

Extreme alkali bicarbonate- and carbonate-rich fluid inclusions in granite pegmatite from the Precambrian Rønne granite, Bornholm Island, Denmark

Rainer Thomas · Paul Davidson · Christian Schmidt

Received: 12 November 2009 / Accepted: 29 April 2010
© Springer-Verlag 2010

Abstract Our study of fluid and melt inclusions in quartz and feldspar from granite pegmatite from the Precambrian Rønne granite, Bornholm Island, Denmark revealed extremely alkali bicarbonate- and carbonate-rich inclusions. The solid phases (daughter crystals) are mainly nahcolite [NaHCO_3], zabuyelite [Li_2CO_3], and in rare cases potash [K_2CO_3] in addition to the volatile phases CO_2 and aqueous carbonate/bicarbonate solution. Rare melt inclusions contain nahcolite, dawsonite [$\text{NaAl}(\text{CO}_3)(\text{OH})_2$], and muscovite. In addition to fluid and melt inclusions, there are primary CO_2 -rich vapor inclusions, which mostly contain small nahcolite crystals. The identification of potash as a naturally occurring mineral would appear to be the first recorded instance. From the appearance of high concentrations of these carbonates and bicarbonates, we suggest that the mineral-forming media were water- and alkali carbonate-rich silicate melts or highly concentrated fluids. The coexistence of silicate melt inclusions with carbonate-rich fluid and nahcolite-rich vapor inclusions indicates a melt-melt-vapor equilibrium during the crystallization of the pegmatite. These results are supported by the results of hydrothermal diamond anvil

cell experiments in the pseudoternary system H_2O – NaHCO_3 – SiO_2 . Additionally, we show that boundary layer effects were insignificant in the Bornholm pegmatites and are not required for the origin of primary textures in compositionally simple pegmatites at least.

Keywords Pegmatites · Fluid and melt inclusions · Carbonate melt · Carbon dioxide · HDAC experiments

Introduction

From melt and fluid inclusion studies and experimental work, we know that in some types of granite melts concentrations of B, F, P, Li, and water can reach weight percent levels. The further enrichment of these components can proceed to extreme levels in evolved granite pegmatites, whereby the characteristics of these sometimes exotic and enigmatic igneous rocks can be explained. The following features are partial characteristics of pegmatites: extremely coarse and variable grain-size, anisotropic fabrics, chemical heterogeneity at several different scales, and strong chemical fractionation within the pegmatites, indicated by enrichment of some elements by factors of 10^3 – 10^4 compared to typical granites (London 1992, 2005).

One common view of pegmatite formation is that the melt fluxing effects of B, F, P, Li, and water are responsible for pegmatite textures by significantly reducing the silicate solidus and permitting an extended crystallization interval. However, this cannot be the only mechanism as is evident from simple pegmatites containing only quartz and feldspar. Pegmatites associated with Precambrian granites, formed at greater depths (7–11 km) are an example, since the typical pegmatite-forming elements (F, B) are present only in trace quantities.

Communicated by J. Hoefs.

Electronic supplementary material The online version of this article (doi:10.1007/s00410-010-0533-z) contains supplementary material, which is available to authorized users.

R. Thomas (✉) · C. Schmidt
Helmholtz Centre Potsdam, German Research Centre
for Geosciences GFZ, Telegrafenberg, Potsdam, Germany
e-mail: thomas@gfz-potsdam.de

P. Davidson
ARC Centre of Excellence in Ore Deposits,
University of Tasmania, Hobart 7001, Australia

The search for a suitable mechanism for the formation of such simple pegmatites is a challenge, because water and carbon dioxide alone have insufficient solution capacity for aluminosilicate components, and normally the solubility of CO_2 in granite melts is very low. We must seek a transport and crystallization medium without fluorine and boron, or any other of the typical fluxing elements characteristic of evolved rare-element pegmatites.

One approach comes from experimental work done by Mustart (1972). His studies of the phase relations in the peralkaline portion of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ have shown that peralkaline melts may contain much higher quantities of dissolved water than is normally indicated by the solubility experiments performed with haplogranite or peraluminous granite composition. The addition of any amount of sodium disilicate to, for example, the albite- H_2O system increases the water solubility dramatically: 15% (g/g) at 700°C, 21% (g/g) at 600°C, and up to 43% (g/g) at 530°C.

This experimental work raises the question of whether we find in nature evidence that peralkaline melts play a crucial role in the formation of the simple pegmatites? To answer this question we have studied a very simple pegmatite, the quartz-feldspar pegmatites in the Precambrian Rønne Granite, Bornholm Island, Denmark: composed of quartz, feldspar, and only traces of mica.

Petrology and sample descriptions

The Rønne granite, about 1,400 Ma in age, is a medium-grained, equigranular rock, where plagioclase dominates over microcline feldspar (so-called “red admirals”). This rock is a typical lower crustal I-type granite, and according to the nomenclature of Streckeisen it is a granite *sensu stricto*. This rock contains abundant subhorizontal and vertical pegmatite veins with thicknesses from centimeters up to more than 1 meter (Jørgard 2001). The very fresh pegmatite sample (Bo 22/1) used in this study from the Klippeløkke quarry, 3 km ENE of Rønne (Bornholm Island, Denmark), is a simple quartz-feldspar pegmatite with a conspicuous graphic texture and only minor amounts of mica. The potassium feldspar (microcline) is flesh-red and the quartz glyphs are smoky-colored. Fluorite is only a very rare accessory mineral in the granite. There are no indications that elements (F, B, P), typical for evolved pegmatite, are present in elevated concentrations. Surprisingly, we found remnants of graphite schist both in the granite and in the pegmatite. Raman spectra of the first-order region ($1,100-1,800\text{ cm}^{-1}$) of this graphite gave a minimum R2 ratio of 0.115, corresponding to a maximum graphite disequilibrium temperature of 590°C (Beyssac et al. 2002).

For the inclusion study we used samples containing only quartz and feldspar from the graphic granite. In

quartz and potassium feldspar, there are isolated clusters of daughter crystal-rich fluid inclusions, in addition to numerous CO_2 -bearing secondary fluid inclusions, mostly arranged in trails. Rarely, there are also small quartz grains (2–3 mm in diameter) densely filled with all of the primary inclusion types: silicate melt inclusions, carbonate/bicarbonate crystal-rich inclusions, and nahcolite-bearing CO_2 inclusions. In this case, the number of nahcolite-bearing inclusions is high: $\sim 1.4 \times 10^7$ inclusions/ cm^3 . Under crossed Nicols, such grains look like a star-studded sky.

Secondary fluid inclusions show no Raman spectroscopic indication of carbonate or bicarbonate in solution. There are three types of primary inclusions. The first and most striking inclusion type consists of extremely nahcolite- and zabuyelite- $[\text{Li}_2\text{CO}_3]$ -rich inclusions (Figs. 1a, b, d, 2). In some cases these inclusions contain up to 80–90% (vol/vol) carbonates and/or bicarbonates as well as a carbonate and/or bicarbonate saturated solution and only a very small vapor bubble. The water-rich phase occupies only about 10–20% of the volume. The second type are CO_2 -rich water-poor vapor inclusions, often containing a small nahcolite crystal $[\text{NaHCO}_3]$ typically of about 2–5% (vol/vol) (Fig. 1c). The third type are volatile-rich (H_2O , CO_2) aluminosilicate melt inclusions, composed mainly of muscovite, dawsonite, and nahcolite (Fig. 3). These appear

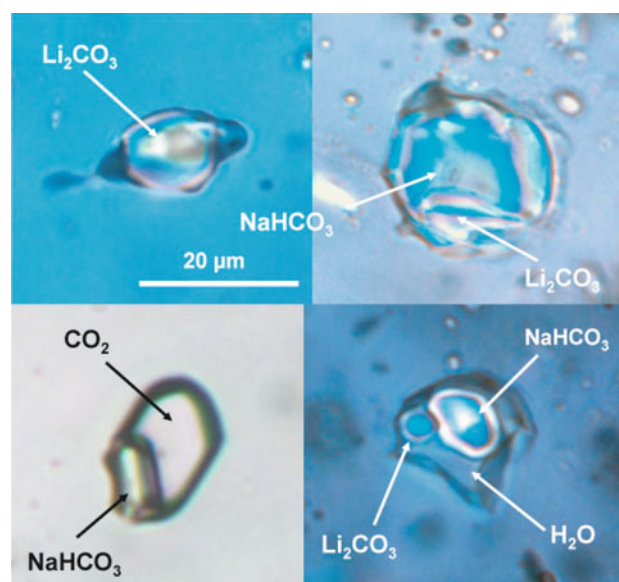


Fig. 1 Li_2CO_3 - and NaHCO_3 -rich inclusions in quartz in graphic pegmatite from Rønne, Bornholm Island/Denmark: **a** zabuyelite-rich inclusion in quartz, **b** nahcolite- and zabuyelite-rich inclusion in pegmatite quartz, **c** a CO_2 -rich inclusion with a nahcolite crystal, and **d** an inclusion containing nahcolite and zabuyelite and minor bicarbonate-rich solution. The identification is based on agreement of the optical and Raman data with synthetic standards

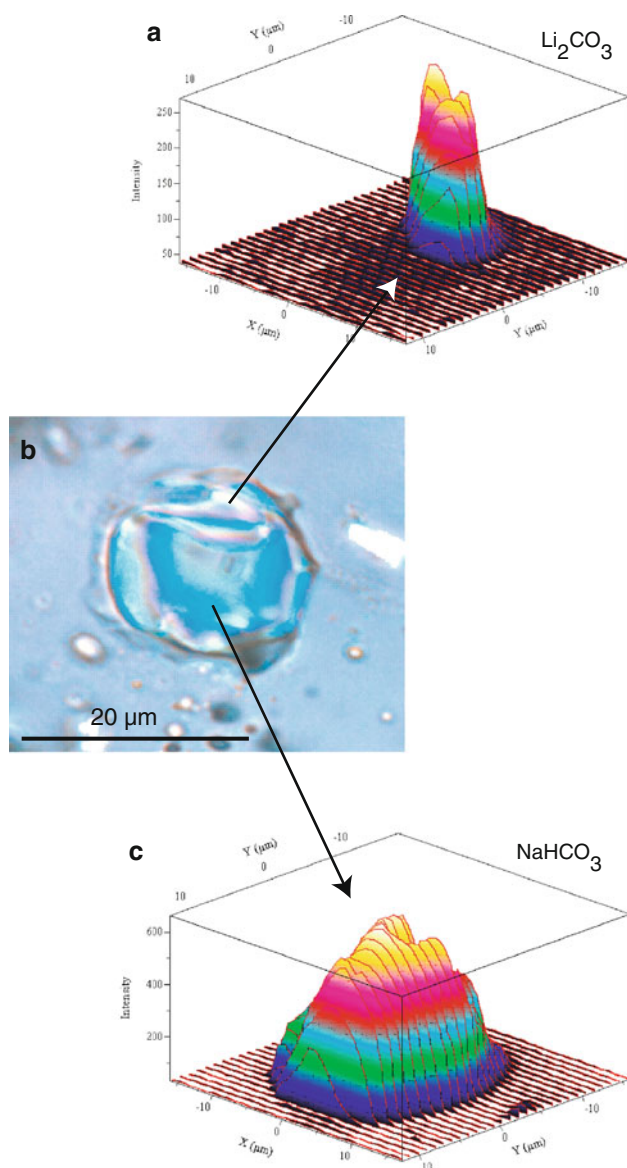


Fig. 2 High spectral resolution image of the inclusion in Fig. 1b using the ν_1 Raman bands for nahcolite ($1,046\text{ cm}^{-1}$) and zabuyelite ($1,090\text{ cm}^{-1}$). The intensity distribution of the two Raman bands is shown over the whole inclusion. The figure shows the high spatial resolution of the confocal arrangement of the Raman spectrometer used and demonstrates that both phases can be clearly distinguished: **a** distribution of zabuyelite, **b** optical image of the inclusion, and **c** distribution of nahcolite in the inclusion

to differ from the first type mainly in the presence of a significant aluminosilicate component.

Carbonate daughter crystals are characterized by high interference colors and are soluble with heating. If a microscope heating stage is used, most daughter crystal-rich inclusions decrepitate before total homogenization is attained. The small size ($<10\text{ }\mu\text{m}$) of the most inclusions also prevents study of the homogenization behavior using a hydrothermal diamond anvil cell (HDAC).

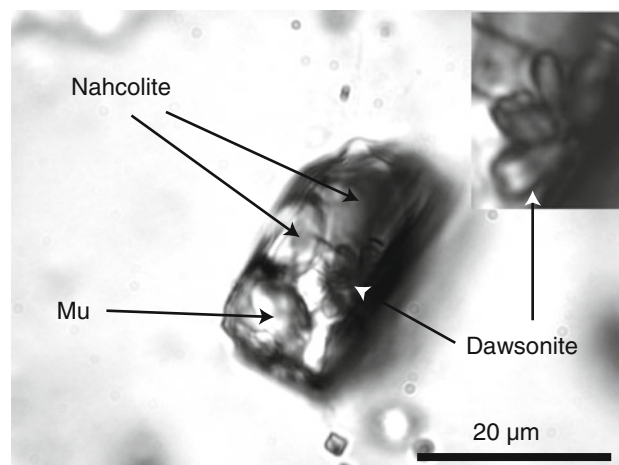


Fig. 3 A carbonate—bicarbonate-rich melt inclusion in pegmatite quartz from Rønne, Bornholm Island/Denmark containing nahcolite, dawsonite, and muscovite (Mu)

Analytical techniques

Micro-Raman spectroscopy

Raman spectroscopy is a very sensitive technique, which requires minimal sample volume and preparation. In addition, Raman spectroscopy is generally non-destructive and can be used to identify a wide range of minerals (Downs 2006). Because water is a weak scatterer of Raman radiation, Raman spectra can be obtained from daughter minerals immersed in water (i.e., in aqueous fluid inclusions). Modern confocal Raman microprobes have a lateral resolution of $\sim 1\text{ }\mu\text{m}$ and a depth resolution of $\sim 2\text{ }\mu\text{m}$ which allow confocal spectral measurements from selected regions inside mineral samples, and this enables the identification and characterization of daughter minerals in inclusions.

Raman spectra were recorded with a Jobin–Yvon LabRam HR800 spectrometer (grating: $1,800\text{ g/mm}$), equipped with an Olympus optical microscope and a long-working-distance LMPlanFI $100\times/0.80$ objective. We used a 488 nm excitation of a Coherent Ar^+ laser Model Innova 70C, a power of 300 mW (about 14 mW on sample). The spectral resolution was $\leq 0.6\text{ cm}^{-1}$. Using edge filters, we could take Raman spectra down to a wavenumber of 50 cm^{-1} . Each unpolarized spectrum represents the accumulation of six acquisitions of 20 s each. The spectra were collected at a constant laboratory temperature (20°C) with a Peltier-cooled CCD detector (-70°C), and the positions of the Raman bands were controlled and if necessary corrected using the principal plasma lines in the Argon laser. The difference between recommended and measured positions of the plasma lines in the fingerprint spectral region was not larger than 0.6 cm^{-1} .

For identification of the carbonate/bicarbonate daughter minerals we used a multistep process. The first step was to take spectra in the frequency region around $1,100\text{ cm}^{-1}$ (C–O and C–OH stretching) to test whether the solid was a carbonate or bicarbonate. Then, Raman spectra were taken in other frequency regions to identify the species based on other bands. As an example, the Raman band at 95 cm^{-1} is characteristic Li_2CO_3 (Anderson et al. 2001).

For the determination or estimation of the carbonate concentration according to Oliver and Davis (1973) in the water-rich part of the first inclusion type, we used the same device setup, except for a grating of $2,400\text{ g/mm}$. The background-corrected spectra with a second-degree polynomial were fitted using the Levenberg-Marquart method implemented in the LabSpec software by HORIBA Jobin–Yvon. The peaks were fitted with the Gauss/Lorentz function. The given calibration was verified by dilution of saturated sodium, potassium, rubidium, and cesium carbonates stock solutions with distilled water.

Microthermometry of aqueous fluid inclusions

Microthermometric measurements were performed using a calibrated LINKAM THMS 600 heating and freezing stage, together with a TMS92 temperature programmer and a LNP2 cooling system mounted on an Olympus microscope. The stage was calibrated with synthetic fluid inclusions (SYNFLINC—Goldstein and Reynolds (1994) p. 92) and melting points of different standards. All measurements were performed under argon. The standard deviation depends on absolute temperature and is always less than $\pm 2.5^\circ\text{C}$ for temperatures greater 100°C and is $\leq 0.2^\circ\text{C}$ for cryometric measurements lesser than 20°C . Samples were $300\text{-}\mu\text{m}$ -thick, doubly polished smoky quartz, and potassium feldspar chips.

The microthermometric measurements were performed to obtain information on the solute concentration in the inclusions.

Hydrothermal diamond anvil cell experiments in the pseudoternary system $\text{SiO}_2\text{--NaHCO}_3\text{--H}_2\text{O}$

General remarks

Because of the tendency of the nahcolite-rich inclusions to decrepitate, and thus the inability to easily study homogenization behavior using conventional microscope heating stages, hydrothermal diamond anvil cell experiments have been performed to provide additional evidence. Experiments in the system $\text{SiO}_2\text{--NaHCO}_3\text{--H}_2\text{O}$ provide confirmation for the assumption that such four-phase melt inclusions with CO_2 -vapor, liquid CO_2 , H_2O -rich solution,

and peralkaline silicate glass were stable as a single homogeneous volatile-rich silicate melt at high temperatures and pressures, and thus do not require formation by heterogeneous trapping (Thomas et al. 2006a). This is in accord with the consistent phase ratios in such inclusions, which also argue for trapping of a single homogenous melt, rather than heterogeneous co-trapping. Furthermore, the experiments should also show that the quartz solubility in such peralkaline solutions/melts is significantly higher than in normal hydrothermal solutions.

The experiments

A chip of natural quartz, several nahcolite crystals, and distilled water were loaded into the sample chamber of an externally heated Bassett-type hydrothermal diamond anvil cell (HDAC) (Bassett et al. 1993) equipped with ultra-low fluorescence grade diamond anvils (culet diameter 0.9 mm). Before the sample chamber, formed by the two diamonds and the Ir gasket, was sealed, an air bubble was allowed to grow by controlled leaking until the desired initial fluid density was approximately achieved. The actual NaHCO_3 concentration in the solution in the sealed sample chamber was determined from the nahcolite dissolution temperature in the presence of vapor using solubility data (Linke and Seidell 1965) and the solution model by Haynes (2003). The sample was then studied at different temperatures and pressures using visual observation and Raman spectroscopy.

The temperature in the sample chamber of the HDAC was measured using K-type thermocouples attached to the diamonds and calibrated based on the α - β quartz transition temperature (574°C at 0.1 MPa) and the triple point of H_2O (0.01°C , 0.6 kPa). The power input to the resistive heaters was controlled using Eurotherm® 2408 temperature controllers. The pressure was obtained from the calibrated frequency shift of the 464 cm^{-1} Raman line of quartz (Schmidt and Ziemann 2000; Eqs. 2 and 3 therein).

Raman spectra of sample phases in the HDAC at different P and T were acquired as described previously, except that a Nikon MPlan SLWD $40\times$ objective was used, that the laser power at the source was set to 275 mW , and that collection times (usually 10 or 20 s) and number of accumulations (usually 10 or 20) were selected such that the background was low and the signal to noise ratio was satisfactory.

Results

Melt and fluid inclusion study

Reconnaissance studies using the cold-seal pressure vessel homogenization technique (Thomas et al. 2009b,

supplementary material) were performed at 700°C, 1 kbar and 20 h to investigate the behavior of the rare volatile-rich silicate melt inclusions with heating. These experiments show that the nahcolite-bearing CO₂ inclusions do not decrepitate up to 700°C, and nahcolite is soluble at those conditions in the CO₂-phase (Fig. 4a). Figure 4b and c show melt inclusions after rehomogenization. After

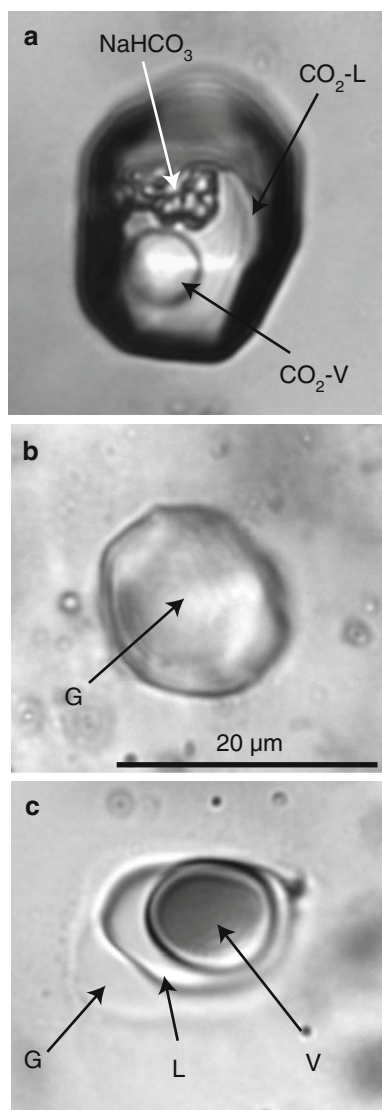


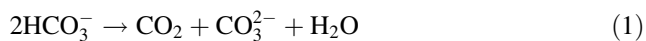
Fig. 4 Melt inclusions in pegmatite quartz from Rønne, Bornholm Island/Denmark after rehomogenization (700°C, 1 kbar, 20 h). **a** A nahcolite-bearing CO₂ inclusion after rehomogenization at 700°C. Prior to homogenization this inclusion contained a single, well-formed nahcolite crystal. The now dispersed small crystals may suggest that nahcolite completely dissolved at 700°C in the system according to the reaction $2\text{NaHCO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{melt}$. The $\pm$ volume constant ratio is also consistent with this interpretation. **b** A small, completely homogenized, relatively water-poor melt inclusion; **c** a water-rich melt inclusion containing a water-rich glass (G), a water-rich liquid phase (L), and a CO₂-rich vapor phase (V)

quenching, the melt inclusions contain a silicate glass and volatiles (H₂O-rich solution + CO₂-rich bubble).

According to Raman spectrometric studies, the inclusions in pegmatite quartz and feldspar from the Bornholm pegmatite contain mainly daughter crystals of carbonates and bicarbonates (Figs. 1, 2). The identification of the solid carbonates and bicarbonates with Raman spectroscopy is simple and unequivocal. Table 1 gives a survey of the Raman bands of interest.

From a small number of homogenization experiments on large nahcolite-rich fluid inclusions, we determined a maximum disappearance temperature of nahcolite of 253°C. The ice melting temperature of this inclusion is −6.6°C. This corresponds to about 8.0% (g/g) NaCl and 2.7% (g/g) NaHCO₃ in solution (Borisenko 1977). The nahcolite melting temperature for the solid phase corresponds to about 67.2% (g/g) nahcolite. However, this value is only an estimate, because the phase diagram of NaCl–NaHCO₃–H₂O for this temperature range is incomplete and the proportion of solid nahcolite is highly variable between inclusions. The total homogenization of these inclusions could not be determined because the inclusions always decrepitate at about 290°C. From the reduction in bubble diameter at 290°C, we estimate that the total homogenization temperature in the liquid phase should be about 320°C.

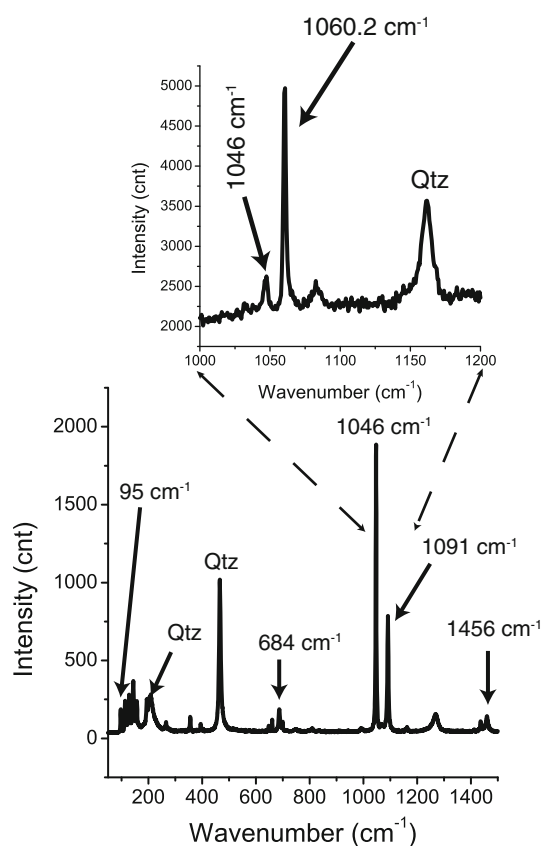
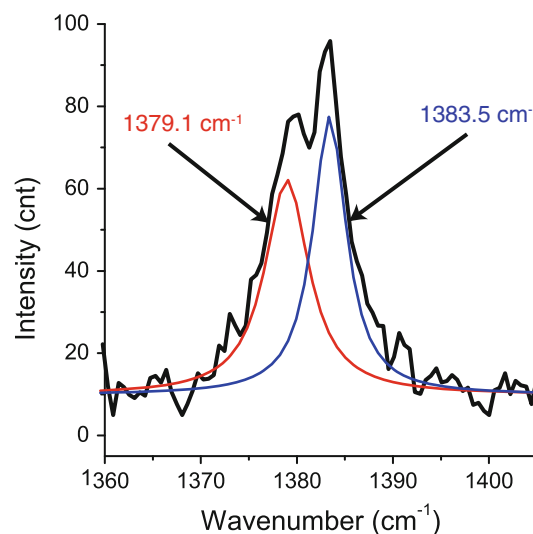
Raman spectroscopy showed that the solid phases (volumetric determined/estimated) consist mainly of nahcolite (50% (vol/vol)) and zabuyelite (10–30% (vol/vol)) in the salt-rich inclusions, and small amounts of natrite [Na₂CO₃], potash [K₂CO₃], kaliginite [KHCO₃], and nahcolite (2–5% (vol/vol)) in the H₂O-poor CO₂-rich inclusions (Fig. 5). In the water-rich phase of the first inclusion type, we determined a relatively high carbonate concentration. From measurements on 11 large inclusions (~30 µm) we obtained a plasma line-corrected position of the carbonate band ν_3 of $1,379.1 \pm 1.4 \text{ cm}^{-1}$ (Fig. 6). According to Oliver and Davis (1973), this value corresponds to a carbonate concentration of about 2.7 mol/l (mean). Because the carbonate frequencies are virtually independent of the alkali metal cation, determination of the species in solution is not possible by Raman spectroscopy, but some estimations are possible. Since about 10% of the bicarbonate decomposes to CO₂ and carbonate (Oliver and Davis 1973)



when it is dissolved in water at 25°C, a small part of the carbonate is then linked to Na₂CO₃. Since we could not identify visually Na₂CO₃ as soda crystals during cooling on a microscope cooling stage, the largest part of the carbonate must be a highly soluble alkali carbonate. The solubility at 20°C of Na₂CO₃ and K₂CO₃ is 1.71 and

Table 1 Raman main frequencies (cm^{-1}) for some carbonates and bicarbonates in fluid and melt inclusions (in this work, determined with the Jobin–Yvon LabRam HR800 spectrometer)

Species	Main Raman bands (cm^{-1})	Supplementary bands (cm^{-1})	Reference
CO_2 (gas)	1,285, 1,388, 1,370	1,409	Burke (2001)
CO_2 (solution)	1,276, 1,384		Davis and Oliver (1972)
CO_3^{2-}	684, 1,062, 1,376, 1,438		Oliver and Davis (1973)
HCO_3^-	632, 672, 1,017, 1,302, 1,360		Oliver and Davis (1973)
Li_2CO_3	1,091	96, 712, 746, 1,459	Anderson et al. (2001)
Na_2CO_3	1,078	698, 1,428	This work
K_2CO_3	1,060	234, 686	This work
Rb_2CO_3	1,062	221, 685	This work
Cs_2CO_3	1,040, 1,048	227, 662, 672, 679	This work
NaHCO_3	1,046	684, 1,266, 1,432	Downs (2006)
KHCO_3	1,028	635, 675, 1,277	This work
Calcite	1,085	156, 283, 711	Downs (2006)
Dawsonite	192, 1,091, 1,506	590, 728	Downs (2006)

**Fig. 5** Raman spectra of the main daughter phases in fluid inclusions in quartz from the Bornholm pegmatite. The lower spectrum shows the typical spectra of nahcolite [NaHCO_3] and zabuyelite [Li_2CO_3] in an inclusion (Fig. 2). The bands at 95, 1,091, and $1,456\text{ cm}^{-1}$ are typical for zabuyelite, and the band at 684 and the strong band at $1,046\text{ cm}^{-1}$ are very characteristic of nahcolite. The upper spectrum shows the wavenumber range from 1,000 to $1,200\text{ cm}^{-1}$ and the strong band at $1,060.2\text{ cm}^{-1}$ for K_2CO_3 and a weaker band at $1,046\text{ cm}^{-1}$ for the nahcolite in a CO_2 -rich inclusion in the same quartz crystal**Fig. 6** Typical resolved Raman spectrum at $1,380\text{ cm}^{-1}$ from the fluid in a carbonate/bicarbonate-rich fluid inclusion in quartz from the Bornholm pegmatite. The spectrum shows two components centered at $1,379.1$ and $1,383.5\text{ cm}^{-1}$, which corresponds to the carbonate ions and CO_2 dissolved in the solution, respectively

3.8 mol/l (Nyvt 1977), respectively. This implies that a large part of the carbonate ions are associated with potassium as K_2CO_3 . The other high-soluble carbonates (Rb_2CO_3 and Cs_2CO_3) should only be present in traces. If we recalculate the total carbonate concentration into K_2CO_3 , then we obtain 37.3% (g/g) K_2CO_3 . This value is lower than the solubility of K_2CO_3 at 20°C , which is 52.5% (g/g) in water (Nyvt 1977). Therefore, we only find solid K_2CO_3 as daughter crystals in water-free, CO_2 -rich inclusions because the solubility of K_2CO_3 in CO_2 is very low or if the concentration of K_2CO_3 is greater than 52.5% (g/g).

Based on the identified minerals in the inclusions, the fluid phase can be modeled by the pseudoternary

$\text{K}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$, or the pseudoquaternary system $\text{K}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--Li}_2\text{CO}_3\text{--H}_2\text{O}$. SiO_2 is an important component, which also enters into these systems at higher temperatures; this makes the exact treatment of such systems extremely difficult.

Raman spectroscopy shows that the gas phase of the last type of inclusions is almost pure CO_2 . All other gas components are near or below the detection limit. Based on the determined reduced peak areas (Burke 2001), the gas phase in the secondary CO_2 inclusions without any trace of nahcolite has the following composition: $X_{(\text{CO}_2)} = 0.988$, $X_{(\text{O}_2)} = 0.002$, $X_{(\text{CO})} = 0.008$ and $X_{(\text{N}_2)} = 0.002$. The Raman band of CO at $2,140\text{ cm}^{-1}$ is very characteristic for this inclusion type and demonstrates more reduced conditions. In the case of nahcolite-bearing CO_2 -rich inclusions, the composition is similar:

$$X_{(\text{CO}_2)} = 0.993, X_{(\text{O}_2)} = \text{d.l.}, X_{(\text{CO})} = 0.003, \\ X_{(\text{N}_2)} = 0.003 \text{ and } X_{(\text{H}_2)} = 0.001.$$

Methane (CH_4) is only present in trace concentration. However, a dramatic change in the composition was observed with increasing accumulation time (from 10 to 100 s) at the same laser power (14 mW on sample):

$$X_{(\text{CO}_2)} = 0.028, X_{(\text{O}_2)} = 0.048, X_{(\text{CO})} = 0.288, \\ X_{(\text{N}_2)} = 0.322 \text{ and } X_{(\text{H}_2)} = 0.314.$$

At the same time, graphite formed at the expense of CO_2 in the inclusions which had to be taken into account when determining laser settings. Such behavior has already been observed by e.g., van den Kerkhof et al. (1991) and can be explained by the simple reduction reactions:



In addition to the very alkali bicarbonate-rich inclusions in the pegmatite quartz, there are also complex inclusions mainly containing nahcolite, dawsonite $[\text{NaAl}(\text{CO}_3)(\text{OH})_2]$, and muscovite $[\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH},\text{F})_2]$ (Fig. 3). This inclusion type is relatively rare, and in our view probably represents a primary carbonate-rich silicate melt. This inclusion type contains about 20% (vol/vol) muscovite, 25% (vol/vol) nahcolite, and 12% (vol/vol) dawsonite plus an aqueous solution. A significant amount of SiO_2 was probably deposited on the inclusion wall (Thomas et al. 2008). Figure 4a and b show two melt inclusions with different glass/fluid ratio, possibly representing type-A and type-B melt inclusions in analogy to the terminology used by Thomas et al. 2000 and following papers.

Fluid-rich inclusions in clear red pegmatite feldspar (microcline) crystals sometimes also contain calcite as well

as nahcolite and zabuyelite. Presumably calcite is formed by an ion-exchange reaction of the sodium-enriched solution with anorthite component of the feldspar.

In contrast to the pegmatite, the inclusions in granite quartz contain only nahcolite- and Mg-rich calcite daughter minerals, zabuyelite was not detected.

Results of hydrothermal diamond anvil cell experiments

Several experiments were performed in the pseudoternary system $\text{H}_2\text{O} + \text{NaHCO}_3 + \text{SiO}_2$ using a hydrothermal diamond anvil cell. Phase relationships at relatively low bulk densities and temperatures to 600°C were studied on aqueous solutions with NaHCO_3 concentrations ranging from 3.0 to 5.5 molal (20.0–31.8% (g/g)), with quartz present at all conditions. As an example, the experiment on a 4.7 molal NaHCO_3 solution with quartz is documented in Fig. 7 and in the supplementary video.

For low to intermediate pressures ($<500\text{ MPa}$), important qualitative results from optical observation and Raman spectroscopy include the following:

1. at the lowest bulk densities, coexistence of two fluids in the high temperature region of the experiments: carbonate melt (usually formed by melting of natrite) and aqueous fluid,
2. a high quartz solubility at least at temperatures $>400^\circ\text{C}$ as indicated by clearly discernible changes in the size of the quartz crystal upon heating and cooling, by the formation of sodium silicate or silica quench globules, and by a much higher normalized integrated intensity of the Raman band at $\sim 770\text{ cm}^{-1}$ in the aqueous fluid compared to that from experiments with quartz and water at similar conditions,
3. a strongly enhanced conversion of $\text{HCO}_3^-(\text{aq})$ in the aqueous fluid to $\text{CO}_3^{2-}(\text{aq})$ with increasing temperature,
4. an increasing concentration of CO_2 in the vapor phase upon heating,
5. no detectable CO_2 in the aqueous liquid at temperatures $>400^\circ\text{C}$ and $<300^\circ\text{C}$.

Additional information on the cause of the strongly enhanced silica solubility was obtained from an earlier experiment with a Re gasket (Thomas et al. 2006a) at similar conditions. In this experiment, it was possible to quench the dispersed globules (similar to those in Fig. 7f) to a metastable glass with different silicate components ($\text{Na}_2\text{Si}_2\text{O}_5$, Na_2SiO_3 , and H_4SiO_4) (Fig. 8). It needs to be noted, however, that such an experiment with a Re gasket is not directly comparable to experiments using Ir gaskets, because of the shift to more alkaline conditions due to the reaction of the carbonate solution with the Re gasket,

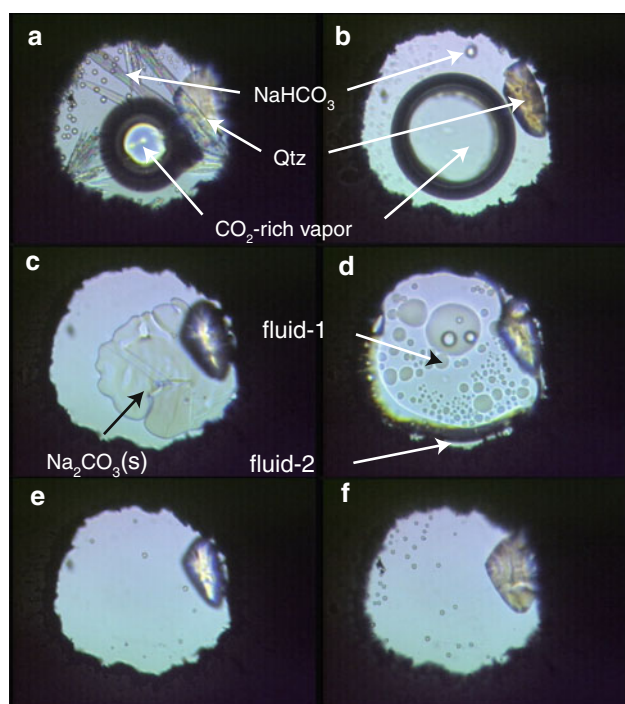
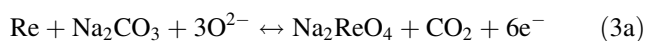


Fig. 7 Sequence of photographs of the sample chamber of the HDAC during a series of experiments with $\text{H}_2\text{O} + 4.7$ molal $\text{NaHCO}_3 + \text{quartz}$. **a** A quartz crystal, acicular crystals of nahcolite, aqueous saturated NaHCO_3 solution, a CO_2 -rich vapor bubble, and small globules of a silica-rich quench phase at 100°C after cooling from 555°C , 230 MPa. **b–e** snapshots during heating of phase assemblage shown in **(a)**, **b** the last small nahcolite crystal just before its dissolution at 155°C . This temperature corresponds to a NaHCO_3 concentration of about 4.7 molal ($\sim 28.5\%$ (g/g)). The vapor bubble disappeared at 390°C and ~ 90 MPa. **c** Twinned natrite [Na_2CO_3] crystals shortly before onset of melting at 434°C , ~ 130 MPa. The first solid that nucleated upon heating was wegscheiderite [$\text{Na}_5(\text{CO}_3)(\text{HCO}_3)_3$] at $\sim 250^\circ\text{C}$. At 370°C , natrite crystallized at the expense of wegscheiderite. **d** At about 500°C , after final melting of natrite at 459°C and ~ 150 MPa, two fluids are present—fluid 1, aqueous solution and fluid 2, a dense carbonate melt (probably with a significant sodium silicate component), mostly attached at the gasket and the quartz crystal, but also as small blebs at the diamond surface **(e)** just before complete dissolution of fluid 2 in fluid 1 at 551°C , ~ 230 MPa. Heating was stopped at this point and the sample was cooled down slowly. This resulted in formation of small amount of sodium silicate globules **(f)**. Natrite did not nucleate during cooling. Note the large volume change of the quartz crystal during heating and cooling, which indicates strongly enhanced silica solubility

forming the green metastable sodium rhenate [Na_2ReO_4] in the presence of NaOH (Noddack and Noddack 1933):



The reaction responsible for the presence of the oxide ion O^{2-} in carbonate melts is as follows:



The complete sequence of this HDAC experiment is shown in Fig. 9. During cooling, we observe a metastable

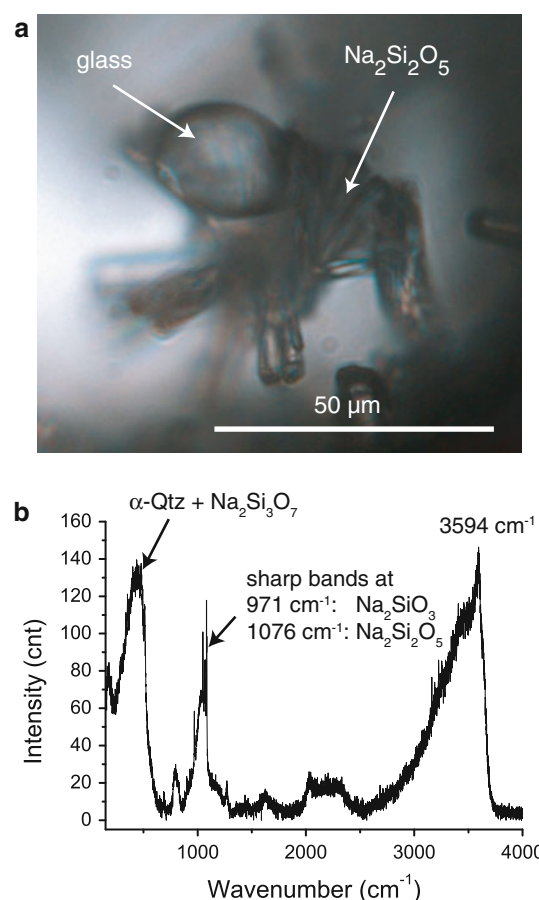


Fig. 8 **a** Detail of the sample from a HDAC experiment using a Re gasket, after quenching to room temperature. The photograph shows a glass globule attached to needles of sodium disilicate. **b** The Raman spectrum of the glass globule indicates that the quenched melt consists of sodium silicates, mostly trisilicate [$\text{Na}_2\text{Si}_3\text{O}_7$], orthosilicate [Na_2SiO_3] and disilicate [$\text{Na}_2\text{Si}_2\text{O}_5$]. The very broad band at about 410 cm^{-1} can be interpreted as a complex band with components of Na-trisilicate, α -quartz and nano-sized crystallites of SiO_2 (Krol and Janssen 1982). In the high frequency region, the broad asymmetric H_2O –OH stretching band is clearly visible. In addition, there is a strong Raman band at $3,594\text{ cm}^{-1}$, which is typical for NaOH (Zakiryanova et al. 1999). After several weeks at room temperature, the glass, and the sodium disilicate had dissociated and formed quartz crystals

well-ordered suspension of gel-like corpuscles at 448°C (Fig. 9), which is destroyed immediately after a small decrease in temperature (3°C).

Discussion

Boundary layer effect

One potential issue with any melt inclusion study is the boundary layer effect (London 2005, 2008, 2009). As a crystal grows, it will tend to create a boundary layer in which elements compatible with the growing crystal will

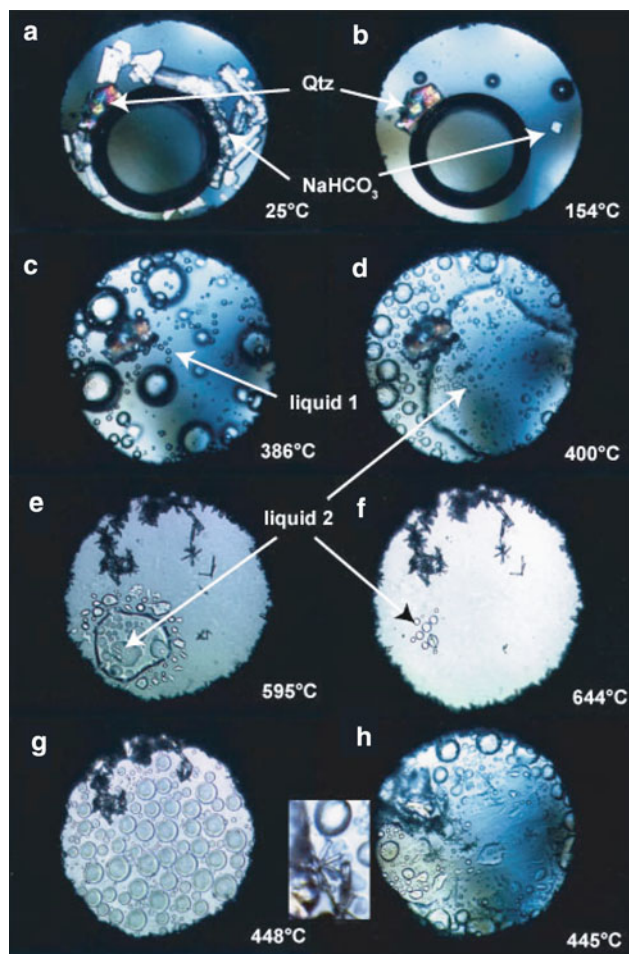


Fig. 9 Photographs of a HDAC experiment with a Re gasket and quartz, nahcolite, and water as starting materials—view into the sample chamber at different temperatures: **a** at 25°C at the start of the experiment. The sample chamber is filled with a small piece of a quartz crystal, strongly birefringent nahcolite crystals, saturated solution, and a vapor bubble. Upon heating, the vapor bubble enriches in CO_2 . **b** Just before the temperature of complete nahcolite dissolution at 154°C. This temperature corresponds to a solution concentration of about 28.2% (g/g) NaHCO_3 . (Haynes 2003). **c** Formation of abundant small bubbles of CO_2 due to the reaction $2\text{HCO}_3^-(\text{aq}) \rightarrow \text{CO}_3^{2-}(\text{aq}) + \text{CO}_2 + \text{H}_2\text{O}$. **d** A second carbonate-rich liquid phase (liquid 2) forms at about 480°C. This phase consumed all quartz upon heating to 480°C, and converted to a Na-silicate fluid (liquid 2) coexisting with an aqueous fluid (liquid 1). **e, f** The Na-silicate fluid dissolved completely in the aqueous fluid at 646°C. Upon cooling to 448°C, this homogeneous solution separated suddenly into two liquid phases (**g**), one form resembles erythrocytes suspended in blood plasma. Gaseous CO_2 was only present at temperatures less than 400°C, above this temperature CO_2 was present as carbonate/bicarbonate complexes. **h** At 445°C, the suspension changed suddenly into a more gel-like suspension. Furthermore, very small needle-like crystals of $\text{Na}_2\text{Si}_2\text{O}_5$ crystallized (for detail, see photograph). The needle-like black crystals are Re oxides formed from the Re gasket

be depleted, and incompatible elements will be enriched. Melt inclusions trapped from this layer will therefore be to some degree unrepresentative of the bulk melt. However,

this layer is limited by the diffusion rate, the melt viscosity, and possibly various forms of external stirring. In viscous silicate melts this effect may or may not be significant (Baker 2008). However, in very low viscosity melts the boundary layer should be negligible in extent, and physically unstable, points which have been dealt with at length in (Thomas et al. 2009a, b) among others. In the present case we will restrict ourselves to some points particularly pertinent to Bornholm. If the melt inclusion compositions are representative of a boundary layer, then that boundary layer has a viscosity probably less than 10^{-2} Pa•s, and possibly much less, which can be compared with the viscosity of water at 20°C of 10^{-3} Pa•s. As such it would be gravitationally unstable and would inevitably pond on the chamber roof. Moreover, while melt inclusions with carbonate/bicarbonate-rich silicate melts are abundant, melt inclusions with low H_2O concentrations (3–5% (g/g)) supposed some authors (e.g., London 2009) to be typical of pegmatite melts have not been observed at Bornholm, or indeed in any of the suites examined by the authors (Thomas et al. 2008, 2009a, b; Thomas and Davidson 2008). On the issue of viscosity we would also observe that low H_2O melts proposed as “characteristic” pegmatite forming melts would have viscosities of $\sim 10^5$ Pa•s at 700°C and very much higher (10^8 Pa•s) if undercooled to 450°C (London 2009) would have been very difficult to emplace in the forms and conditions at Bornholm, and almost impossible at any distance from a batholith (e.g., the Froland pegmatites in Norway—in preparation). Thus, in the conditions present in the Bornholm pegmatites we do not consider that significant boundary layers could develop, and that the melt inclusions are representative of the bulk melt in the melt pocket in which the crystals grew.

Crystallization media of fluorine- and boron-poor pegmatites

The discovery of primary alkali carbonate/bicarbonate-rich inclusions provides possible constraints on the media responsible for crystallization of fluorine- and boron-poor pegmatites. Eutectic carbonate melts in the system $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ have a very low viscosity. According to Ejima et al. (1987) the viscosity of the ternary carbonate eutectic at 500, 700, and 900°C is 18.66, 6.36, and 3.14 mPa•s, respectively. Water has a viscosity of 1.0 mPa•s at 20°C. In a water-bearing alkali carbonate melt the viscosity should be further reduced, as we can conclude from all of our HDAC experiments, which show highly mobile particles and bubbles.

In the HDAC experiment documented in Fig. 7 and the video in the supplementary material we show, as well as some interesting phase changes, that quartz is highly soluble in such a nahcolite-rich fluid, and that the

dissolved quartz (in the simplest case as $\text{Na}_2\text{Si}_2\text{O}_5$) will be deposited on the same crystal. Only a very small amount of the Si-rich melt is dispersed in the chamber. This means for a natural melt inclusion in quartz with such a water-rich silicate melt that during cooling SiO_2 is deposited on the inclusion wall and makes an apparent fluid inclusion from what was a primary melt inclusion. In contrast to fluid inclusion of the system $\text{NaCl-H}_2\text{O}$, the HDAC experiments show clearly that NaHCO_3 -bearing inclusions show very different homogenization behavior and also that in the presence of alkali bicarbonate/carbonate at high temperatures the inclusion system is not isochoric due to the high solubility of the quartz host. Furthermore, the experiments demonstrate that the dissolved quartz is already deposited epitaxially on the remaining quartz crystal at cooling—similar to the deposition on the inclusion wall in the case of natural inclusions. Our HDAC experiments with almost the same composition show that small variations in the bulk density produce dramatically different system behavior on cooling and heating. The reason for this can be seen from the three-dimensional phase diagram for the ternary system $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--H}_2\text{O}$ at 425°C given by Urusova and Valyashko (2005). Variation in temperature, pressure, and density has a large influence on the phase behavior.

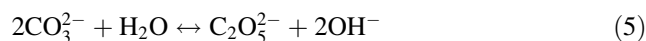
Furthermore, the experimental setup can have a dramatic influence—by using Re gaskets we have observed a different behavior of the system as a result of the formation of NaOH by the reaction of the carbonate solution with the gasket. Thus, the presence of high-field strength elements in natural inclusions can have also a profound influence to the chemical behavior in the inclusion system.

From hydrothermal diamond anvil cell (HDAC) experiments (Thomas et al. 2006a and the present work) on the $\text{SiO}_2\text{--NaHCO}_3\text{--H}_2\text{O--CO}_2$ system with about 30% (g/g) NaHCO_3 we know that such fluid can react very rapidly with quartz at about $400\text{--}600^\circ\text{C}$, forming in the simplest case an aqueous Na disilicate fluid, coexisting with a carbonate-rich fluid. Before the reaction starts, sodium hydroxide forms as an intermediate phase at about 450°C , which would indicate a sudden and significant increase in reactivity of the fluid. This was demonstrated on the first runs where we used a Re gasket in the HDAC experiments. This produced strong green coloring of the alkali-bearing melt with cooling (which indicates increased oxidation) immediately before the formation of sodium perhenate via reaction with sodium hydroxide (Noddack and Noddack 1933), which is a very strong Raman scatterer (Thomas et al. 2006a). In subsequent experiments we used Ir gaskets to prevent dissolution of the gasket. The Na disilicate dissolves at about 550°C into a homogeneous liquid phase. CO_2 is completely dissolved up to this temperature.

Gaseous CO_2 is only formed at temperatures lower than 400°C , above this temperature CO_2 is completely consumed as carbonate/bicarbonate complexes and later dissolved as CO_2 in the liquid. According to Claes et al. (1996), the solubility of CO_2 in carbonate melts is unusually high. The results of this study demonstrate also a very high solubility of CO_2 in highly concentrated alkali carbonate solutions at high temperatures. We can assume that carbon dioxide occurs in the water-rich melt partly as the molecular species CO_2 but principally as a dicarbonate ion $\text{C}_2\text{O}_5^{2-}$ produced by an addition reaction of CO_2 with carbonate ions (Claes et al. 1996):

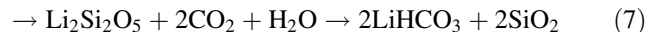
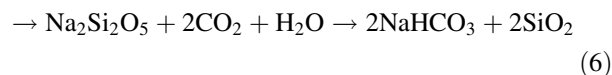


Zeller et al. (2005) discussed an almost complete conversion of carbonate into dicarbonate according to the overall reaction (5):

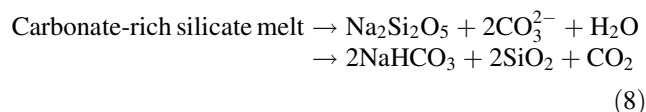


The presence of the daughter mineral phases nahcolite [Na_2CO_3] and zabuyelite [Li_2CO_3] in natural inclusions in high concentrations suggests further important reactions during the crystallization of the pegmatite-forming melt:

Carbonate-rich silicate melt



Another similar reaction can be derived from the observation of CO_2 -rich inclusions in quartz with small nahcolite crystals:



The SiO_2 component crystallized on the inclusion wall; only nahcolite and dense CO_2 remain visible.

Li bicarbonate is not a stable compound at room temperature, and on cooling it forms the stable phase Li_2CO_3 which has a low and reciprocal solubility in water (Anderson et al., 2001). At low temperatures ($<400^\circ\text{C}$) the alkali disilicates are not stable at presence of CO_2 . According to Eqs. 6 and 8 the released SiO_2 will be deposited epitaxially on the inclusion wall. Thus, the originally water- and carbonate-rich melt inclusion is transformed into an apparent fluid inclusion (Thomas et al. 2008). If one does not recognize this mimicry, the interpretations of the inclusion data can lead to completely erroneous conclusions.

Using Eq. 6 we can calculate from the nahcolite concentration the equivalent SiO_2 concentration, 30% (g/g) NaHCO_3 corresponds to 21.5% (g/g) SiO_2 .

The detection of significant amounts of natrite [Na_2CO_3], potash [K_2CO_3], kaliginite [KHCO_3], and nahcolite (2–5% (vol/vol)) in pure CO_2 -rich inclusions suggests that these inclusions are genetically linked to the nahcolite- and zabuyelite-rich inclusions. Because of low water concentrations in these CO_2 -rich inclusions the alkali carbonates and bicarbonates [Na_2CO_3], potash [K_2CO_3], and kaliginite [KHCO_3] could be unequivocally detected. According to Nyvlt (1977) the solubility of these compounds in water is very high: at 20°C they are 18.1, 52.5, and 25.0% (g/g), respectively.

According to Oliver and Davis (1973), the position of the ν_3 Raman band ($\sim 1,380\text{ cm}^{-1}$) for alkali carbonate solutions is independent of the alkali metal cations and show a small shift with the concentration, from $1,383\text{ cm}^{-1}$ at a concentration of 0.1 mol/l to $1,376\text{ cm}^{-1}$ at 8.0 mol/l. Likewise, the major Raman band ($\sim 1,017\text{ cm}^{-1}$) for alkali bicarbonates in H_2O shows a similar behavior. This means, at relatively low concentrations the alkali carbonates [Na_2CO_3] and potash [K_2CO_3] as well as kaliginite [KHCO_3] should not be found as daughter mineral phases in H_2O -dominated inclusions. However, in CO_2 -rich inclusions the solubility of these compounds is at room temperatures very low, and we found these phases as daughter minerals in CO_2 -rich inclusions in pegmatite quartz from Bornholm. The detection of potash [K_2CO_3] as a separate phase in CO_2 -rich inclusions presents a first description of the well-known compound as a new mineral in nature. Experimental work on the system $\text{NaAlSi}_3\text{O}_8\text{--Na}_2\text{CO}_3\text{--H}_2\text{O}$ by Koster van Groos and Wyllie (1968) has studied among other things the join $\text{NaAlSi}_3\text{O}_8\text{--Na}_2\text{CO}_3$ with 30% (g/g) H_2O at 3 kbar. From these studies it follows that the low-temperature boundary of the miscibility gap $L_1 + L_2 + V$ lies between 690 and 700°C (with L_1 —silicate-rich liquid, L_2 — Na_2CO_3 -rich liquid, V — H_2O and CO_2 -rich vapor). The closing of the miscibility gap was not attained, or more probably not observed, using the cold-seal pressure vessels of the Tuttle type.

From inclusion work, using rapid quench and cold-seal pressure vessels homogenization experiments on natural melt inclusions and from hydrothermal diamond anvil cell experiments with the synthetic $\text{SiO}_2\text{--NaHCO}_3\text{--H}_2\text{O}$ system, it follows that closing of the miscibility gap at reasonable pressure and temperature conditions is possible. However, more work is necessary for further clarification.

According to our observation the largest number of the carbonate/bicarbonate-rich inclusions in the Bornholm pegmatite was found in the graphic quartz within microcline crystals, and only insignificant secondary events (late hydrothermal overprinting) overprint the original state. Due to the crystallization of the K-feldspar from the original carbonate- and water-rich silicate melt, the residual

melt was gradually enriched in sodium, for example, as Na disilicate, from which the graphic quartz crystallized. In this quartz we find extremely abundant randomly dispersed nahcolite-rich inclusions of different sizes, and with very different crystal/fluid ratio. Moreover, the quartz also contains abundant submicroscopic fluid inclusion ($\sim 3 \times 10^{10}$ inclusions/ cm^3) which gave the quartz a cloudy appearance.

Between crossed Nicols, interference colors in basal sections of quartz crystals show curved lamellae with flamboyant extinction in more or less radial strips around quartz cores. This internal structure of the quartz together with the dispersed nahcolite crystals and the submicroscopic inclusions suggests crystallization from a gel-like media, rich in silica, and with abundant sodium and carbonates (Fig. 10). Rare melt inclusions in the same crystal may demonstrate incomplete melt/gel separation. Evidence for the existence of silica or silica-based gels in pegmatites

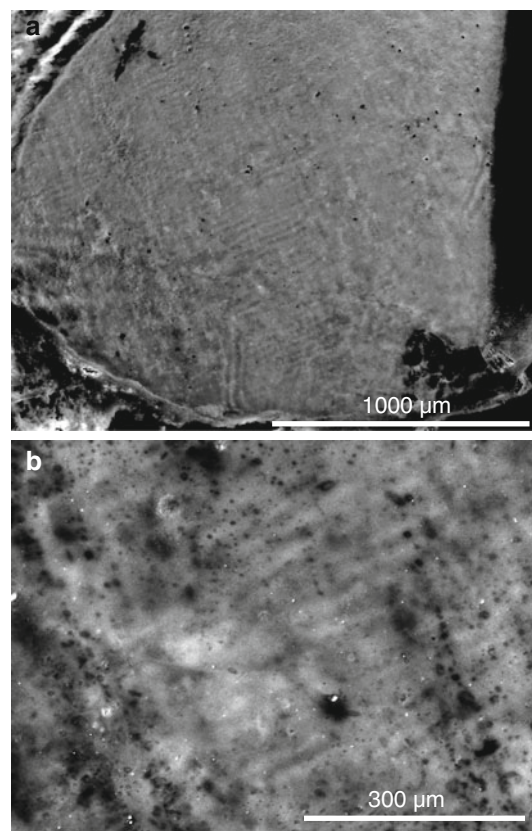


Fig. 10 Photomicrograph of a quartz grain in the graphic granite from the Rønne pegmatite/Bornholm **a** showing micelle-like crystallites. The fringes are transition phases between the crystalline and amorphous regions. This quartz grain contains abundant of nahcolite-rich primary fluid inclusions, as well as melt inclusions. **b** Is a magnified detail of the upper photograph, demonstrating that the micelle-like crystallites are not the result of strain-induced birefringence

remains tantalizing, and experimental work (e.g., HDAC) on melts at high (and poorly constrained) temperatures, pressures, and compositions remains inconclusive. We hypothesize that during crystallizations of extremely water-rich melts, commonly enriched in other volatile components, a final silica- and water-dominated residual melt passes into a state more closely resembling a gel than a conventional melt. However, much more work will be required if we are to understand the nature and behavior of high temperature silica gels. In passing we note that HDAC methods provide a much enhanced experimental capability, since they allow observation, and even analyses, of transient intermediate states. This is in distinct contrast to most high temperature and pressure experiments which permit only those states which can be quenched to be preserved.

From experimental investigations of phase equilibria in the system $\text{Na}_2\text{CO}_3\text{--K}_2\text{CO}_3\text{--H}_2\text{O}$ by Urusova and Valyashko (2005), it follows that from a homogeneous supercritical fluid with high contents of Na_2CO_3 and K_2CO_3 a strong and simple separation between Na and K by heterogenization is possible. Moreover, such hot alkali- and carbonate-rich fluids can react as metasomatic agents and could conceivably transform silicate protoliths into pegmatites. This could provide a mechanism for pegmatite formation in terrains where large granite batholiths, typically considered as necessary sources for heavy concentrations of pegmatites, are missing (e.g., the Froland pegmatites in Norway). This effect would also tend to push final compositions to more quartz-rich values.

Other examples of carbonate/bicarbonate-rich granite pegmatites

Generally, alkali carbonate/bicarbonate-rich fluids are not rare in granite pegmatites. Similar zabuyelite-bearing carbonate-rich fluids were found in spodumene-hosted fluid inclusions from Bikita and Kamativi, Zimbabwe, and Tanco, Manitoba, Canada (Anderson et al. 2001). We have observed fluid inclusions in spodumene (taken during the PEG2009 field trip) from the Capoeira 1 pegmatite, Borborema/Brazil which contain only daughter crystals of quartz, mica and zabuyelite, and a bicarbonate-rich solution, showing the crystallization of the spodumene from a water- and Li-rich aluminosilicate melt. Nahcolite-rich fluid inclusions were found in Tanco, Canada, and Orlovka, Transbaikalia, Russia (35.0% (g/g) NaHCO_3 , 5.3% (g/g) NaCl), in the Borboremea pegmatite field, Brazil, and also at Zinnwald, E-Erzgebirge, as well as in the tungsten deposit Pechtelsgrün, W-Erzgebirge, both in Germany. In the case of Pechtelsgrün, as an example, from the study of ten large fluid inclusions the following temperatures of phase changes were determined (Thomas et al. 2006b):

Eutectic melting temperature: -21.7°C

Ice melting temperature: $-10.0 \pm 0.2^\circ\text{C}$

Nahcolite melting temperature: $146 \pm 3^\circ\text{C}$.

According to the ternary system $\text{NaHCO}_3\text{--NaCl--H}_2\text{O}$ (Borisenko 1974, 1977), the composition of the fluid phase is for the measured temperatures:

20.9% (g/g) NaHCO_3 , 10.3% (g/g) NaCl, and 68.8% (g/g) H_2O .

The homogenization behavior of these fluid inclusions from Pechtelsgrün with a bulk salt content of about 31% (g/g) is even more unusual. At room temperature the vapor bubble occupies a volume of about 28% (vol/vol). During heating, the bubble shrink up to about 400°C and then enlarge quickly to a volume of about 50% (vol/vol). At 403°C , a new vapor bubble forms inside the large initial vapor bubble, now transformed into a liquid phase; thus, at this temperature three different phases are present: two liquids phases and a vapor phase. The homogenization occurs into the vapor phase by increase of the newly formed vapor bubble at $500 \pm 10^\circ\text{C}$. The homogenization behavior is reproducible. The following sequence of phase transition could be observed: at room temperature, solid + liquid + vapor; heating up to 400°C , liquid + vapor; at 403°C , liquid 1 + liquid 2 + vapor; further heating, liquid 1 + vapor; 500°C , vapor only.

KHCO_3 -rich fluid inclusions (with up to 40% (g/g) KHCO_3) were described by Schmidt and Thomas (1990) from Nb-Ta-pegmatites from the northern part of Mozambique. The study of samples from the quartz core from the Muiane pegmatite, Mozambique, has shown that nahcolite- and dawsonite-rich inclusions are very common. Typically the dawsonite-rich inclusions are surrounded by satellite-like, smaller nahcolite-rich inclusions, probably formed by decrepitation of the originally homogeneous melt inclusion shortly after trapping, possibly as a result of the pressure increase caused by the change in the speciation of the carbonate to CO_2 .

Dawsonite-rich inclusions were described by Sirbescu and Nabelek (2003a, b) from the Harney Peak granite-pegmatite system of the Black Hills, South Dakota from which these authors proposed a crystallization of a compositionally complex melt at very low temperatures ($\sim 400\text{--}350^\circ\text{C}$). However, these authors do not appear to have considered the epitaxial growth of quartz on the inclusion wall from silica dissolved in the alkali-rich melt. In our view, the failure to recognize this has produced a number of erroneous conclusions for the temperature of pegmatite-forming processes.

Carbonate- and water-rich melts trapped as H_2O - and CO_2 -rich melt inclusions (Fig. 11) were also found in the quartz core of the Hühnerkobel pegmatite near Bodenmais,

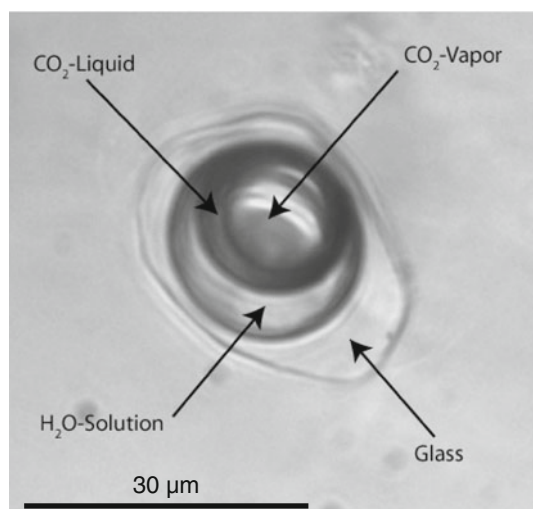


Fig. 11 A volatile-rich melt inclusion in pegmatite quartz from Zwiesel near Bodenmais, S-Germany. After homogenization at 650°C and a pressure of 3 kbar the homogenous, but metastable water-rich glass, decomposed during quenching into four phases. At room temperature, we observe a peralkaline water-rich glass, an aqueous carbonate-rich as well as liquid and gaseous carbon dioxide. The phases in the inclusion are arranged according density solution

Bavaria, Germany (Thomas et al. 2006a). After rehomogenization at 700°C and 3 kbar and following quenching, these large inclusions are characterized by four different phases at room temperature: (i) a water-rich glass with 21.9% (g/g) H₂O and with a low refractive index (like Fig. 4c). The glass component of the inclusion occupies 53% (vol/vol), (ii) an aqueous liquid phase (22% (vol/vol)), (iii) a liquid CO₂ phase (25% (vol/vol)) and (iv) a CO₂-vapor bubble. The bulk water content is 36.5% (g/g), and the bulk density is about 1.34 g/cm³ (Thomas et al. 2006a). These large inclusions, which can be homogenized using the rapid quench technique to a metastable glass without decrepitation, are very important because here the four different phases can be seen. In large inclusions the metastable glass disassociates during quenching into the four different phases. Small inclusions, which are the rule, are not generally so instructive.

Conclusions

The alkali carbonate/bicarbonate concentrations in fluid (formerly melt) inclusions in pegmatite quartz and feldspar reported in this study are currently the highest observed concentration found in granite-pegmatite systems. However, the occurrence of such alkali carbonates and bicarbonates in pegmatite minerals is not rare and has been reported in the literature. Our own research has found such inclusions in almost all granite pegmatites that we have studied worldwide. Although high concentrations

of alkali carbonate/bicarbonate concentrations in fluid inclusions in pegmatite minerals are common, the significance of such media for the formation of granite pegmatite has been little appreciated. This in part may be due to the fact that extremely water, and alkali carbonate- and bicarbonate-rich melts dissociate into vapor, liquid, and daughter mineral phases on cooling, and silica is largely deposited epitaxially (and thus invisibly) on inclusion wall, converting a true primary MI into an inclusion which erroneously resembles a high density fluid inclusion.

Being highly soluble in water at all temperatures alkali carbonates and bicarbonates are fugitive in pegmatites, so evidence may only survive where trapping as MI or FI has occurred. They, plus water and other volatiles, may be the significant difference between the composition of parental melts for granites and granitic pegmatites, when the post-magmatic composition of both are so similar.

The presence of high carbonate/bicarbonate concentrations permits highly volatile-rich melts to be stable under geologically reasonable conditions for pegmatites, as shown by HDAC experiments. In such melts, the extremely low viscosity, and thus very high diffusion rates, makes boundary layer effects unlikely to be significant.

Carbonate/bicarbonate-rich fluids can be extremely reactive depending on pressure and have the potential to acquire silica at or near the site of emplacement, and they have extremely low viscosities, which may help explain very thin, laterally extensive, compositionally simple pegmatites emplaced into relatively cool rocks at great distance from any felsic magma bodies (London 2008, pp. 104–105; Ihlen and Müller 2009; Müller et al. 2009).

Carbonate/bicarbonate inclusions are also abundant in the quartz core of pegmatites. Although controversial, textures have been described herein suggestive of crystallization from a silica-rich gel. We speculate that this may mean that the extreme enrichment of SiO₂ in the quartz core of some pegmatites can be traced back to highly mobile alkali silicates as sols or gels.

Although this paper has concentrated on simple granitic pegmatites, alkali carbonate- and bicarbonate-rich solutions are also very important transport media for many ore-forming elements such as Be, Nb, Ta, W, Sn, Au and others (e.g., Letnikov 2009). Thus, where REE and rare metals are present in the source melts, carbonate- and bicarbonate-rich fluids could make efficient metal transport media, so this mechanism for pegmatite formation may provide a link to REE and rare metal pegmatites.

Acknowledgments We thank P. and E. Bankwitz (Potsdam) for key samples from the Bornholm Island, Denmark, taken in the years 1993 and 2005 and T. Jogart for the introduction into the basement geology

of Bornholm during the field excursion in October 1993, as well as A. Müller and P. Ihlen for the introduction into the Froland pegmatite field in S-Norway in 2007. Critical reviews by two anonymous reviewers, which helped to improve the manuscript, are greatly appreciated.

References

- Anderson AJ, Clark AH, Gray S (2001) The occurrence and origin of zabuyelite (Li_2CO_3) in spodumene-hosted fluid inclusions: implications for the internal evolution of rare-element granitic pegmatites. *Can Mineral* 39:1513–1527
- Baker DR (2008) The fidelity of melt inclusions as records of melt composition. *Contrib Mineral Petrol* 156:377–395
- Bassett WA, Shen AH, Bucknum M, Chou I-M (1993) A new diamond anvil cell for hydrothermal studies to 2.5 GPa, from -190 to $1,200^\circ\text{C}$. *Rev Sci Instrum* 64:2340–2345
- Beyssac O, Coffé B, Chopin C, Rouzaud JN (2002) Raman spectra of carbonaceous material in metasediments: a new geothermometer. *J Metamorphic Geol* 20:859–871
- Borisenko AS (1974) Determination of sodium carbonates and bicarbonates in solutions of gas–liquid inclusions in minerals. *Akad Nauk SSSR Doklady* 214:917–920 (in Russian)
- Borisenko AS (1977) Cryometric technique applied to studies of the saline composition of solution in gaseous fluid inclusions in minerals. *Geologiya i Geofizika AN SSSR SO* 8:16–27 (in Russian)
- Burke EAJ (2001) Raman microspectrometry of fluid inclusions. *Lithos* 55:139–158
- Claes P, Thirion B, Glibert J (1996) Solubility of CO_2 in the molten Na_2CO_3 – K_2CO_3 (42 mol%) eutectic mixture at 800°C . *Electrochim Acta* 41:141–146
- Davis AR, Oliver BG (1972) A vibrational-spectroscopic study of the species present in the CO_2 – H_2O system. *J Sol Chem* 1:329–339
- Downs RT (2006) The RUFFTM Project: an integrated study of the chemistry, crystallography, Raman and infrared spectroscopy of minerals. Program and abstracts of the 19th general meeting of the international mineralogical association in Kobe, Japan, O03-13
- Ejima T, Sato Y, Yamamura T, Tamai K, Hasebe M, Bohn MS, Janz GJ (1987) Viscosity of the eutectic Li_2CO_3 – Na_2CO_3 – K_2CO_3 melt. *J Chem Eng Data* 32:180–182
- Goldstein RH, Reynolds TJ (1994) Systematics of fluid inclusions in diagenetic minerals. *SEPM ShortCourse* 31. *SEPM (Society for Sedimentary Geology)*, 199 p
- Haynes HW (2003) Thermodynamic solution model for trona brines. *AIChE J* 49:1883–1894
- Ihlen PM, Müller A (2009) Rare-metal pegmatites in the Sveconorwegian orogen (0.9–1.1 Ga) of southern Norway. *Estud Geol* 19:140–144
- Jørgart T (2001) Bornholms Grundfjelds Geologi. Excursion guide, University Roskilde, Denmark, Publication 111:1–38 (in Danish)
- Koster van Groos AF, Wyllie PJ (1968) Liquid immiscibility in the join $\text{NaAlSi}_3\text{O}_8$ – Na_2CO_3 – H_2O and its bearing on the genesis of carbonatites. *Am J Sci* 266:932–967
- Krol DM, Janssen RK (1982) Raman study of the chemical reactions during the melting of a 15 Na_2CO_3 –10 BaCO_3 –75 SiO_2 batch. *J Phys Colloque C9, Suppl* 12(43):347–350
- Letnikov FA (2009) Autonomous fluid systems of the continental crust. *Doklady Earth Sci* 427A:947–949
- Linke WF, Seidell A (1965) Solubilities of inorganic and metal-organic compounds, vol II, 4th edn. *Am Chem Soc, Washington*
- London D (1992) The application of experimental petrology to the genesis and crystallization of granitic pegmatites. *Can Mineral* 30:499–540
- London D (2005) Granitic pegmatites: an assessment of current concepts and directions for the future. *Lithos* 80:281–303
- London D (2008) Pegmatites. *Can Miner Special Publication* 10
- London D (2009) The Origin of primary textures in granitic pegmatites. *Can Miner* 47:697–724
- Müller A, Ihlen PM, Larsen RB, Spratt J, Seltmann R (2009) Quartz and garnet chemistry of south Norwegian pegmatites and its implications for pegmatite genesis. *Estud Geol* 19:20–24
- Mustart DA (1972) Phase relations in the peralkaline portion of the system Na_2O – Al_2O_3 – SiO_2 – H_2O . Dissertation, Stanford University, USA
- Noddack I, Noddack W (1933) *Das Rhenium*. Leipzig, 86 p
- Nyvt J (1977) *Solid-liquid equilibria*. Elsevier, Amsterdam, 248 p
- Oliver BG, Davis AR (1973) Vibrational spectroscopic studies of aqueous alkali metal bicarbonate and carbonate solutions. *Can J Chem* 51:698–702
- Schmidt W, Thomas R (1990) Zur Genese von Seltenmetall-Granitpegmatiten auf der Grundlage von Einschlußuntersuchungen und geochemischen Betrachtungen. *Z Geol Wiss Berlin* 18:301–314
- Schmidt C, Ziemann MA (2000) In situ Raman spectroscopy of quartz: a pressure sensor for hydrothermal diamond-anvil cell experiments at elevated temperatures. *Am Miner* 85:1725–1734
- Sirbescu M-LC, Nabelek P (2003a) Crustal melts below 400°C . *Geology* 31:685–688
- Sirbescu M-LC, Nabelek P (2003b) Crystallization conditions and evolution of magmatic fluids in the Harney Peak Granite and associated pegmatites, Black Hills, South Dakota—evidence from fluid inclusions. *Geochim Cosmochim Acta* 67:2443–2465
- Thomas R, Davidson P (2008) Water and melt/melt immiscibility, the essential components in the formation of pegmatites; evidence from melt inclusions. *Z Geol Wiss Berlin* 36:347–364
- Thomas R, Webster JD, Heinrich W (2000) Melt inclusions in pegmatite quartz: complete miscibility between silicate melts and hydrous fluids at low pressure. *Contrib Mineral Petrol* 139:394–401
- Thomas R, Schmidt C, Veksler I, Davidson P, Beurlen H (2006a) The formation of peralkaline pegmatitic melt fractions: evidence from melt and fluid inclusion studies. *Anais da Academia Brasileira de Ciencias* 16:61–67
- Thomas R, Webster JD, Davidson P (2006b) Understanding pegmatite formation: the melt and fluid inclusion approach. Melt inclusion in Plutonic rocks, *MAC Short Course* 36, Chap 9, pp 189–210
- Thomas R, Davidson P, Hahn A (2008) Ramanite-(Cs) and ramanite-(Rb): New cesium and rubidium pentaborate tetrahydrate minerals identified with Raman spectroscopy. *Am Mineral* 93:1034–1042
- Thomas R, Davidson P, Badanina E (2009a) A melt and fluid inclusion assemblage in beryl from pegmatite in the Orlovka amazonite granite, East Transbaikalia, Russia: implications for pegmatite-forming melt systems. *Mineral Petrol* 96:129–140
- Thomas R, Davidson P, Rhede D, Leh M (2009b) The miarolitic pegmatites from the Königshain: a contribution to understanding the genesis of pegmatites. *Contrib Mineral Petrol* 157:505–523
- Urusova MA, Valyashko VM (2005) Supercritical phase equilibria in the ternary water-salt system Na_2CO_3 – K_2CO_3 – H_2O . *Russ J Inorg Chem* 50:1754–1767
- van den Kerkhof AM, Touret JLR, Maijer C, Jansen JBH (1991) Retrograde methane-dominated fluid inclusions from high-temperature granulites of Rogaland, southwestern Norway. *Geochim Cosmochim Acta* 55:2533–2544

Zakiryanova ID, Khokhlov VA, Kochedykov VA (1999) Raman spectra and microdynamics of the hydroxide-ion in molten NaOH and NaCl-NaOH mixtures. *J Molecular Liquids* 83: 153–162

Zeller K-P, Schuler P, Haiss P (2005) The hidden equilibrium in aqueous sodium carbonate solutions—evidence for the formation of the dicarbonate anion. *Eur J Inorg Chem* 2005:168–172