LETTER

Water solubility in albite-orthoclase join and JR-1 rhyolite melts at 1000°C and 500 to 2000 bars, determined by micro-analysis with SIMS

ISOJI MIYAGI*, HISAYOSHI YURIMOTO and EIICHI TAKAHASHI

Earth and Planetary Sciences, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152, Japan

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Water solubilities in albite (Ab)-orthoclase (Or) join and JR-1 rhyolite melts at 1000°C and up to 2000 bars were determined by the "excess of water" method using an internally heated pressure vessel (IHPV) with rapid quenching and a secondary ion microprobe mass spectrometer (SIMS). We have found that secondary hydration of run product glass with coexisting aqueous fluid occurs during quenching. The hydration is significant in sodium-rich glass. The bulk analysis of such secondary hydrated run-products will cause overestimation of the water solubility, while the true water solubility can be obtained by micro-analysis on non-attacked portion of the glass. The apparent compositional dependence in the published water solubility data could be due to the secondary hydration of run product glass. Newly determined water solubility for the Ab-Or join and rhyolite melts is expressed as H_2O (mol%) = $0.19\sqrt{P_{H_2O}}$ (bar), at 1000°C.

INTRODUCTION

Water in magmas is important in the understanding of mechanism of violent eruption (e.g., Sparks, 1978; Wilson, 1980), as well as the formation of hydrothermal ore deposits (e.g., Hedenquist and Lowenstern, 1994). Since the pioneering work by Goranson (1931), the water solubility in silicate melts has been investigated as a function of water pressure, temperature, and melt composition (Burnham, 1975; Oxtoby and Hamilton, 1978; Dingwell *et al.*, 1984; Hamilton and Oxtoby, 1986; McMillan *et al.*, 1986; Holtz *et al.*, 1992; Paillat *et al.*, 1992; Romano *et al.*, 1996). Burnham (1975) proposed the well-known water dissolution model of that hydrolytic reaction of a molecular water with the bridging oxygen between two tetrahedral cations (Si, Al) produces two hydroxyls. More highly polymerized melts become less polymerized structure by the reaction,

which explains the dramatic changes in fluidity, electrical conductivity, and cationic diffusion rate. If the hydrolytic reaction is essential, the equimolar, isothermal, isobaric water solubilities in Ab, Or, $CaAl_2Si_2O_8$ (An), and Si_4O_8 (Qz) melts should be essentially the same. However, it has been reported that the water solubilities depend significantly upon the anhydrous composition of melts (Oxtoby and Hamilton, 1978; Dingwell *et al.*, 1984; McMillan and Holloway, 1987; Holtz *et al.*, 1992; Romano *et al.*, 1996). For example, the highest solubility values along the Ab-Qz join are obtained for the most Ab-rich melts, whereas the solubility remains almost constant along the Or-Qz join, and this solubility is much smaller than that of Ab (Dingwell *et al.*, 1984; Holtz *et al.*, 1992). In spite of large efforts, the dissolution mechanism of water in melts is still not well understood at the molecular level. The composition dependence is one key. However, some of the

*Now at Geological Survey of Japan, Higashi 1-1-3, Tsukuba, Ibaraki 305, Japan

previous measurements may involve a problem; overestimation of water solubility due to secondary hydration of run product glass during quenching (Miyagi, 1995). In this paper, we present the evidence for the overestimation, and provide new water solubility data for Ab-Or and rhyolite melts, where the secondary hydration could happen.

EXPERIMENTAL PROCEDURES

In this study, the solubility was determined by the "excess of water" method that measures water content of hydrous run product glasses synthesized under water saturated conditions at 1000°C and

500 to 2000 bars, with gold or Ag₅₀Pd₅₀ alloy casing. Starting materials were Ab, Ab₂₅Or₇₅, Ab₅₀Or₅₀, Ab₇₅Or₂₅ and Or gel, and JR-1 rhyolite glass, a geochemical reference sample of the Geological Survey of Japan. High pressure runs were performed using a rapid-quenching IHPV, SMC-2000, at the Tokyo Institute of Technology. Quenching capability of the SMC-2000 is estimated to be >200°C/sec (Takahashi and Tomiya, 1992).

In order to measure the secondary glass hydration rate, glass bead specimens were sealed together with distilled water in gold tubes, and then placed at the bottom of the SMC-2000 furnace (i.e., 2000 bars and 70°C) for 50 hours. The

Fig. 1. A BEI of Ab glass synthesized in water-saturated conditions (~10 wt.%H₂O, at 1000°C and 2000 bars) which contains a few bubbles. Bright and dark areas correspond to those water-rich and -poor, respectively. The figures in bold indicate water contents (in wt.%) analyzed by SIMS. The dotted oval outlines a secondary hydrated glass rind formed around an elongated bubble. The histogram (inset) shows the results of SIMS carpet bombardment hydrogen analysis on this specimen (after Miyagi, 1995). A: water content of non-hydrated portion of this specimen by SIMS. B: bulk water content of this specimen determined by the hydrogen manometry with a vacuum extraction line. C: published water solubility at 1000°C and 2000 bars by Hamilton and Oxtoby (1986).

starting glass materials (albite, rhyolite, dacite, and andesite glass) were nearly anhydrous glass beads pre-heated at 1000 to 1300°C in atmospheric furnace.

Run product glasses were observed by an EPMA, JEOL JXA-8800, and then measured for their hydrogen contents by a SIMS, Camera IMS-3F, at the Tokyo Institute of Technology (Miyagi and Yurimoto, 1995).

RESULTS AND DISCUSSION

Rapid glass hydration

In a backscattered electron image (BEI) of Ab glass synthesized under water saturated condition, numerous dark spots are observed (Fig. 1). They formed around the vesicles, and have almost the same chemical composition as the surrounding glass, except that they are water-rich. Since the experimental duration (~100 hours) is long enough to homogenize the melt in terms of dissolved water, the rinds could not exist during the high pressure runs, but could have formed during the quenching due to hydration with remaining water.

The thickness of the rinds is about 60 μm , 40 μm and 0 μm in Ab, Ab₇₅Or₂₅ and Or glass, respectively (Figs. 1 and 2). We also found that the hydration occurred on the surface of nearly dry glass beads (Ab, JR-1 obsidian, JA-1 andesite) at 70°C and $P_{\text{H}_2\text{O}} = 2000$ bars. The thickness of the rims formed within 50 hours is >100 μm , 20 μm and <5 μm for Ab, rhyolitic and andesitic glasses, respectively. The glass hydration rate $k (=x^2/t)$ was >4800, 190 and <12 ($\mu\text{m}^2/\text{day}$) in Ab, JR-1, and JA-1, respectively, at 70°C and $P_{\text{H}_2\text{O}} = 2000$ bars, where x is the hydration depth (μm), and t is the duration of hydration (day). These figures are surprisingly greater than previous measurements. For example, an extrapolation of the glass hydration rate in a Cerro de las Navajas obsidian under $P_{\text{H}_2\text{O}} = 5\text{--}40$ bars (Michels *et al.*, 1983) gives $k \approx 2.5 \times 10^{-3}$ ($\mu\text{m}^2/\text{day}$) at 70°C, i.e., $\sqrt{kt} = 0.07$ $\mu\text{m}/50$ hours. Thus the glass hydration rate appears to depend on $P_{\text{H}_2\text{O}}$, as well as the glass chemical compositions.

As mentioned above, the thickness of the rinds on Ab glass during quenching in this study is 60

Fig. 2. BEI and Scanning Electron Microscope (SEM) images of Ab₇₅Or₂₅ (upper) and Or (lower) glasses, both synthesized in water-saturated conditions at 1000°C and 2000 bars.

μm . Assuming that the effective re-hydration time is 1 sec, the hydration rate during the quenching is calculated to be 310×10^6 ($\mu\text{m}^2/\text{day}$). Note that average $P_{\text{H}_2\text{O}}$ for the glass hydration in our isobaric quenching is $\ll 2000$ bars because of a rapid drop in the internal pressure of rigid bubbles. The glass hydration will proceed at a significant speed at higher $P_{\text{H}_2\text{O}}$ conditions, for example, in case of isobaric quenching of bubble-free glass pellet with excess water. In an extreme case, water concentration of run product glass may be re-homogenized by the rapid glass hydration during quenching. This may be a reason why such glass hydration has not been reported before.

Water solubility in aluminosilicate melts

The histogram (Fig. 1, inset) shows the results of carpet bombardment hydrogen analysis on the

Ab glass shown in Fig. 1. The bulk water content of the specimen (arrow B, 6.5 wt.%H₂O, by hydrogen manometry) is close to the published water solubility in Ab melt under the experimental conditions (arrow C, 6.9 wt.%H₂O, Hamilton and Oxtoby, 1986). In contrast, the water content of the non-hydrated portion at the left end of this histogram (arrow A, 5.1 wt.%H₂O) is much lower than the above measurements. Bulk analysis of such secondary-hydrated run-products will clearly overestimate the water solubility. On the other hand, the true water solubility will be preserved in the non-hydrated glass, away from the rinds. In this case, the lowest concentration (arrow A, 5.1 wt.%H₂O) may represent the true solubility. Our water solubility data (Fig. 3) show virtually no composition dependence, and are consistent with the published data for Or, Qz, and CaO-Al₂O₃-

Fig. 3. Water solubilities (wt.%H₂O, one melt oxygen basis) in aluminosilicate melts. All our data given by the symbols for different chemical compositions are at 1000°C and 500–2000 bars. They are approximated by a single regression line (shaded line). Line CAS represents the data for a melt, 28.5CaO + 5.6Al₂O₃ + 65.9SiO₂, at 1180°C (McMillan *et al.*, 1986). Line QAO is data for a suite of melts ranging in composition from 0.3SiO₂ + 0.7KAlSi₃O₈ (left end) to 0.3SiO₂ + 0.7NaAlSi₃O₈ (right end) at 800°C and 2000 bars (Holtz *et al.*, 1992). Line SS is a calculated water solubility in Ab melt at temperatures along its wet solidus (Fig. 16 in Silver and Stolper, 1989). Dashed lines are published solubility data from a compilation by McMillan and Holloway (1987). Qz = SiO₂; Or = KAlSi₃O₈; Ab = NaAlSi₃O₈; Ne = NaAlSiO₄; 4Na = 0.36Na₂O + 0.09Al₂O₃ + 0.55SiO₂; BD = Beinn and Dubhaich granite; HP = Harding Pegmatite.

SiO₂ melts, in which the secondary hydration effect may be negligible. Calculated water solubility in Ab melt by Silver and Stolper (1989) based on spectroscopic data obtained from water undersaturated glass specimens is also in concordance with the present results. A simple regression line through our data is determined with H₂O (mol%) = $0.19\sqrt{P_{\text{H}_2\text{O}}}$ (bar), at 1000°C. It is possible that the apparent composition dependence in the published solubility data is caused mainly by the secondary glass hydration with variable tendency as a function of melt composition.

CONCLUSIONS

In the "excess of water" method, the rapid secondary hydration of run product glass occurs with coexisting aqueous fluid during quenching, which results in possible overestimation of water solubility. This problem can be overcome using both rapid quenching and rapid depressurizing techniques, followed by a careful micro-analysis of water concentration in the run product glass. Our data indicate that the equimolar, isobaric and isothermal water solubility in the compositional range of Ab-Or and rhyolite melts has virtually no compositional variation.

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