

BEHAVIOR OF B_xO_y COMPLEXES IN ALKALINE HYDROTHERMAL SOLUTIONS (EXPERIMENTAL AND SYNTHETIC FLUID INCLUSION STUDY)

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Introduction

The finding of sassolite daughter crystals in fluid inclusions in pegmatite minerals from around the world (Smirnov et al., 2000; Peretyazhko et al., 2000; Thomas et al., 2000) entails an important conclusion that boron could be major component of hydrothermal fluids. This further raises a host of questions regarding boron behavior and speciation under natural conditions associated with crystallization of hydrothermal minerals. This work represents the results of the fluid inclusion study of quartz grown from sodium-borate hydrothermal solutions.

Experimental setup and results

For investigation of boric acid behavior under hydrothermal conditions we have chosen compositions within well-characterized system Na₂O-B₂O₃-H₂O. Quartz crystals were grown on seed at 520°C and 1.5 kbars. The compositions of starting solutions are shown in the Table. The starting composition was chosen with the aim of obtaining fluid inclusions containing borate daughter crystals in quartz. Inclusions obtained in quartz overgrowth have been studied microthermometrically and by Raman spectroscopy within 20–350°C temperature range.

The growth of quartz and fluid inclusion entrapment have been observed in solutions containing 0.1– 6.5 wt. % of NaOH. Seeds and charge completely dissolved in experimental solution with 12 wt. % NaOH, and, after the run, the system consisted of water solution and glass-like phase. The formation of glass-like phase (GLP) was also observed in experiments with 6.5 wt. % of NaOH along with quartz growth.

Quartz overgrowths contain abundant primary two-phase fluid inclusions, ranging in size from 10 to >100 μm. The inclusions consist of water solution and a gas bubble. The glass-like phase was not observed in fluid inclusions. Daughter crystals of sassolite were observed only in inclusions corresponding to 0.1 and 0.8 wt. % NaOH in the starting solution. The last melting crystals in inclusions obtained in other runs appear to be ice. Eutectic temperatures of inclusions decrease progressively with increasing NaOH content in the starting solution.

Table. Starting solution compositions and results of the study

| Starting solution | | Fluid inclusions | | | | Glass-like phase | | | | |
|-------------------|--------------------------------|------------------|--------------------------|--|--------------------|----------------------|-------------------|-------------------------------|------------------|-------|
| wt. % | | Te | Tm | Raman lines within borate region, cm ⁻¹ | | wt. % | | | | |
| NaOH | H ₃ BO ₃ | °C | °C | 20°C | 350°C | SiO ₂ | Na ₂ O | B ₂ O ₃ | H ₂ O | Total |
| 0.1 | 10.8 | -3 | 39-45* | 876 | 871 | No GLP formation | | | | |
| 0.8 | 10.9 | -5.1 - -6.3 | 20* | 876 | 867 | | | | | |
| 1.8 | 10.8 | -8.4 - -9.0 | -2.1 - -2.7 [‡] | 879 | 870 | | | | | |
| 3.1 | 10.8 | -12.7 | -1.8 [‡] | 876 | 874 | GLP was not analysed | | | | |
| 6.5 | 21.3 | -35 | -17.5 [‡] | 874 | 867 | | | | | |
| 6.5 | 10.8 | -11 | -2.7 [‡] | 766, 788, 969 | 759, 781, 959, 867 | 57.84 | 15.43 | 8.37 | 7.64 | 89.28 |
| 12.9 | 10.7 | No quartz growth | | | | 56.99 | 16.76 | 8.70 | 6.50 | 88.95 |
| 12.9 | 21.3 | No quartz growth | | | | 46.61 | 16.38 | 16.71 | 7.48 | 87.18 |

Te – eutectic temperature; Tm - temperature of final melting; * - dissolution of sassolite; [‡] - ice melting

GLP is typically located at the bottom of container and substitute for charge particles. The results of electron microprobe and SIMS microanalyses are presented in Table. The Table shows that GLP consists primarily of SiO₂, Na₂O and B₂O₃. Common feature of all samples is a prominent deficit of analytical totals. The GLP is highly unstable under electron beam, indicating that some constituents may be lost in the course of analysis. Typically alkaline metals and water are very mobile in hydrous glass structure. In order to eliminate the loss of Na during the analysis, we used defocused (20 μm) electron beam at low beam current (10 nA). Thus, the Na loss would not be greater than 10 rel.%. It is apparent from the Table, that after combination of SIMS data with electron microprobe analysis analytical totals still remain below 100%. We believe that the most possible reason for this is the failure to determine water by SIMS, which was previously reported by Ihinger et al. (1994) for hydrous glasses with water content >5 wt. %. Assuming that the total deficit is due to water loss, the water content can be assessed as 16 to 20 wt. %.

Raman and IR-spectroscopy of inclusions and GLP

On the basis of presence of 876-867 cm^{-1} band in Raman spectra of fluid inclusions within the explored temperature range, we concluded that the only detectable species in solution is H_3BO_3 . Integral intensity of this band decreases as NaOH content increases in the starting solution. Heating of inclusions up to 350°C does not result in appearance of new bands within the 500 – 1200 cm^{-1} range, typical of the Raman spectra of alkali-borate and polyborate species. The only exceptions to this rule are inclusions in quartz grown in solution with 6.5 wt. % NaOH and 10 wt. % H_3BO_3 (see Table). The bands at 766-759 and 969-959 cm^{-1} in these inclusions indicate the presence of boron in four- and three-fold coordination respectively, whereas H_3BO_3 appears only on heating in small amounts. The decrease of integral intensity of the 876 cm^{-1} band is observed from 100 to 350°C for experiments with 0.1 – 3.1 wt.% NaOH and 10 wt. % H_3BO_3 ; for experiment with 6.5 wt. % NaOH and 21 wt. % H_3BO_3 , the integral intensity of the 876 cm^{-1} band increases in this temperature range.

IR spectra of GLP samples with highest B_2O_3 content consist of broad bands centered at 450 and 1050 cm^{-1} that could be assigned to vibration of Si-O-Si bonds, bands at 1650, 3400 and 3600 cm^{-1} that could be assigned to H_2O and OH vibrations, and less intensive at 680, 1340 and 1400 cm^{-1} . The bands at 670 cm^{-1} of borosilicate glasses are typically assigned to Si-O-B vibrations (Sigoli et al., 2001). Band at 1340 cm^{-1} is probably due to B(3)-O-B(4) and 1400 cm^{-1} could be assigned to B(3)-O vibrations (Valyashko, Vlasova, 1966). B(4)-O vibrations can not be detected by IR spectroscopy, because they are usually masked by stronger Si-O-Si vibrations.

Discussion

According to the published experimental data, the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ contains three non-variant eutectic points within the range of expected fluid-inclusion compositions. For inclusions in quartz grown in solutions with NaOH/ H_3BO_3 of <0.3 the expected eutectic points are close to each other at -1 and -1.5°C. For compositions with NaOH/ H_3BO_3 of 0.3 to 0.6, the expected eutectic point is -5.8°C. Daughter phases of sassolite and hydrous sodium tetraborate should exist up to ~50°C or appear on cooling. Our thermometric data given in the Table show that the behavior of fluid inclusions does not correspond to what would be expected on the basis of phase diagram for the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. We interpret this phenomenon as an indication of formation of a new soluble substance, lowering eutectic and ice-melting temperatures and decreasing H_3BO_3 content in the solution. The data suggest that this substance most probably is comprised of sodium, boron and silica.

Raman spectroscopy data support the presence of new borate-containing substance, expressing it through the decrease of integral intensity of H_3BO_3 band that follows the increase of NaOH content. Further decrease of integral intensity observed on heating probably indicates slight increase of the content of new species as quartz gets dissolved from inclusion walls. The absence of new bands (apart from 876 cm^{-1}) in borate vibration region shows clearly that in contrast to $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ system alkali-borate complexes do not appear in significant amounts within the explored temperature range.

The appearance of the GLP in final experiment product indicates that liquid immiscibility occurs in the course of quartz growth at NaOH content >6.5 wt. %. This is the evidence for liquid immiscibility, which is a common feature for $\text{Na}_2\text{O}-\text{SiO}_2-\text{H}_2\text{O}$ and $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ systems (Valyashko, 1990, Haller et al., 1970). Our analyses show that GLP represents hydrous sodium borosilicate liquid. According to SIMS and IR analyses, boron partitions between GLP and water solution. Boron in GLP exists in three- and, probably, four-coordinated forms, and could be partially incorporated into silicon-oxygen network. The absence of GLP in primary fluid inclusions indicates that it forms along with quartz growth rather than at cooling after experiment. Heavier sodium borosilicate liquid accumulates at the bottom of the growth container. Quartz seeds, suspended in the container, grow from water solution and do not trap this liquid.

Conclusions

Our experiments have shown that in the course of the quartz growth, sodium-borate components of hydrothermal fluid reacts with dissolved silica to form highly soluble substance. The effect is prominent even at very low NaOH contents and manifests itself through decrease of eutectic ice melting and sassolite dissolution temperatures. Apparently, the chemistry of the fluid inclusions corresponds to the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$, rather than $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. H_3BO_3 remains one of the dissolved boron forms along with other forms, which differ from sodium meta- and tetraborate complexes. The fraction of H_3BO_3 complexes decreases with increasing NaOH content and the temperature, and increase with increasing H_3BO_3 content. At high NaOH content boron partitions between water solution and heavy sodium borosilicate liquid, where it probably exists in three- and four-coordinated forms, and partially is bounded to silicon-oxygen network, corroborating the presence of sodium-boron-silica complexes inferred from micro-thermometric and spectroscopy data.

Our data show an important role of heavy immiscible liquids for boron partitioning under hydrothermal conditions. During the growth of crystals in natural alkaline environment, crystals growing on the ceilings of cavities would not trap heavy liquid. Studies of such crystals could lead to underestimation of the boron contents in the system. Another source of underestimation is the formation of sodium-boron-silica species in even slightly alkaline sodium solutions.

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