Observations on the crystallization of spodumene from aqueous solutions in a hydrothermal diamond-anvil cell

J. LI, I.-M. CHOU, S. YUAN AND R. C. BURRUSS

MLR Key Laboratory of Metallogeny and Mineral Assessment, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing, China; U.S. Geological Survey, National Center, Reston, VA, USA; Laboratory for Experimental Study Under Deep-sea Extreme Conditions, Sanya Institute of Deep-sea Science and Engineering, Chinese Academy of Sciences, Sanya, China

ABSTRACT

Crystallization experiments were conducted in a new type of hydrothermal diamond-anvil cell (HDAC; type V) using LiAlSi₂O₆ (S) gel and H₂O (W) as starting materials. A total of 21 experiments were performed at temperatures up to 950°C and pressures up to 788 MPa. In the samples with relatively low W/S ratios, many small crystals formed in the melt phase during cooling. In those with high W/S ratios, only a few crystals with smooth surfaces crystallized from the aqueous fluid in the presence of melt droplets, which were gradually consumed during crystal growth, indicating rapid transfer of material from the melt to the crystals through the aqueous fluid. The nucleation of crystals started at 710 (±70°C) and 520 (±80) MPa, and crystal growth ended at 570 (±40°C) and 320 (±90) MPa, with the cooling P-T path within the stability field of spodumene + quartz in the S-W system. The observed linear crystal growth rates in the aqueous phase, calculated by dividing the maximum length of a single crystal by the duration of the entire growth step, were 4.7 × 10⁻⁶ and 5.7 × 10⁻⁶ cm s⁻¹ for the cooling rates of 0.5 and 1°C min⁻¹, respectively. However, a rapid crystal growth rate of 3.6 × 10⁻⁵ cm s⁻¹ in the aqueous fluid was observed when the components were supplied by nearby melt droplets. Our results show that when crystals nucleate in the aqueous fluid instead of the melt phase, there are fewer nuclei formed, and they grow much faster due to the low viscosity of the aqueous fluid, which accelerates diffusion of components for the growth of crystals. Therefore, the large crystals in granitic pegmatite can crystallize directly from aqueous fluids rather than hydrosilicate melt.

Key words: aqueous solution, crystallization medium, hydrothermal diamond-anvil cell, pegmatite

INTRODUCTION

Granitic pegmatite is one of the most attractive rocks in the world because it not only contains many industrial minerals (Glover et al. 2012) and strategic metals (Linnen et al. 2012), but also exhibits a striking texture of giant crystals (London & Kontak 2012 and references therein). Some crystals in pegmatite are not only large, but also pristine and even of gem quality (Simmons et al. 2012). It is widely accepted that pegmatite dikes crystallize at a large degree of liquidus undercooling, and pegmatitic magma cools from emplacement temperature to their solidus temperature at the dike centers in a few days to a few months with a crystal growth rate of 10⁻⁶–10⁻⁵ cm s⁻¹ (Chakoumakos & Lumpkin 1990; Morgan & London 1999; Webber et al. 1999; Sirbescu et al. 2008). However, it is still not clear how and what type of liquid can transfer components so fast to crystal growth fronts to keep up with the fast growth rate and formation of giant crystals. In the model of Jahns & Burnham (1969), an aqueous fluid of low viscosity that exsolved from H₂O-saturated granitic magma is the key factor for the internal evolution of pegmatite and the rapid diffusion of constituents through the aqueous phase aids to the formation of inner giant crystals (Walker et al. 1986). In the ‘constitutional zone-refining’ model, London (2005a, 2008, 2009) hypothesized that, during crystallization, a flux-rich boundary layer exists between the crystal growth front and...
silicate melt and regarded this flux-rich hydrosilicate melt as the ideal crystallization medium for giant crystals in pegmatites due to their exceedingly high material-transport properties in terms of mass and rate (London 2009; London & Morgan 2012).

London (2008) placed the role of an aqueous fluid in the pegmatite formation as the top unknown factor among many larger geochemical issues in the earth sciences. He also believed that the growth rates of silicate crystals in pegmatite are underestimated and that it will not be possible to know the true rates of growth in silicate systems until experiments are carried out to measure the nucleation delay and to determine when (and why) a crystal stops growing while the new ones of the same phase nucleate. He suggested that experiments in diamond-anvil cells offer the possibility to view and record the actual nucleation and growth of crystals, from which improved growth rates could be obtained.

In this study, we made in situ observations of the nucleation and crystallization of spodumene in aqueous solutions in the system LiAlSi2O6–H2O in a new type of hydrothermal diamond-anvil cell (HDAC; type V). The choice of our starting material was based on the results of 30 homogenization experiments in an HDAC for crystal-rich inclusions in spodumene from Jiajika lithium pegmatite deposit in China (Li JK, Chou I-M, Yuan SD, Burruss RC, submitted). During heating in these experiments, decrepitation of the crystal-rich inclusions was prevented by applying external pressures (2.7–5.6 MPa) to the inclusions in the sample chamber of HDAC. In these inclusions, the H2O–CO2–NaCl fluid phase homogenized mostly around 290°C (between 272°C and 304°C), followed by the melting of zabuyelite (Li2CO3) and other daughter minerals (i.e., quartz, calcite, spodumene, and unidentified minerals) during heating. Finally, the melt dissolved totally (between 510 and 720°C) into the H2O–CO2–NaCl fluid, from which the host spodumene crystallized. In other words, the spodumene crystals in the Jiajika pegmatite deposit crystallized from flux-rich aqueous fluids instead of hydrosilicate melt.

**EXPERIMENTAL PROCEDURES**

LiAlSi2O6 gel (from Stewart 1978), prepared based on the method of Hamilton & Henderson (1968), and Milli-Q water (18 MΩ cm1) were loaded in the sample chamber the HDAC (Fig. 1; Anderson et al. 2010). The sample chamber is a hole (1.0 mm diameter) at the center of a Re gasket (3 mm diameter and 0.25 mm thick), sealed by compressing the gasket with two parallel diamond-anvil faces (1.6 mm diameter). Sample temperatures, controlled by a Linkam temperature controller (TMS 94) with the heating or cooling rate set at the values ranging from 0.5 to 50°C min−1, were measured by two type-K thermocouples with their individual sensing tips attached to each of the two diamonds. These thermocouples were calibrated by the triple point of H2O (0.01°C) and the melting points of NaNO3 (306.8°C) and NaCl (800.5°C); the reported temperatures were accurate to ± 3°C.

As shown in Fig. 2, the sample in the HDAC was observed using an inverted microscope with a Leitz (5×, 10×, or 20×) or a Mitutoyo (20× or 50×) long-working-distance objective lens, which was cooled by a stream of compressed air. The images of the sample were recorded continuously with a video system.

The sample was first heated at 5°C min−1 until the LiAlSi2O6 gel melted to form droplets and then totally

---

© 2013 John Wiley & Sons Ltd, *Geoﬂuids, 13*, 467–474
dissolved into the aqueous fluid. After holding the totally homogenized fluid at a temperature slightly higher than the homogenization temperature for 15 min, the sample was cooled at 1 °C min⁻¹ rate until melt droplets exsolved from the homogeneous fluid. The sample was then heated again at 1 °C min⁻¹ rate to record the temperature at which the last melt droplet dissolved into the aqueous solution. This temperature (TMS) was assigned as the saturation temperature of silicate melt in aqueous fluid. Then, we recorded in situ crystallization parameters as the sample cooled at a set rate of 0.5, 1.0, 5.0, 10, or 50 °C min⁻¹. The parameters included the initial and final crystal growth temperatures, number of crystals, rate and direction of crystal growth, and distribution and disappearance temperature of silicate melt droplets. With further cooling, a vapor bubble appeared in the HDAC sample chamber. We heated the sample once more at 1 °C min⁻¹ and recorded the disappearance temperature of the vapor bubble, which

Table 1 Experimental results for the crystallization of spodumene from aqueous solution containing dissolved Li-aluminosilicate in HDAC.

<table>
<thead>
<tr>
<th><em>No</em></th>
<th><em>TThDC</em> (°C)</th>
<th><em>TTS</em> (°C)</th>
<th><em>R_Cooling</em> (°C min⁻¹)</th>
<th><em>TCN</em> (°C)</th>
<th><em>TMS-CN</em> (°C)</th>
<th><em>M_TMS-CN</em> (°C)</th>
<th><em>N</em></th>
<th><em>V_Crystal/H_2O</em></th>
<th><em>PMS</em> (MPa)</th>
<th><em>PCN</em> (MPa)</th>
<th><em>PCS</em> (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>276</td>
<td>950 50</td>
<td>720 590 570 230 38 1.24% 788 537 363</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-1</td>
<td>307</td>
<td>810 1</td>
<td>780 725 530 30 2 0.97% 501 473 230</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-2</td>
<td>308</td>
<td>805 5</td>
<td>745 715 530 60 10 0.78% 506 447 235</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-3</td>
<td>306</td>
<td>790 10</td>
<td>734 540 56 16 0.39% 500 444 250</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-1</td>
<td>263</td>
<td>851 5</td>
<td>710 141 9 736 572</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-2</td>
<td>273</td>
<td>860 5</td>
<td>695 Exs 555 165 16 1.89% 707 519 353</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-1</td>
<td>288</td>
<td>810 1</td>
<td>775 670 549 35 1 0.93% 591 554 306</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-2</td>
<td>290</td>
<td>810 1</td>
<td>720 1 701 90 3 0.85% 581 487</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-1</td>
<td>294</td>
<td>847 5</td>
<td>752 735 95 3 602 506</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-2</td>
<td>293</td>
<td>840 1</td>
<td>744 740 526 96 4 1.61% 599 501 267</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-3</td>
<td>292</td>
<td>833 5</td>
<td>765 744 580 68 2 0.41% 596 527 329</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5-4</td>
<td>291</td>
<td>822 1</td>
<td>740 706 609 82 4 0.80% 589 504 364</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>288</td>
<td>819 0.5</td>
<td>723 707 550 96 1 3.35% 598 497 306</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-1</td>
<td>276</td>
<td>740 1</td>
<td>706 691 550 34 2 2.03% 634 592 395</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-2</td>
<td>258</td>
<td>750 1</td>
<td>720 710 550 30 3 638 602 389</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-3</td>
<td>263</td>
<td>755 1</td>
<td>722 716 569 33 5 2.31% 625 586 399</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7-4</td>
<td>268</td>
<td>760 5</td>
<td>709 668 595 51 10 2.00% 612 553 416</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-1</td>
<td>221</td>
<td>793 5</td>
<td>648 662 532 142 22 2.72% 662 490 347</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-2</td>
<td>221</td>
<td>814 1</td>
<td>733 81 7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8-3</td>
<td>265</td>
<td>880 5</td>
<td>740 709 540 140 9 2.65% 761 600 357</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>258</td>
<td>745 5</td>
<td>698 677 540 47 5 1.65% 633 574 376</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Experiment number. A total of 21 experiments in nine groups. Experiments in each group used the same sample but with different cooling rates.*

© 2013 John Wiley & Sons Ltd, Geofluids, 13, 467–474
is the homogenization temperature of the aqueous fluid in HDAC. This temperature was used to calculate the bulk H$_2$O density and therefore the pressure in the HDAC sample chamber at any temperature from the equation of state of H$_2$O (Haar et al. 1984) assuming constant volume (isochoric) of the sample chamber.

After a crystallization experiment was completed at a specified cooling rate, without unloading the sample from the HDAC sample chamber, we repeated the experimental procedures described above, except with a different cooling rate, to determine the effect of cooling rate on the crystallization process. The crystals in the sample chamber of HDAC were identified with a JY Horiba LabLam HR Raman system either in situ or after the sample was cooled down to room temperature and retrieved from the sample chamber.

RESULTS

A total of 21 experiments were performed at temperatures up to 950°C and pressures up to 788 MPa in the HDAC in the system LiAlSi$_2$O$_6$–H$_2$O with high H$_2$O content. Results were listed in Table 1 in nine groups, including the $P$-$T$ conditions during crystal growth and the volume ratios between the final crystals and H$_2$O in the HDAC cell at room temperature. The same sample was used in each group but with different cooling rates.

Among all of our experiments listed in Table 1, experiment No. 6 was performed at the lowest cooling rate and it produced the highest volume ratio between the final crystals and H$_2$O. Fig. 3 shows images of experiment No. 6 taken at various temperatures. The pressure ($P$) and temperature ($T$) conditions for the initial and final growth of spodumene for all crystallization experiments are listed in Table 1 and shown in Fig. 4. We calculated the linear crystal growth rate in aqueous solution by dividing the maximum length of a single crystal by the duration of the entire nucleation and growth step, as described by Fenn (1977) and Swanson (1977). Through observation and measurement in situ, the linear growth rates of a single spodumene crystal in aqueous fluid containing Li-alumino-silicate for two experiments, where only one crystal was nucleated, were obtained and are listed in Table 2 with errors and other parameters.

Figure 5 shows images taken between 722°C (Fig. 3C) and 707°C (Fig. 3D) for experiment No. 6, illustrating the distribution and disappearance of melt droplets during crystal growth. Examples of pristine crystals grown from the aqueous fluid are shown in Fig. 6. In situ Raman anal-

![Fig. 3. Images of experiment No. 6 taken at various temperatures: (A) at 285°C during heating at 5°C min$^{-1}$ rate showing the residual LiAlSi$_2$O$_6$ gel at the upper-right corner and two vapor bubbles, which disappeared at 288°C; (B) at 819°C, the last exsolved melt droplet disappeared during heating at the rate of 1°C min$^{-1}$; (C) at 722°C, one degree below the nucleation temperature of spodumene, the single spodumene crystal (near the top of the view) grew in the presence of melt droplets; (D) at 707°C, the last melt droplet was consumed; (E) at 551°C, the crystal growth stopped; and (F) at 288°C, the exsolved vapor bubble was almost homogenized into the aqueous fluid, indicating the bulk H$_2$O density of 0.736 g cm$^{-3}$, which was used to calculate the sample pressures at elevated temperatures (see those listed in Table 1) using the EOS of H$_2$O and assuming isochoric relations in the HDAC sample chamber.]

© 2013 John Wiley & Sons Ltd, Geofluids, 13, 467–474
Li-aluminosilicate is very similar to that of pure water with the bulk H$_2$O (to liquid) temperature near 283 °C. Virgilite (Li$_{0.5}$Al$_{0.5}$Si$_{2.5}$O$_6$ or LixAlxSi$_{3-x}$O$_6$) in the H$_2$O diagram (London 1984). Eucryptite (LiAlSiO$_4$), petalite (LiAlSi$_4$O$_{10}$), and TMD. The data listed in Table 1. The crystallization of spodumene in HDAC. The P-T conditions for the initial (diamonds) and final (squares) crystallization of spodumene in HDAC. The data listed in Table 1. The arrow represents the general P-T path during the crystallization of spodumene in aqueous solution, and the shaded area represents the inferred entrapment conditions of crystal-rich inclusions in Jiajika deposit, based on 30 homogenization experiments in HDAC (Li JK, Chou I-M, Yuan SD, Burrus RC, submitted). Our previous in situ calibrations of pressures in HDAC using α-β quartz transition indicate that when the homogenization (to liquid) temperature is near 283 °C, the isochores of the fluid containing Li-aluminosilicate is very similar to that of pure water with the bulk H$_2$O density of 0.754 g cm$^{-3}$. However, use of the isochores of pure water may generate up to 5% uncertainties for other sample fluids in this study with their homogenization temperatures far from 283 °C. Note that most of our experimental P-T conditions are within the stability field of spodumene plus quartz, based on the quartz-saturated phase relations of Li-aluminosilicate minerals of London (1984) shown here and also near the inferred entrapment conditions of crystal-rich inclusions in Jiajika deposit (shaded area). Based on the observed total homogenization temperatures of the crystal-rich inclusions and the corresponding stable pressure in the LiAlSiO$_4$-SiO$_2$-H$_2$O diagram (London 1984). Eucryptite (LiAlSiO$_4$), petalite (Li$_3$AlSiO$_4$), virgilite (Li$_{0.3}$Al$_{0.7}$Si$_{2.5}$O$_6$ or Li$_3$Al$_{1.5}$Si$_{3.5}$O$_6$), and TMD. The use of HDAC allows in situ observation and sample characterization by Raman spectroscopy. Therefore, we were able to eliminate uncertainties associated with ‘quench’ in previous experiments (Fenn 1977; Swanson 1977; London 1984; Swanson & Fenn 1986; Sirbescu et al. 2009) using conventional high-pressure apparatus, such as cold-seal pressure vessels, for the study of granitic pegmatite formation. As shown in Fig. 3, all crystallization processes can be observed, including the P-T condition for the saturation of silicate melt in aqueous fluid, the nucleation T of crystals, and the number and growth rate of crystals. As shown in Table 2 and Fig. 3C,D, the average crystal growth rate was 3.6 × 10$^{-5}$ cm s$^{-1}$ between 723 and 707 °C in Exp. No. 6 when mass transfer from nearby melt droplets was possible. The distribution and consumption of melt droplets between 722 and 707 °C (Fig. 5) indicate that the nutrient for the growth of the crystal was derived mainly from the nearby melt droplets with relatively high mass transfer and crystal growth rates. As shown in Fig. 3D,E, the average crystal growth rate dropped to 9.6 × 10$^{-7}$ cm s$^{-1}$ in the 156 °C temperature interval between 707 and 551 °C when no melt droplets were present and components were totally derived from the aqueous fluid with much lower nutrient content (Table 2). The average growth rate of spodumene crystals for the entire growth process is 4.7 × 10$^{-6}$ cm s$^{-1}$. As shown in Table 2, this average growth rate is not significantly different from 5.7 × 10$^{-6}$ cm s$^{-1}$ for the crystal in Exp. 4-1 with a cooling rate of 1°C min$^{-1}$ instead of 0.5°C min$^{-1}$. From the relations between crystal size and cooling history of volcanic and plutonic rocks, pegmatite had been expected to form in a slow cooling process with low nucleation density. As shown in Fig. 8, if the number of crystals of all results is averaged at a given cooling rate, there is a clear correlation between nucleation density and cooling rate, but in Table 1, the data at 5°C min$^{-1}$ cooling rate show large uncertainties. However, the cooling rate may influence the volume ratio between the final crystals and H$_2$O in the HDAC cell, and these ratios became higher.

One additional experiment was performed for the same binary system but with low H$_2$O/LiAlSi$_2$O$_6$ ratio. The results are shown in Fig. 11.

**DISCUSSION**

The use of HDAC allows in situ observation and sample characterization by Raman spectroscopy. Therefore, we were able to eliminate uncertainties associated with ‘quench’ in previous experiments (Fenn 1977; Swanson 1977; London 1984; Swanson & Fenn 1986; Sirbescu et al. 2009) using conventional high-pressure apparatus, such as cold-seal pressure vessels, for the study of granitic pegmatite formation. As shown in Fig. 3, all crystallization processes can be observed, including the P-T condition for the saturation of silicate melt in aqueous fluid, the nucleation T of crystals, and the number and growth rate of crystals. As shown in Table 2 and Fig. 3C,D, the average crystal growth rate was 3.6 × 10$^{-5}$ cm s$^{-1}$ between 723 and 707 °C in Exp. No. 6 when mass transfer from nearby melt droplets was possible. The distribution and consumption of melt droplets between 722 and 707 °C (Fig. 5) indicate that the nutrient for the growth of the crystal was derived mainly from the nearby melt droplets with relatively high mass transfer and crystal growth rates. As shown in Fig. 3D,E, the average crystal growth rate dropped to 9.6 × 10$^{-7}$ cm s$^{-1}$ in the 156 °C temperature interval between 707 and 551 °C when no melt droplets were present and components were totally derived from the aqueous fluid with much lower nutrient content (Table 2). The average growth rate of spodumene crystals for the entire growth process is 4.7 × 10$^{-6}$ cm s$^{-1}$. As shown in Table 2, this average growth rate is not significantly different from 5.7 × 10$^{-6}$ cm s$^{-1}$ for the crystal in Exp. 4-1 with a cooling rate of 1°C min$^{-1}$ instead of 0.5°C min$^{-1}$. From the relations between crystal size and cooling history of volcanic and plutonic rocks, pegmatite had been expected to form in a slow cooling process with low nucleation density. As shown in Fig. 8, if the number of crystals of all results is averaged at a given cooling rate, there is a clear correlation between nucleation density and cooling rate, but in Table 1, the data at 5°C min$^{-1}$ cooling rate show large uncertainties. However, the cooling rate may influence the volume ratio between the final crystals and H$_2$O in the HDAC cell, and these ratios became higher.

---

**Table 2** The growth rate of a single spodumene crystal in aqueous fluid containing Li-aluminosilicate.

<table>
<thead>
<tr>
<th>No.</th>
<th>T$_{MD}$ (°C)</th>
<th>L$_{CN-MD}$ (mm)</th>
<th>V$_{CN-MD}$ (10$^{-6}$ cm s$^{-1}$)</th>
<th>T$_{MD-CS}$ (°C)</th>
<th>L$_{MD-CS}$ (mm)</th>
<th>V$_{MD-CS}$ (10$^{-6}$ cm s$^{-1}$)</th>
<th>V$_{ave}$ (10$^{-6}$ cm s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>707</td>
<td>0.7</td>
<td>36</td>
<td>0.32</td>
<td>0.96</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>4-1</td>
<td>670</td>
<td>0.69</td>
<td>11</td>
<td>0.1</td>
<td>1.4</td>
<td>5.7</td>
<td></td>
</tr>
</tbody>
</table>

*Experiment number.* Disappearance temperature of silicate melt droplets upon cooling and during crystallization. †Length of crystal formed between T$_{CN}$ and T$_{MD}$. ‡Growth rate of crystal between T$_{CN}$ and T$_{MD}$.* Length of crystal formed between T$_{MD}$ and T$_{CS}$. **Growth rate of crystal between T$_{CN}$ and T$_{MD}$. ††Average growth rate of crystal for the entire growth process.

© 2013 John Wiley & Sons Ltd, Geofluids, 13, 467–474
with decreasing cooling rates (Table 1). Other than experiment No. 6 that produced the highest ratio with the lowest cooling rate of 0.5°C min\(^{-1}\), experiments of different bulk compositions, such as series 2, 5, and 7, all showed this trend (Fig. 9). The experiments are therefore consistent with the expectation that fewer, larger crystals result from the natural cooling rates of pegmatites, which may be hundredths to thousandths of degrees per minute (Sirbescu et al. 2008). On the other hand, as shown in Fig. 10, oversaturation is a potential factor controlling nucleation density in aqueous solution, similar to those reported previously for the role of undercooling on the crystallization of silicate melt (Lofgren 1974; Fenn 1977; London 1992).
As shown in Figs 5 and 6, crystals that grew from aqueous fluid tend to be large and pristine. On the other hand, as shown in Fig. 11, crystals that grew from hydrosilicate melt tend to be small with poorly developed crystal surfaces. In the experiment of crystallization in hydrosilicate melt, the crystal growth rates were reported in the range of 0.1–6.5 × 10^{-6} cm s^{-1} (Fenn 1977), 3 × 10^{-6} cm s^{-1}–1 × 10^{-10} cm s^{-1} (Swanson 1977), 1.4–2.2 × 10^{-6} cm s^{-1} with an undercooling of 40–70°C (Swanson & Fenn 1992), and 1 × 10^{-8} and 5 × 10^{-7} cm s^{-1} (Baker & Freda 2001). These growth rates are all equivalent or lower than the average crystal growth rates in aqueous solution observed in this study and much lower than the observed rate when the nutrient was available from the nearby melt droplets suspended in aqueous solution, indicating that the low viscosity of aqueous fluid accelerates the supply of components and therefore speeds up the growth rate of the crystals.

CONCLUSION

Crystallization experiments were performed in a new type of HDAC for the binary system LiAlSi_2O_6–H_2O at temperatures up to 950°C and pressures up to 788 MPa, with cooling rates ranging from 0.5 to 50°C min^{-1}. Samples were observed in situ, and images were recorded continuously with a video system. An average crystal growth rate of 3.6 × 10^{-5} cm s^{-1} was reached in the 16°C temperature interval between 723 and 707°C when components were available from nearby melt droplets. Our experimental results show that crystallization from aqueous solution causes low nucleation density and high mass transfer rates, which meet the requirements for the formation of large pristine crystals in pegmatite. This conclusion is consistent with results from our homogenization experiments in HDAC for crystal-rich inclusions in spodumene from Jiajiaka lithium pegmatite deposit in China (Li JK, Chou I-M, Yuan SD, Burruss RC, submitted), where hydrous silicate melt homogenized into the H_2O-CO_2-NaCl fluid. This water-rich fluid is similar to the final ‘boundary-layer...
liquid’ during crystallization described by Simmons (2007) and London (2005b) and to the silicate-dissolved aqueous fluid evolved from H2O-saturated silicate melt described by Jahns & Burnham (1969), and from which the host spodumene crystallized. Similar experiments in the future, with different bulk compositions in HDAC, will certainly help formulate acceptable models for the genesis of granitic pegmatite.

ACKNOWLEDGEMENTS

We would like to thank Prof. W. A. Bassett for providing HDAC (type V), Dr. David B. Stewart for providing LiAlSi2O6 gel, and Robert Seal and Harvey Belkin of the U. S. Geology Survey (USGS), two anonymous reviewers, and Editors, Prof. Craig Manning and Prof. Robert Bodnar, for their constructive reviews. Jiankang Li and Shunda Yuan would like to thank CAGS for financial support and also Ms. Haiping Qi for her support and encouragement during their one-year visit at the USGS. This study was supported by the Mineral Program and Energy Program of U.S. Geological Survey, the Chinese National Non-profit Institute Research Grant of CAGS-IMR (K1001), the National Natural Science Foundation of China (40702014), the Chinese SinoProbe Project (SinoProbe-03-01), and the Knowledge Innovation Program of Chinese Academy of Sciences (SIDSSE-201302). The use of trade, product, industry, or firm names in this report is for descriptive purpose only and does not constitute endorsement by the USGS and the U.S. Government.

REFERENCES


CONTENTS

395 EDITORIAL: Introduction to thematic issue on fluid and melt inclusions
R.J. Bodnar, T.P. Mernagh, I.M. Samson and C.E. Manning

398 Role of fluid and melt inclusion studies in geologic research
S.E. Kesler, R.J. Bodnar and T.P. Mernagh

405 Nanogranite inclusions in migmatitic garnet: behavior during piston-cylinder remelting experiments
O. Bartoli, B. Cesare, S. Poli, A. Acosta-Vigil, R. Esposito, A. Turina, R.J. Bodnar, K.I. Angel and J. Hunter

421 Melt inclusion evidence for magma evolution at Mutnovsky volcano, Kamchatka
K. Robertson, A. Simon, T. Petke, E. Smith, O. Selyangin, A. Kryukhin, S.R. Mulcahy and J.D. Walker

440 Investigation of long-term geochemical variations and magmatic processes at Mount St. Helens
M.J. Severs, K.J. Gryger, S.A. Makin, R.J. Bodnar and W.B. Bradford

453 Zircon-bearing, crystallized melt inclusions in peritectic garnet from the western Adirondack Mountains, New York Slate, USA
R.S. Darling

460 Are silicate-rich inclusions in spodumene crystallized aliquots of boundary layer melt?
A.J. Anderson

467 Observations on the crystallization of spodumene from aqueous solutions in a hydrothermal diamond-anvil cell
J. Li, I.-M. Chou, S. Yuan and R.C. Burruss

475 Fluid inclusion evidence for a genetic link between simple antimony veins and giant silver veins in the Coeur d’Alene mining district, ID and MT, USA
A.H. Hofstra, E.E. Marsh, T.J. Todorov and P. Emsbo

484 An evaluation of hydrogen sulfide in orogenic gold fluids and the uncertainties associated with vapor-rich inclusions
T.P. Mernagh and E.N. Bastrakov

506 Geology, fluid inclusion, and isotope constraints on ore genesis of the Neoproterozoic Jinshan orogenic gold deposit, South China
C. Zhao, P. Ni, G.-G. Wang, J.-Y. Ding, H. Chen, K.-D. Zhao, Y.-T. Cai and Y.-F. Xu

528 Fluid inclusions at different depths in the Sanshandao gold deposit, Jiaodong Peninsula, China

542 Boiling as a mechanism for colour zonations observed at the Byrud emerald deposit, Eidsvoll, Norway: fluid inclusion, stable isotope and Ar–Ar studies
L. Loughrey, D. Marshall, P. Ilen and P. Jones

559 A fluid inclusion study of diagenetic fluids in Proterozoic and Paleozoic carbonate rocks, Victoria Island, NWT
J. Mathieu, D.J. Kontak and E.C. Turner

579 Acid saline fluid inclusions: examples from modern and Permian extreme lake systems
K.C. Benison

594 Multiple hydrocarbon charging events in Kuh-e-Mond oil field, Coastal Fars: evidence from biomarkers in oil inclusions
Z. Shariatinia, S. Feiznia, A. Shafiei, M. Haghighi, A. Mousavi Dehghani, M. Memariani and N. Farhadian