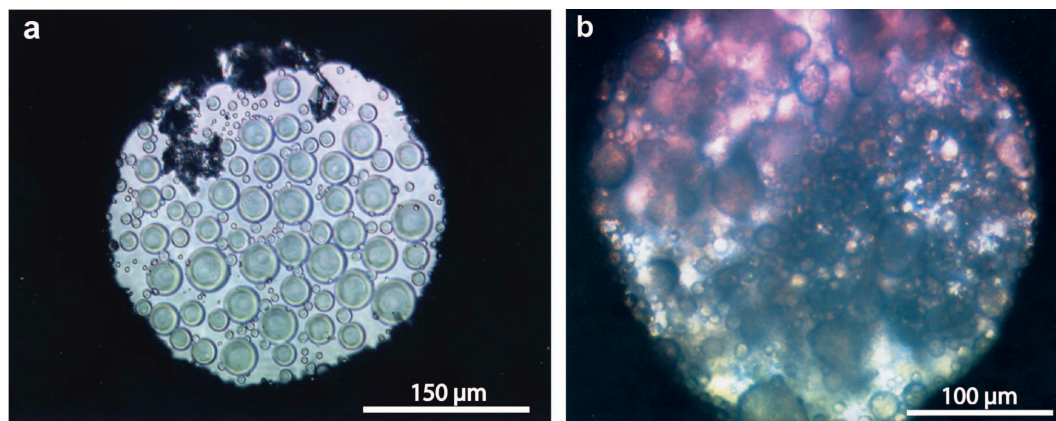
Fig. 9. (*a*) Photomicrograph from a series taken during a HDAC experiment in the $SiO_2-NaHCO_3-H_2O-CO_2$ system at 448ºC (Thomas *et al*. 2011*b*). At this temperature the homogeneous solution suddenly separates into a suspension of a gel-like substance completely filling the chamber formed by the two diamonds and the Re gasket. On further cooling the platelets disappear completely at 430ºC. (*b*) Formation of a metastable suspension-like hydrated melt phase suddenly at 630ºC during rapid cooling from 650ºC. At 650ºC the system was a homogeneous water-rich melt system.

graphic quartz and feldspars which form at the beginning of pegmatite crystallization. Similar inclusions were found also in the root zone of smoky quartz crystals from miarolitic pegmatites in the Königshain granite. All these observations demonstrate that the water content during the pegmatite formation is very high at the beginning of crystallization and increases over time (Thomas and Davidson, 2012*a*).

Why is the formation of silica sols and gels at high temperatures possible?

Thomas *et al*. (2011*b*) have shown that the quartz in the Rønne pegmatite is characterized by fluid inclusions that are very rich in nahcolite ($NaHCO_3$) and zabuyelite (Li_2CO_3). A large percentage of these fluid inclusions contain between 60 and 80 vol.% of alkali carbonates (Fig. 8). We interpret these fluid inclusions as
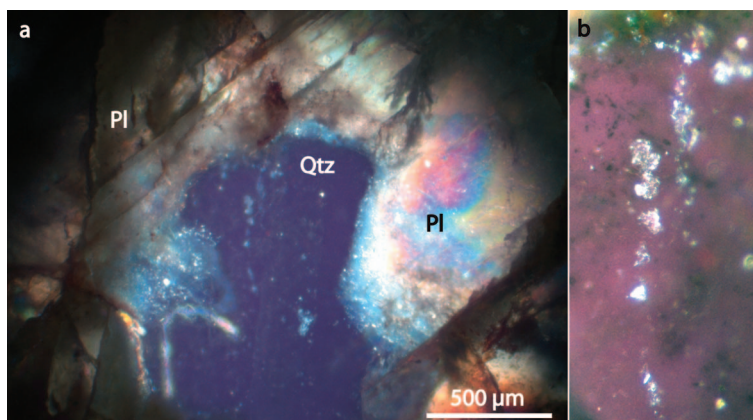

Fig. 10. (*a*) Replacement of plagioclase (Pl) by quartz (Qtz) in the graphic zone of the Rønne pegmatite by a nahcolite-rich solution. The bright tracks in quartz in the magnified image (*b*) mark the original plagioclase by remnant feldspar and calcite.

quartz- and alkali-carbonate-rich melt inclusions, which, by deposition of quartz on the inclusion wall during cooling, have been transformed from melt inclusions into apparent fluid inclusions (Fig. 8b). Using equation (1), 30 wt.% nahcolite corresponds to ~21.5 wt.% SiO_2. As these inclusions are present at an early stage of the Rønne pegmatite evolution, as indicated by the transfer of calcite into the wall zone of the host rock and by the high concentration of nahcolite-rich inclusions in quartz of the graphic zone, we can conclude that the primary pegmatite-forming melt was rich in alkali carbonates and water. Moreover, as we have also found coexisting aluminosilicate-rich melt inclusions we can infer that these alkali carbonate-rich inclusions were formed as a result of a melt−melt−fluid immiscibility process from a primary water-rich and carbonate-bearing silicate melt.

At high temperatures a carbonate-rich fluid or water-rich melt can dissolve a large amount of SiO_2. The HDAC experiments of Thomas et al. (2006; 2011b) show that such fluids promote the formation of SiO_2 colloids. In such systems the alkalis remain in solution as ions, providing a simple mechanism for the strong separation of the silica gel. For example, Smirnov et al. (2012) showed experimentally that a minimum of 2 wt.% Na_2O was required to produce a colloidal form of silica (a hydrosilicate liquid or HSL in their terminology), and that above that value the amount of HSL formed was proportional to the amount of Na_2O present.

Mustart (1972) demonstrated a possible alternative to melt−melt−fluid immiscibility processes by using a hydrous albite and sodium disilicate melt as a model for peralkaline magmas. At temperatures $\leqslant 540$ºC and closed system conditions a fluid can contain 38 wt.% H_2O and continues to increase in H_2O content to a maximum of 50 wt.% at 290ºC, at which point analcime begins to form at the expense of albite (Mustart, 1972: p. 116 and also summary on p. 126). Crystallization of albite produces an increase in the sodium disilicate and water concentrations in the melt and the dissolution of vapour. The water content can increase to very high levels (50 wt.%) down to low temperatures (<300ºC) without formation of a vapour phase. This model should also be applicable nahcolite-bearing systems if alkali carbonate is used in place of sodium disilicate.

What is the source of the high alkali carbonate concentrations?

Previous studies have suggested the existence of a sol/gel state during pegmatite-forming processes (e.g. Brotzen 1959; Taylor 2005, 2006), but they have had little influence on recent pegmatite studies. We have found gel-like inclusions in several pegmatites or pegmatitic granites including those at: Borborema; Bornholm; Ehrenfriedersdorf; Königshain; Malkhan; Muiane; and Naipa, suggesting that they might be unrecognized rather than rare (Thomas and Davidson, 2008). A question which arises from the conclusions presented in this study, and those of Thomas et al. (2011a,b, 2012) and from Thomas and Davidson (2012a) is, where does the carbonate-rich pegmatite-forming fluid come from?

The solubility of carbonate in silicate melts of typical granitic composition is very low and decreases with decreasing temperature (Sood, 1981; Liu et al., 2005). According to Sood (1981) the solubility of CO_2 in a granitic melt is 2500−3500 ppm at 1200ºC. At lower temperatures (~750ºC) the solubility is only about 500 ppm.

As the Rønne granite is modally poor in carbonates, and their abundance near the pegmatite veins increases significantly, the alkali carbonates are clearly an important primary component of the pegmatite-forming system. Three different sources for alkali carbonates in the granite−pegmatite system can be considered First, the parental granite melt carried considerably more alkalis in proportion to alumina (cf. Tuttle and Bowen, 1958: p. 88−89) and therefore may have been saturated in carbonates at high temperatures, as indicated by the primary calcite crystals in feldspars. With cooling the alkali carbonates would strongly fractionate into the mobile pegmatite-forming system as a result of their differing solubilities in granitic and peralkaline pegmatite-forming fluids. The experimental work of Mustart (1972) is important in this respect as data for the system $Na_2Si_2O_5–NaAlSi_3O_8−H_2O$ showed clearly that excess alkalis increase the maximum solubility of water and CO_3^{2-} significantly (Thomas and Davidson, 2012b). Secondly, it might be that during melting of nahcolite-rich sediments (Kempe and Degens, 1985) in the lower crust the granite-forming melt was enriched or saturated in alkali carbonates. Thirdly, the alkali carbonate-rich pegmatite-forming fluid originates directly from a CO_2 metasomatized mantle source (Bonin, 2005; B. Bonin, pers. comm.).

The data of table 2 in Noe-Nygaard (1963) show that the carbonate concentration at the granodiorite−pegmatite contact is 0.76 wt.%, whereas in the granodiorite away from the contact the concentration is below the detection limit. The inference is that the high carbonate concentration is a direct result of transfer from the pegmatite. This conclusion is also consistent with the common observation of calcite crystals in the feldspars and quartz of the pegmatite and with the presence of nahcolite-rich fluid inclusions in quartz and the rarity or absence of these inclusions in the undisturbed rock.

According to McKenzie (1985) small amounts of carbonate-bearing melt can be effectively extracted from a bulk granite/granodiorite system because of its very low viscosity. For the separation and influx of a pegmatite-forming melt from the granodiorite matrix into the dilation veins the viscosity must be sufficiently low. Using the model of McKenzie (1985) this threshold viscosity is 10^2 Pa s (Thomas and Davidson, 2012a). At 700°C this equates to a minimum water content of about 12.5 wt.%. Further crystallization of quartz and K-feldspar will dramatically increase the water and carbonate content in the system, forming a low viscosity Na-alkaline carbonate fluid which can dissolve large amounts of SiO_2. The excess alkalis and alkali carbonates prevent the formation of a vapour phase down to low temperatures, as indicated by the absence of miarolitic cavities in the Rønne pegmatite.

More problematically, if the source is according to the third hypothesis, fluids rich in alkali carbonates/bicarbonates would be expected outside of the alkali carbonate-rich pegmatite-bearing granites. However, the reaction of such fluids with Ca^{2+}-bearing fluids or rocks to produce calcite might mask their primary nature. Previous fluid inclusion studies (Newton et al. 1998) discussed only simple $CO_2−H_2O−NaCl$ fluids and might have led to an underestimation of the importance such carbonate-bearing fluids. Note that alkali carbonate-bearing or rich fluids would be excellent vehicles for the transport of alkalis and large ion lithophile elements upward through the crust.

Implications of evidence of the high temperature formation of silica gels

Evidence of the presence of silica gels at high temperatures demonstrates that at such temperatures high concentrations of alkali carbonates are not of only theoretical interest. However, current attention has focused on simple systems such as $CO_2−H_2O$ or $CO_2−H_2O−NaCl$ with the low solubility capacity for aluminosilicate compounds. This is true not only of pegmatite-forming systems, as for example Smirnov et al. (2012) and Touret et al. (2007) have shown. Water-rich alkali-carbonate fluids have a high transport capacity for silica and numerous other molecules (Thomas et al., 2011a), a change into a sol/gel state would result in a separation of the alkalis from SiO_2, producing, among other effects, almost pure SiO_2 in pegmatite quartz cores. Moreover, the transport and extreme enrichment of SiO_2 in large quartz veins no longer requires the so called "little red wagon effect" to deposit large quantities of silica from low solute-carrying capacity aqueous fluids, as discussed by London (2009).

The high concentrations of Na that are present when sol/gel forms can also serve as a source for the formation alkali-replacement minerals such as the saccharoidal masses of albite or cleavelandite (Brotzen, 1959) that are commonly found in pegmatites. For example, in cleavelandite from the Naipa pegmatite in Mozambique we have found direct evidence of a gel-like phase (Fig. 11), in addition to large and very flat (up to $200 \times 15 \times 3$ μm) nahcolite-bearing (8.3 wt.%) fluid inclusions.

In economic terms, the enrichment of Li in this stage might lay the foundations for the Na-Li mineralization (Fig. 8b). Similarly, studies such as those of Smirnov et al. (2012) imply Ta might have high solubilities in alkaline gels or sodium silicate gels, with obvious applications to the formation of high field strength element and rare metal deposits, including the tantalite-type mineralization (Thomas et al., 2011a) that is commonly found in pegmatites.

Conclusions

Low temperature gel inclusions have been described in chalcedony and agate (Prokofiev et al., 2008). In this study of the pegmatites associated with the Rønne granodiorite, especially in the quartz-rich central parts of the pegmatite veins and their cores, we have found clear and surprising indications of former gel inclusions in both quartz and feldspars; these appear to represent the mineral-forming or re-forming medium at this stage. Furthermore, we have also found former gel inclusions in earlier-formed
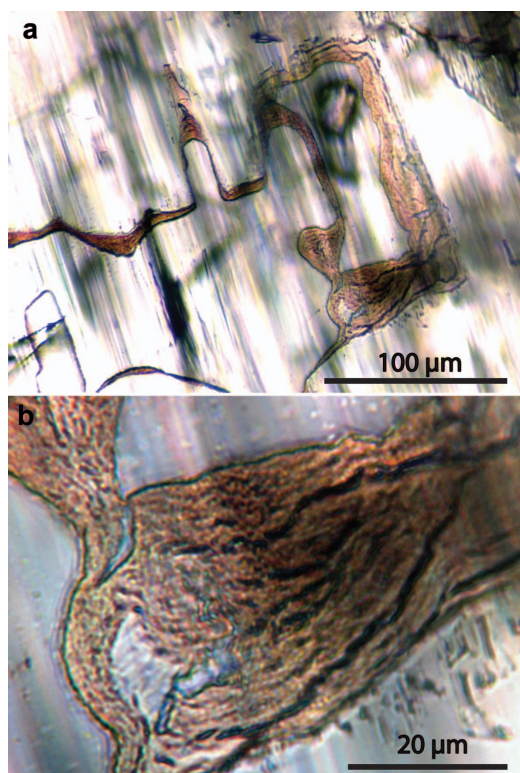
FIG. 11. (*a*) Cleavelandite from the Naipa pegmatite, Mozambique, showing a brownish pattern of gel inclusions. The photo (*b*) is an enlargement of area above the scale bar in (*a*).

quartz of the graphic granite zone, with a significant increase in the number of these inclusions in the direction of the quartz core, indicating the presence of high alkali and water concentrations at an early stage of pegmatite formation. The textural relationships of the former gel inclusions imply that the gel state was directly connected to the primary mineral-forming processes at temperatures from ~700ºC to ~550ºC, and thus that the sol/gel phase is not of secondary post-magmatic origin. The coexistence of silicate melt inclusions with gel inclusions in some stages of the pegmatite formation does not imply that silicate sol/gel states are dominant in pegmatite formation, nonetheless the high water and alkali carbonate contents allow temporary transitions into this state. The high primary alkali carbonate contents of some pegmatites poses questions regarding the origin of these

compounds, which require further studies using stable isotope methods.

In general terms, the addition of a possible sol/gel state into discussions of pegmatite-forming processes widens its physical and chemical basis considerably. The interplay of these different processes enables the large variety in the appearance of pegmatites and their chemical, mineralogical and textural development, which commonly appear to be independent of the host rocks, to be better understood. The diversity of parameters such as temperature, pressure, concentration and speciation within wide limits differentiates the pegmatite-forming process from all other magmatic or hydrothermal processes.

Acknowledgements

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