

Water contents and hydrogen isotopic ratios of rocks and minerals from the 1991 eruption of Unzen volcano, Japan

Minoru Kusakabe ^{a,*}, Hiroaki Sato ^b, Setsuya Nakada ^c, Toshihiro Kitamura ^a

^a Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori-ken 682-0193, Japan

^b Department of Earth and Planetary Sciences, Kobe University, 1-1 Rokkodai, Nada-ku, Kobe-shi 657-8501, Japan

^c Volcano Research Center, Earthquake Research Institute, University of Tokyo, 1-1-1 Yayoi, Bunkyo-ku, Tokyo 113-0032, Japan

Received 1 September 1997; received in revised form 29 June 1998; accepted 10 September 1998

Abstract

Water contents and hydrogen isotopic ratios were determined for blocks from pyroclastic flow deposits, and bread-crust bombs and blocks from the 1991 Vulcanian eruptions of Unzen volcano, Japan. Groundmass water contents and δD values of samples were calculated by subtracting the contribution of major hydrous minerals (hornblende and biotite) from the bulk rock analyses, and range from 0.1 to 0.5 wt.% and -83 to -49% , respectively. The samples do not show a systematic H_2O – δD relationship, although the block samples tend to have lower δD values than the bomb samples. The non-systematic H_2O – δD relationship is likely a result of near surface, kinetically-controlled gas loss. High viscosity of this magma would hinder attainment of hydrogen isotopic equilibrium between exsolved vapor and melt in the final degassing stage. The near surface degassing, however, was accompanied by kinetic fractionation resulting in enrichment of deuterium in the final products as exemplified by bread-crust bombs with high H_2O –low δD margins and low H_2O –high δD cores. Relatively high δD values of the blocks and bombs as well as high temperature volcanic gas (-30 to -35%) suggest a closed system degassing of an initial water-rich magma ($H_2O = 6$ wt.%) until its water content was reduced to 0.5 wt.%. The pre-eruptive δD value (-46%) was estimated from the volcanic gas data and D/H analysis of hornblende phenocrysts coupled with assumed isotopic equilibration in the initial hydrous magma. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: water content; hydrogen isotopes; Unzen volcano; degassing

1. Introduction

The degree and effectiveness of degassing in silicic magma is closely related to eruption style. For example, explosive eruptions result from rapid ascent of water rich magma, whereas effusive eruptions (or dome formation) result from slow ascent of effectively degassed magma (Eichelberger et al., 1986; Jaupart and Allegre, 1991; Woods and Koyaguchi, 1994). Only one explosive eruption, a Vulcanian eruption in June 1991, occurred during the recent activity at Unzen volcano (November 1991–February 1995). The eruptive activity of

* Corresponding author. Tel.: +81-858-43-1215; Fax: +81-858-43-3450; E-mail: kusakabe@misasa.okayama-u.ac.jp

Unzen volcano is characterized by the formation of a dacite dome, associated with frequent pyroclastic flows generated by dome collapse (Sato et al., 1992). Description of the 1991–1995 Unzen eruptions is found in the papers by Nakada and Fujii (1993) and Nakada et al. (1995). The typically effusive nature of eruption suggests that the Unzen magma underwent extensive degassing before it erupted as dome lava.

When a silicic magma ascends from depth, it may be saturated with water and eventually vesiculate at a shallower depth to form bubbles. At magmatic temperatures as high as 800–900°C, hydrogen isotopic fractionation between water vapor and water dissolved in the magma is significantly large (Kuroda et al., 1982; Taylor and Westrich, 1985; Richet et al., 1986), and the D/H ratio of the magma changes as degassing proceeds. It is known that water in silicate glasses/melts exists as hydroxyls (OH) and molecular water (H₂O), the relative proportion of which changes as a function of water content (Stolper, 1982) and temperature (Nowak and Behrens, 1995; Shen and Keppler, 1995). These characteristics provide the basis for modeling the degassing of magma in terms of water content and hydrogen isotopic ratio variations of the erupted products. Degassing of explosive rhyolitic eruptions was investigated by correlated H₂O– δ D variations in glassy tephra and obsidians (Taylor et al., 1983; Newman et al., 1988; Dobson et al., 1989; Taylor, 1991; Wilding et al., 1993). Ash and pumice erupted early in the eruption cycle are relatively enriched both in H₂O and deuterium, whereas later lavas and obsidians are depleted. The above studies showed that the H₂O– δ D relationship of the glassy tephra and obsidians is described either by single stage degassing (open system degassing), two-stage degassing (closed system degassing followed by open system degassing), or multi-stage degassing (repetition of closed/open system degassing). The H₂O– δ D relationship of lavas and bombs from dome-forming rhyo-dacitic eruptions has also been explained by the above listed mechanisms (Hoblitt and Harmon, 1993; Anderson et al., 1995) with a final stage of kinetically-controlled degassing (Anderson and Fink, 1989).

To constrain the degassing processes of the Unzen magma we analyzed water contents and hydrogen isotopic compositions (D/H ratio) of blocks collected from the pyroclastic flows and bombs from the Vulcanian eruption in June 1991. Some ash samples from the pyroclastic flows were also analyzed. The D/H ratios of some hydrous minerals (hornblende and biotite) separated from the blocks and bombs were determined to constrain the D/H ratio of water dissolved in magma at deeper levels.

2. Samples and analytical methods

The samples analyzed include blocks from pyroclastic flows, bread-crust bombs from Vulcanian explosion and ash derived from pyroclastic flows (Table 1). Bread-crust bombs from the June 11 Vulcanian explosion are generally more porous than the blocks in the pyroclastic flow deposits. The bread-crust bombs have dense outer margins, 5–10 mm thick, compared to the inner part. The blocks and bombs commonly contain phenocrysts of plagioclase, hornblende, biotite, quartz, iron oxides and pyroxenes, in decreasing order of abundance. The modal analysis indicated that the crystal content was approximately 25 vol.% on the dense-rock basis (Nakada, 1996a). The groundmass is composed of glass, plagioclase, hornblende, pyroxene and magnetite (Sato, 1996; Nakada and Motomura, 1997). The block and bomb samples were fresh, and there was no sign of secondary alteration. An ash fall sample from the phreatic eruption of April 9, 1991, before the dome emergence, consists of some vesicular glass fragments and lithic accessories. Ash fall samples from pyroclastic flows consist mainly of glassy, vesicular grains accompanied by some accessory grains of unknown origin. For these reasons, we excluded the ash samples from discussion, although the analytical results are similar to the bulk values of the bomb and block samples (Table 1).

Large blocks were crushed on an iron plate with an iron hammer. The powdered samples (60–80 mesh) were analyzed for water content and hydrogen isotopic ratio on a bulk rock basis. Hydrogen in the samples was quantitatively extracted as H₂O by inductively heating to 1200°C in vacuum after adsorbed water was removed at 200°C for 2 h. A small amount of H₂, if any, produced by reaction of water vapor with ferrous iron in the sample was oxidized to H₂O by passing through a CuO furnace at 400°C. The extracted water was passed

Table 1
Water and hydrogen isotopic ratios of blocks, bombs and ash from 1991 Unzen eruption

Sample	Sample type	Date of eruption	Bulk rock		Groundmass	
			H ₂ O (wt.%)	δD (‰)	H ₂ O ^a (wt.%)	δD ^b (‰)
K-91-5-24-E	Block in pfd	May 24, 1991	0.20	−59.5	0.10	−83.0
K-91-5-24 (gms)	Block in pfd	May 24, 1991	–	–	0.12 [†]	−88.9 ^c
K-91-5-27-B	Block in pfd	May 27, 1991	0.22	−60.3	0.13	−79.9
K-91-5-27-C	Block in pfd	May 27, 1991	0.24	−63.0	0.15	−82.2
K-91-6-1-B	Block in pfd	June 1, 1991	0.21	−60.0	0.12	−81.2
K-91-6-1-E	Block in pfd	June 1, 1991	0.23	−58.8	0.15	−74.5
K-91-6-9-A4	Block in pfd	June 9, 1991	0.40	−59.0	0.38	−65.1
K-91-6-9-B1	Block in pfd	June 9, 1991	0.33	−53.2	0.29	−57.9
K-91-9-16-01	Block in pfd	September 16, 1991	0.20	−52.4	0.11	−63.4
92011501CA	Vulcanian bomb, margin	June 11, 1991	0.50	−61.2	0.51	−66.5
92011501CB	Vulcanian bomb, core	June 11, 1991	0.34	−59.0	0.29	−66.9
92031701AA	Vulcanian bomb, margin	June 11, 1991	0.48	−60.0	0.49	−65.1
92031701AB	Vulcanian bomb, core	June 11, 1991	0.28	−54.5	0.21	−61.9
92031701BA	Vulcanian bomb, margin	June 11, 1991	0.51	−60.9	0.53	−65.8
92031701BB	Vulcanian bomb, core	June 11, 1991	0.28	−52.7	0.21	−58.8
91081806	Vulcanian block	June 11, 1991	0.35	−52.9	0.31	−57.0
91081807	Vulcanian block	June 11, 1991	0.38	−59.9	0.35	−66.8
91081808B	Vulcanian block	June 11, 1991	0.30	−61.1	0.24	−72.2
91081810	Vulcanian block	June 11, 1991	0.33	−47.6	0.28	−49.1
92011501A	Vulcanian block	June 11, 1991	0.33	−57.7	0.29	−65.0
92011501B	Vulcanian block	June 11, 1991	0.28	−66.0	0.21	−82.5
K-91-4-9	Ash from phreatic eruption	April 9, 1991	0.96	−67.4	–	–
K-91-6-8	Ash matrix in pfl	June 9, 1991	0.30	−37.1	–	–
K-91-6-9	Ash fall from pfl	June 9, 1991	0.41	−64.0	–	–
K-91-6-18	Ash fall from pfl	June 18, 1991	0.33	−68.5	–	–
K-91-7-16	Ash fall from pfl	July 16, 1991	0.30	−49.2	–	–
K-91-8-13	Ash fall from pfl	August 18, 1991	0.51	−86.8	–	–

^aH₂O content of groundmass of the block and bomb samples was calculated by subtracting the phenocryst contribution.

Mean phenocryst content of 25 vol.% containing 4.6 vol.% hornblende and 1.2 vol.% biotite was assumed.

See Table 2 for H₂O contents of the minerals used for the calculation.

^bδD of groundmass of the block and bomb samples was calculated by subtracting the phenocryst contribution.

See Table 2 for δD values of the minerals used for the calculation.

^cMeasured on a groundmass concentrated using a heavy liquid ($d = 2.65 \text{ g/cm}^3$).

through heated metallic uranium to quantitatively convert to H₂, and the volume of the resulting H₂ was measured using a calibrated manometer (Suzuoki and Epstein, 1976).

Phenocrysts of hornblende and biotite, typically 0.2–1 mm in size, were hand-picked under a binocular microscope from coarsely crushed lava blocks and bombs. Altogether 70–150 mg of mineral separates were obtained. Hornblende was brown to brownish green, suggesting some oxidation of Fe²⁺ due to dehydrogenation (Miyagi et al., 1998). Water was extracted from the mineral separates in the same manner as the bulk rock samples.

Hydrogen was analyzed with a stable isotope mass spectrometer to determine the D/H ratio. The isotopic results are expressed in a δD notation with respect to the V-SMOW standard. Duplicate analyses of water content of the samples agreed within 0.01 wt.%. The repeated analysis ($n = 12$) of the laboratory sericite reference sample during the course of the Unzen sample analysis indicated that the analytical reproducibility of δD measurement was $\pm 1.6\%$.

3. Water contents and hydrogen isotopic ratios

The analytical results are given in Table 1. The H₂O contents and δD values of the blocks and bombs are given on a bulk rock basis and also on a groundmass basis. The groundmass values were acquired to discuss the D/H fractionation between water vapor and melt. They were calculated by subtracting the contribution of phenocrysts using the following equations:

$$H_2O_{gms} = \frac{H_2O_{wr} - H_2O_{hbd} \times Hbd - H_2O_{bi} \times Bi}{Gms} \times 100 \quad (1)$$

and

$$\delta D_{gms} = \frac{\delta D_{wr} \times H_2O_{gms} - Hbd \times H_2O_{hbd} \times \delta D_{hbd} - Bi \times H_2O_{bi} \times \delta D_{bi}}{Gms \times H_2O_{gms}} \quad (2)$$

where subscripts gms, wr, hbd and bi stand for groundmass, whole rock, hornblende and biotite, respectively. Hbd, Bi and Gms indicate their abundance in wt.% calculated using their mode and densities. Densities of 3.2, 3.0 and 2.6 were used for hornblende, biotite and groundmass, respectively. The crystal contents of the Unzen dacite in an early stage of the eruptive activity (i.e., 1991) were constant at about 25 ± 3 vol.% (Nakada, 1996a). The phenocryst mode is fairly constant, hornblende and biotite constituting 4.6 and 1.2 vol.% on the dense rock basis. Water contents and δD values of hornblende and biotite phenocrysts as well as the amount of minerals used for analysis are listed in Table 2. The groundmass H₂O contents thus calculated using the above phenocryst contents and their mean H₂O and δD values given in Table 2 are close to the bulk rock H₂O contents, but the correction resulted in variably lower δD values of groundmass than those of bulk rocks (Table 1). For sample K-91-5-24E, groundmass was concentrated using a heavy liquid with density of 2.65 g/cm³ (a bromoform–alcohol mixture) after large phenocrysts were removed by hand-picking. Hydrogen isotopic exchange between the groundmass and heavy liquid was assumed to be negligible. The water content and δD value of the groundmass separate, 0.12 wt.% and -89% , were in good agreement with the calculated values (Table 1) using the above Eqs. (1) and (2).

The δD vs. H₂O plot of hornblende and biotite phenocrysts shows a trend of increasing δD with decreasing H₂O content (Fig. 1), suggesting that the minerals were partially dehydrated and probably dehydrogenated during magma ascent to the surface. The H₂O– δD trend is consistent with the results of dehydration experiments of hornblende (Miyagi et al., 1998).

The H₂O– δD relationship for the Unzen samples is shown in Fig. 2. The data calculated on the phenocryst-free basis are plotted for block and bomb samples, whereas the whole rock data are plotted for ash samples. The blocks from the pyroclastic flows and bombs from the Vulcanian explosions on June 11, 1991

Table 2
D/H analysis of hornblende and biotite from the 1991 eruption of Unzen volcano

Sample	Hornblende			Biotite		
	Amount used (mg)	H ₂ O (wt.%)	δD (‰)	Amount used (mg)	H ₂ O (wt.%)	δD (‰)
Block in pfl, May 24, 1991	110	1.66	–39.5	–	–	–
Block in pfl, May 29, 1991	153	1.46	–36.7	102	1.83	–39.1
Vulcanian bomb A, June 11, 1991	124	1.52	–44.6	91	1.69	–46.5
Vulcanian bomb B, June 11, 1991	101	1.68	–44.0	67	2.13	–48.7
Block in pfl (630C), June 30, 1991	112	1.49	–40.3	78	1.68	–42.4
Block in pfl, September 15, 1991	133	1.57	–40.6	110	1.67	–43.9
Lava from Dome #3, October 27, 1991	104	1.37	–38.2	92	1.60	–41.1

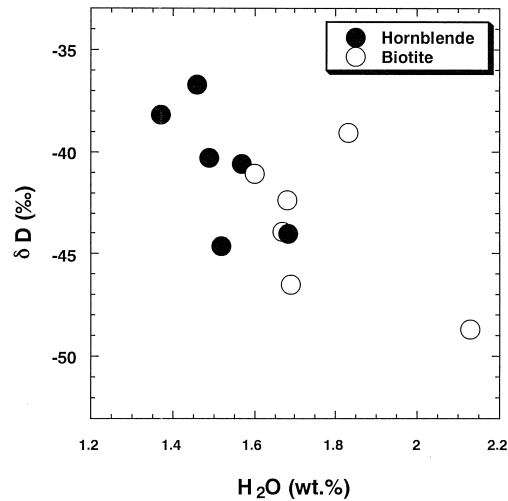


Fig. 1. The δD vs. H_2O plot of hornblende and biotite phenocrysts separated from blocks, bombs and dome lavas of Unzen volcano. See Table 2 for the data.

have H_2O contents ranging from 0.10 to 0.53 wt.%, and δD values from -83 to -49‰ . Ash samples (excluding sample K-91-4-9) show a narrow range of variation in H_2O content (0.30–0.51 wt.%), but a wide range of variation in δD (-87 to -37‰). Sample K-91-4-9 has the highest H_2O content (0.96 wt.%) and is from the phreatic explosion on April 9, 1991. This sample contains fine fragments of basement rocks, vesicular glass, abundant lava coated with fine ash, accretionary lapilli and altered lavas. The other ash samples also

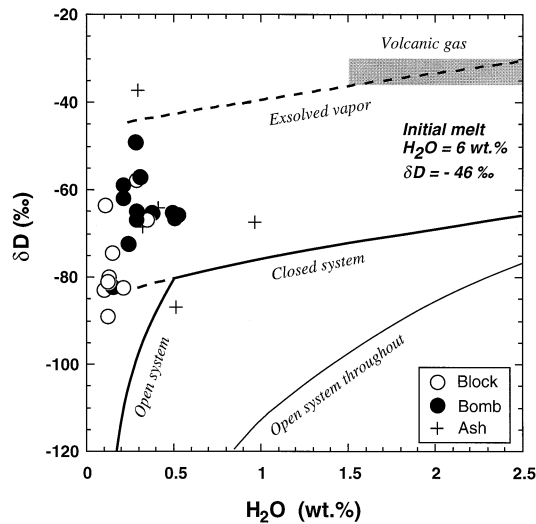


Fig. 2. The δD vs. H_2O plot of the ash and lava blocks from pyroclastic flow deposits and bombs from Vulcanian eruptions on June 11, 1991. The ash data are given on a bulk rock basis, whereas the block and bomb data are shown on a groundmass basis (see text). Two model curves are drawn; (1) close system degassing followed by open system degassing after H_2O content of the magma is reduced to 0.5 wt.% and (2) open system degassing from beginning to end. The δD value of exsolved vapor for the model (1) is shown by dashed curves as a function of H_2O content of the melt. The H_2O and δD values of the pre-eruption melt were assumed to be 6 wt.% and -46‰ , respectively. Hatched area indicates the range of δD values of magmatic gases, corresponding to the exsolved vapor in the closed system when degassing reached $H_2O = 1.5\text{--}2.5$ wt.%.

contain accessory materials of unknown origin. Their variable glass/crystal ratios make the correction for the phenocryst contribution difficult. For these reasons, the results of ash samples were excluded from the following discussion, although they were plotted in Fig. 2.

The δD value of local meteoric water is around -40‰ (Mizota and Kusakabe, 1994; Scott et al., 1994). Alteration of rock samples by such local meteoric water is not likely, since all samples used here were collected soon after extrusion of lavas (for example, the June 11 Vulcanian bombs and blocks were collected in August 1991 to March 1992, only 2–9 months later).

4. Pre-eruptive H_2O content and δD value

To discuss degassing processes, we must constrain the H_2O content and δD value of the pre-eruptive magma. There is much petrologic evidence that magma mixing took place before and/or during ascent of the magma such as the existence of round-shaped phenocrysts showing resorption, plagioclase phenocrysts showing reversed zoning with sodic core (An40–50) and more calcic rim (An55–65) and higher MgO and FeO concentrations in rim than in core (Sato, 1996), and hornblende and biotite phenocrysts forming pargasite rim (Nakada and Motomura, 1997). These features are explained by mixing of a low temperature, crystal-rich magma of dacitic composition with a high temperature, aphyric magma of slightly more mafic composition (Nakamura, 1996; Sato, 1996). Nakamura (1996) estimated $T = 760^\circ\text{C}$, phenocryst content of 40 wt.% and $\text{SiO}_2 = 67$ wt.% for the low-temperature (LT) magma, and $T = 830\text{--}850^\circ\text{C}$ and $\text{SiO}_2 = 63.5$ wt.% for the high-temperature (HT) magma with the LT/HT magma mixing ratio of 58/42. The timing of the mixing is controversial; the LT magma that existed at a shallow level beneath Unzen volcano was penetrated by and mixed with the andesitic–dacitic HT magma just prior to the eruption (Nakamura, 1995; Sato, 1996), whereas the disequilibrium nature of the phenocryst assemblage of Unzen dacite is suggestive of processes taking place in an already mixed, convecting magma chamber (Nakada and Motomura, 1997). The depth of the main magma reservoir is estimated to be about 11 ± 2 km below the surface on the basis of GPS ground deformation measurements during eruption (Nishi et al., 1995). This depth is consistent with a petrologic pressure estimate of 200 ± 50 MPa for the mixed magma made on the basis of plagioclase geobarometry and assuming water saturation and a temperature of 900°C (Fujii, 1996). Melting experiments of Unzen lavas indicate that more than 4 wt.% H_2O is required for the phenocryst stabilization in the mixed magma (Takahashi et al., 1993). For our purpose, the saturated water content of the mixed magma of 6 wt.% was assumed using the water solubility curve for rhyolite melt at 200 MPa (Silver et al., 1990). This water content is similar to that for recent pre-eruptive magmas of Mount St. Helens (3.7–6.5 wt.%, Gardner et al., 1995) and Mount Pinatubo (5.1–6.4 wt.%, Rutherford and Devine, 1996).

It is difficult to determine an initial δD value of water dissolved in the pre-eruptive, mixed magma, because glassy materials with high water contents are not available. As noted previously, the mixed magma consists of a low temperature, phenocryst-rich, dacitic magma and a high-temperature, aphyric magma whose bulk chemical composition is estimated to be similar to the low temperature magma (Nakamura, 1996). We can constrain a δD value of water in the low temperature magma from the following considerations. If we assume that hornblende phenocrysts were in equilibrium with melt of the low temperature magma, their D/H ratios must have been controlled by D/H fractionation between hornblende and melt ($\alpha_{\text{hbd-melt}}$). If the magma was saturated with water, then $\alpha_{\text{hbd-melt}}$ is related to the following relationship:

$$\begin{aligned} \alpha_{\text{hbd-melt}} &= \alpha_{\text{hbd-vap}} \alpha_{\text{vap-melt}} \\ &= \alpha_{\text{hbd-vap}} \left[X_{\text{OHm}} \alpha_{\text{vap-OHm}} + (1 - X_{\text{OHm}}) \alpha_{\text{vap-H}_2\text{O}} \right] \end{aligned} \quad (3)$$

where $\alpha_{\text{hbd-melt}}$, $\alpha_{\text{hbd-vap}}$, and $\alpha_{\text{vap-melt}}$ are the D/H fractionation factors between hornblende and total dissolved water in the melt, hornblende and vapor, and vapor and total dissolved water in the melt, respectively. The

X_{OH_m} and $X_{\text{H}_2\text{O}_m}$ are hydrogen atomic fractions of OH_m and H_2O_m in the melt (Taylor, 1991). Of these fractionation factors, $\alpha_{\text{vap-melt}} = 1.024$ was experimentally determined for a vapor–natural obsidian melt system with the total water content of 3.1 wt.% at 500 bar and 950°C (Taylor and Westrich, 1985), but $\alpha_{\text{vap-melt}}$ values are not known for other temperatures and H_2O contents. A similar value was reported by Richet et al. (1986) for the vapor–albitic melt system between 850 and 1250°C, although they noted experimental difficulty of attaining a closed system equilibrium due to hydrogen addition from the pressure medium. Thus, accuracy of the $\alpha_{\text{vap-melt}}$ value is difficult to evaluate not only because the experimental details are unavailable (Taylor and Westrich, 1985), but also because the fractionation may vary depending on the relative proportion of OH_m and H_2O_m in the melt as a function of the total water content and temperature (Stolper, 1982; Newman et al., 1988; Taylor, 1991; Nowak and Behrens, 1995; Shen and Keppler, 1995). Dobson et al. (1989) determined $\alpha_{\text{vap-OH}_m} = 1.040$ at 750–850°C for rhyolitic melt under low pressure, OH_m -dominated conditions. They also proposed that $\alpha_{\text{vap-H}_2\text{O}_m} = 1.000$. Nowak and Behrens (1995) measured in-situ speciation of the water dissolved in silicate melt of haplogranitic composition by infrared spectroscopy. If we accept their $\text{OH}_m/\text{H}_2\text{O}_m$ ratio of 0.67/0.33 (hydrogen atomic basis) at 750°C for the melt with total water of 6 wt.%, we obtain $\alpha_{\text{vap-melt}} = 1.027$ from the second term of Eq. (3).

The D/H fractionation factors were determined for various hydrous minerals–water systems as a function of temperature and mineral chemistry by Suzuoki and Epstein (1976) and Graham et al. (1984). The $\alpha_{\text{hbd-vap}}$ value of 0.983 at 750°C was calculated using the Suzuoki–Epstein formulation. The chemical composition of *core* part of Unzen hornblende phenocrysts was taken from Table 1 of Nakada et al. (1995). The $\alpha_{\text{hbd-melt}}$ value is then calculated to be 1.010. Hornblende is stable in dacitic magma at a pressure greater than 130 MPa (Gardner et al., 1995) at the total H_2O concentration of > 5 wt.%. Under the assumption that hornblende in Vulcanian bomb B ($\delta\text{D} = -44\text{‰}$, Table 2) was in equilibrium with the melt of the low-temperature magma, its δD value is calculated to be -53‰ . We chose the highest H_2O content and lowest δD value of the analyzed hornblende recognizing that they most likely represent the hornblende that was subjected to the least dehydration during effusion of the dacite lavas (Fig. 1). The bulk δD value of -52‰ is then calculated for the low temperature magma consisting of 60 wt.% melt and 40 wt.% crystals containing hornblende (21 wt.% of the crystals) and biotite (5 wt.%) as major hydrous minerals (Nakamura, 1996). In this calculation, we again chose the highest H_2O content and lowest δD value of the analyzed biotite, although the contribution of hornblende and biotite to δD value of the low temperature magma is very small. Currently it is difficult to estimate the water content of the high temperature, aphyric magma. Considering the similarity of the bulk chemical composition between the two magmas, the high temperature magma was assumed to have a water content and δD value similar to the low temperature magma. Thus, the melt of pre-eruptive, mixed magma was assumed to have a water content of 6 wt.% and δD value of around -50‰ .

5. Degassing model

The H_2O – δD relationships of volcanic glasses from explosive rhyolitic eruptions have been modeled by open system degassing and/or closed system degassing (Taylor et al., 1983; Newman et al., 1988; Dobson et al., 1989; Taylor, 1991). The former is based on the assumption that gas is removed as it exsolves from the system, and is approximated by Rayleigh fractionation behavior. The latter is based on the assumption that gas always remains in contact with the magma. Rhyolitic lava dome emplacement has been explained by either open system degassing (e.g., Little Glass Mountains; Taylor et al., 1983), closed system degassing followed by open system degassing (Mono Craters; Newman et al., 1988; Dobson et al., 1989), or multi-stage, closed/open system degassing (Inyo Dome; Taylor, 1991). For eruption leading to dacitic lava dome formation, variations of H_2O content and δD of dissolved water are explained by a combination of open-, closed-system, and kinetically-controlled water loss (Anderson and Fink, 1989; Hoblitt and Harmon, 1993; Anderson et al., 1995; this study). Although high initial water contents of dome-forming dacitic magmas (5–6 wt.%) are required for

stabilization of hydrous minerals as noted above, dome lavas generally contain very low H₂O, indicating that extensive degassing has proceeded prior to extrusion. Maximum groundmass H₂O content is 0.53 wt.%. Thus, more than 90% of initial water must have degassed before dome formation. This view is consistent with the mechanism for non-explosive silicic volcanism proposed by Eichelberger et al. (1986). It is difficult to assess the change in δD values of dissolved water in magma during such extensive degassing.

It is known that Unzen lavas are highly vesiculated, with porosity of 20–30 vol.%, and that the vesicles are filled with water vapor under pressure of 1–2 MPa in excess of atmospheric pressure (Sato, 1996). This excess pressure explains high self-explosivity of collapsed lava dome rocks leading to generation of frequent pyroclastic flows (Sato et al., 1992). The amount of such water in the vesicles, calculated using the ideal gas law with the above porosity, pressure and temperature (800°C), is equivalent to 0.1–0.5 wt.% (groundmass based). Adding the groundmass H₂O contents of 0.1–0.5 wt.%, the H₂O content of the lava at the time of extrusion may have been as high as 1 wt.%. Part of the degassed water was obviously discharged to the atmosphere as volcanic gas. The SO₂ emission rate was 140–200 ton/day in 1991 (measured by COSPEC; Hirabayashi et al., 1995). Combination of the SO₂ emission rate with the magma extrusion rate of $0.3\text{--}0.4 \times 10^6 \text{ m}^3/\text{day}$ in 1991 (Nakada, 1996b) gives a ratio of 150–280 g SO₂/10⁶ ton magma (a bulk density of 2.4 g/cm³ was assumed for dome lava). If a SO₂/H₂O weight ratio of 1.6×10^{-2} of volcanic gas (Ohba et al., 1994) is used, the H₂O content of magma before gas loss is calculated to be 0.9–1.7 wt.%. Thus, altogether 1.1–2.7 (ave. 2.0) wt.% H₂O was contained in the magma near the top of the conduit where volcanic gas was liberated. We can use δD values of volcanic gas to constrain the deuterium content of this magma. The δD values of water in high temperature volcanic gases ($T \sim 810^\circ\text{C}$) collected from the summit of Unzen volcano between May–December 1992 are -32.0 , -34.9 , -30.2 and -35.2 , and -36.2‰ (Scott et al., 1994) with the average of -34‰ . If this volcanic gas represents the water vapor exsolved from the melt that experienced a closed system degassing from the initial H₂O content of 6 to 2 wt.%, δD of the initial melt is required to have $\delta D = -46\text{‰}$, close to the assumed value of -50‰ .

To show possible degassing processes of the Unzen magma, two model curves are illustrated in Fig. 2: Closed system degassing starting from 6 wt.% down to 0.5 wt.% H₂O (water content at the time of lava extrusion) followed by open system degassing, and open system degassing throughout. The variation in δD values of exsolved vapor is also shown for the former case. Closed system degassing is described by:

$$\delta D_f = \delta D_i - 10^3 \ln \alpha_{\text{vap-melt}}(1 - F), \quad (4)$$

and open system degassing is described by:

$$\delta D_f = \delta D_i - 10^3(1 - \alpha_{\text{vap-melt}}) \ln F, \quad (5)$$

where δD_f is δD value of melt when fraction of water remaining in the melt is F , δD_i is initial δD value and $\alpha_{\text{vap-melt}}$ is hydrogen isotopic fractionation factor between vapor and total water in the melt at 850°C. δD value of exsolved vapor at fraction F in closed system degassing is calculated from:

$$\delta D_{\text{vap}} = [\alpha_{\text{vap-melt}}(1 + 10^{-3}\delta D_f) - 1] 10^3. \quad (6)$$

Eqs. (4) and (6) were used to evaluate the δD_i value as discussed in the foregoing paragraph where volcanic gas data were used as a constraint. For open system degassing following closed system degassing in the former model, the starting H₂O content and δD value were taken to be 0.5 wt.% and -81‰ , respectively, the final values attained under the closed system degassing starting from the melt having 6 wt.% H₂O and -46‰ δD .

The data points in Fig. 2 plot above and to the left of any model curves constructed under the assumptions previously mentioned, although the samples with δD values lower than -65‰ show a trend shown by an open system degassing, similar to that for the October 1986 lobe of the Mount St. Helens (Anderson et al., 1995). To fit the two stage model curve to the data points, a δD_i value of -30‰ is required. Hoblitt and Harmon (1993) assumed the initial δD value of -34‰ for degassing models of the 1980 Mount St. Helens eruption. However,

it is difficult to find evidence for such isotopically heavy initial water in the case of Unzen volcano. The data points with δD values higher than -65‰ are scattered, and appear to be explained by kinetic hydrogen isotopic fractionation during the last stage degassing as discussed below. The concept behind the degassing models, whether closed or open, requires isotopic communication between exsolving vapor and remaining liquid, i.e., the magma must be homogenized chemically and isotopically as vapor exsolves. This condition may only be achieved in a low viscosity magma of high H_2O content or of high temperature, because water molecules in bubbles can easily interact with melt for exchange to occur. However, as degassing proceeds, the magma becomes more and more viscous at a given temperature. In the case of rhyolitic magma its viscosity increases by approximately 1.5 log unit for every 1 wt.% decrease of H_2O content, and reaches 10^9 – 10^{10} poise at 2–1 wt.% H_2O at 850°C (Lange, 1994). Viscosity of 10^{11} poise was estimated for the Unzen lavas (Seino et al., 1991; Goto et al., 1997). Isotopic communication between exsolved vapor and magma may be highly restricted in highly viscous magma, not only because water molecules in the vapor would be difficult to collide with water in the melt and but also because homogenization of the melt would be restricted. Consequently, the H_2O – δD co-variation due to degassing may no longer take place effectively in such a water-depleted magma in a short period of time. Such difficulty of communication between vapor and magma is likely reflected in general lack of positive correlation between δD and H_2O in dome lavas; Unzen (Fig. 2, this study), Mount St. Helens and Santiaguito (Anderson and Fink, 1989; Hoblitt and Harmon, 1993; Anderson et al., 1995).

When a degassed, highly viscous magma rises through a conduit it may encounter shear stress, resulting in deformation of vesicles and migration of volatiles through numerous cracks (Fink and Manley, 1987). Isotopic change during degassing under such circumstances is expected to be small, but transfer of water from highly viscous melt to open space may be controlled by a kinetic isotopic effect. Fig. 3 shows the δD – H_2O relationship between chilled margins and core of three bread-crust bombs from June 11, 1991 Vulcanian eruption. The chilled margins of two samples A (9231701A) and B (92031701B) have higher groundmass H_2O contents (0.49–0.53 wt.%) and lower δD values (-65 to -66‰) than their cores ($H_2O = 0.21$ wt.%, $\delta D = -62$ to -59‰). Sample C (92011501C) has a lower core H_2O content (0.29 wt.%) than the margin (0.51 wt.%), but the δD value is similar the margin. The isotopic increase during small degree of degassing observed for the bread-crust bombs (Fig. 3) may be ascribed to the kinetic effect as mentioned above, although a more random behavior in the H_2O – δD relationship was observed for bread-crust bombs from May 18, 1980

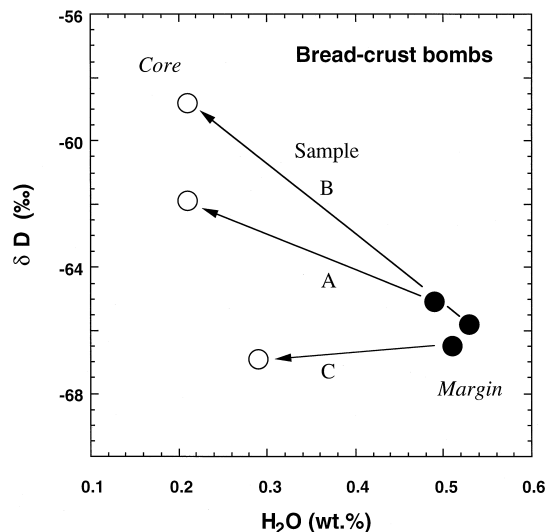


Fig. 3. Comparison of H_2O and δD values between chilled margins and cores of bread-crust bombs from Vulcanian eruptions in June 11, 1991. Note the negative correlation between the margin and core.

eruption of Mount St. Helens (Hoblitt and Harmon, 1993). From the foregoing discussion, we prefer the interpretation that the δD values of block and bomb samples of Unzen volcano that are higher than any of the model curves (Fig. 2) resulted from a kinetic isotope effect superimposed on the isotopic trend that was accomplished by the closed system degassing followed by the last stage open system degassing.

6. Conclusions

(1) Groundmass-based water contents and hydrogen isotopic ratios of lava blocks from pyroclastic flow deposits, and bread-crust bombs and blocks from the 1991 Vulcanian eruptions of Unzen volcano range from 0.1 to 0.5 wt.% and -83 to -49% , respectively. They do not show a systematic trend, although the block samples tend to have lower δD values than the bomb samples.

(2) The non-systematic H_2O – δD relationship is likely a result of near surface, kinetically-controlled degassing of highly degassed magma with H_2O contents as low as 0.5 wt.%. Water-depleted, high viscosity magma would hinder attainment of hydrogen isotopic equilibrium between exsolved vapor and melt in the final stage. The kinetic isotopic fractionation was exemplified by bread-crust bombs with high H_2O –low δD margins and low H_2O –high δD cores.

(3) Relatively high δD values of the blocks and bombs as well as high temperature volcanic gas (-30 to -35%) suggest a closed system degassing of an initial water-rich magma ($H_2O = 6$ wt.%, $\delta D = -46\%$). These pre-eruptive values were estimated from the volcanic gas data and D/H analysis of hornblende phenocrysts coupled with assumed isotopic equilibration in the initial hydrous magma.

(4) Better understanding of near surface degassing processes may be obtained by combining the rock data with the volcanic gas data if available. Further analysis of samples erupted at different times would give a long-term degassing behavior, since the dates of collection of our samples are limited within the total period of the recent Unzen activity (1991–1995; Nakada, 1996a).

(5) Models used in the discussion include some important parameters that are not well known so far. They are hydrogen isotopic fractionation factor between exsolving vapor and melt, and speciation of water dissolved in melt. These parameters need to be known for silicate melts of a wide range of water content and chemical composition. Better knowledge on the water content and δD value of the pre-eruptive magma also plays a critical role in the modeling.

Acknowledgements

We thank T. Nogi and H. Kusakabe for their technical assistance in D/H measurement and mineral separation. Critical comments by two reviewers, S. Anderson and Y. Matsuhisa, are appreciated. English of the early version of the manuscript was improved by M.J. Walter.

References

- Anderson, S.W., Fink, J.H., 1989. Hydrogen-isotope evidence for extrusion mechanisms of the Mount St. Helens lava dome. *Nature* 341, 521–523.
- Anderson, S.W., Fink, J.H., Rose, W.I., 1995. Mount St. Helens and Santiaguito lava domes: the effect of short-term eruption rate on surface texture and degassing processes. *J. Volcanol. Geotherm. Res.* 69, 105–116.
- Dobson, P.F., Epstein, S., Stolper, E.M., 1989. Hydrogen isotope fractionation between coexisting vapor and silicate glasses and melts at low pressure. *Geochim. Cosmochim. Acta* 53, 2723–2730.
- Eichelberger, J.C., Carrigan, C.R., Westrich, H.R., Price, R.H., 1986. Non-explosive silicic volcanism. *Nature* 323, 598–602.
- Fink, J.H., Manley, C.R., 1987. Origin of pumiceous and glassy textures in rhyolite flows and domes. In: Fink, J.H. (Ed.), *The Emplacement of Silicic Domes and Lava Flows*. *Geol. Soc. Am. Spec. Pap.* 212, 77–88.

- Fujii, T., 1996. Eruption of Unzen–Fugendake volcano—petrologic constraints on the magma supply system. *Gekkan Chikyu* 15, 47–51, (in Japanese).
- Gardner, J.E., Rutherford, M., Carey, S., Sigurdsson, H., 1995. Experimental constraints on pre-eruptive water contents and changing magma storage prior to explosive eruptions of Mount St. Helens volcano. *Bull. Volcanol.* 57, 1–17.
- Goto, A., Maeda, I., Nishida, Y., Oshima, H., 1997. Viscosity–equation for magmatic silicate melts over a wide temperature range. *Proc. Unzen International Workshop: Decade Volcano and Scientific Drilling*, Shimabara, Japan, pp. 100–105.
- Graham, C.M., Harmon, R.S., Sheppard, S.M.F., 1984. Experimental hydrogen isotope studies: hydrogen isotope exchange between amphibole and water. *Am. Mineral.* 69, 128–138.
- Hirabayashi, J., Ohba, T., Nogami, K., Yoshida, M., 1995. Discharge rate of SO₂ from Unzen volcano Kyushu, Japan. *Geophys. Res. Lett.* 22, 1709–1712.
- Hoblitt, R.P., Harmon, R.S., 1993. Bimodal density distribution of cryptodome dacite from the 1980 eruption of Mount St. Helens, Washington. *Bull. Volcanol.* 55, 421–437.
- Jaupart, C., Allegre, C.J., 1991. Gas content, eruption rate and instabilities of eruption regime in silicic volcanoes. *Earth Planet. Sci. Lett.* 102, 413–429.
- Kuroda, Y., Hariya, Y., Suzuoki, T., Matsuo, S., 1982. D/H fractionation between water and the melts of quartz, K-feldspar, albite and anorthite at high temperature and pressure. *Geochem. J.* 16, 73–78.
- Lange, R.A., 1994. The effect of H₂O, CO₂ and F on the density and viscosity of silicate melts. In: Carroll, M.R., Rutherford, J.R. (Eds.), *Volatiles in Magmas*. *Rev. Mineral.* 30, 331–369.
- Miyagi, I., Matsubaya, O., Nakashima, S., 1998. Change in D/H ratio, water content and color during dehydration of hornblende. *Geochem. J.* 32, 33–48.
- Mizota, C., Kusakabe, M., 1994. Spatial distribution of δD – $\delta^{18}O$ values of surface and shallow groundwaters from Japan, South Korea and East China. *Geochem. J.* 28, 387–410.
- Nakada, S., 1996a. Unzen–Fugendake eruption: relationships between extrusion rate of magma, growth rate of dome and lava composition. *Gekkan Chikyu* 15, 64–69, (in Japanese).
- Nakada, S., 1996b. Characteristics of lava dome eruption and dome growth model at Unzen volcano. *Mem. Geol. Soc. Jpn.* 46, 139–148, (in Japanese).
- Nakada, S., Fujii, T., 1993. Preliminary report on the activity at Unzen volcano (Japan), November 1990–November 1991: dacite lava domes and pyroclastic flows. *J. Volcanol. Geotherm. Res.* 54, 319–333.
- Nakada, S., Motomura, Y., 1997. Magma chamber of Unzen volcano and origin of phenocrysts and enclaves. *Bull. Volcanol. Soc. Jpn.* 42, S167–S174, (in Japanese).
- Nakada, S., Motomura, Y., Shimizu, H., 1995. Manner of magma ascent at Unzen volcano, Japan. *Geophys. Res. Lett.* 22, 567–570.
- Nakamura, M., 1995. Continuous mixing of crystal mush and replenished magma in the ongoing Unzen eruption. *Geology* 23, 807–810.
- Nakamura, M., 1996. Time scale of magma mixing in Unzen eruption from 1991 to 1993: continuous mixing model of crystal-rich magma and replenished magma. *Mem. Geol. Soc. Jpn.* 46, 127–138, (in Japanese).
- Newman, S., Epstein, S., Stolper, E., 1988. Water, carbon dioxide, and hydrogen isotopes in glasses from the ca. 1340 AD eruption of the Mono Craters, California: constraints on degassing phenomena and initial volatile content. *J. Volcanol. Geotherm. Res.* 35, 75–96.
- Nishi, K., Ishihara, K., Kamo, K., Ono, H., Mori, H., 1995. Positioning of magma reservoir at Unzen volcano by GPS survey. *Bull. Volcanol. Soc. Jpn.* 40, 43–51.
- Nowak, M., Behrens, H., 1995. The speciation of water in haplogranitic glasses and melts determined by in situ near infrared spectroscopy. *Geochim. Cosmochim. Acta* 59, 3445–3450.
- Ohba, T., Hirabayashi, J., Nogami, K., Yoshida, M., 1994. Equilibrium temperature and redox state of volcanic gas at Unzen volcano, Japan. *J. Volcanol. Geotherm. Res.* 60, 263–272.
- Richet, P., Roux, J., Pineau, F., 1986. Hydrogen isotope fractionation in the system H₂O–liquid NaAlSi₃O₈: new data and comments on D/H fractionation in hydrothermal experiments. *Earth Planet. Sci. Lett.* 78, 115–120.
- Rutherford, M.J., Devine, J.D., 1996. Pre-eruption pressure–temperature conditions and volatiles in the 1991 dacitic magma of Mount Pinatubo. In: Newhall, C.G., Punongbayan, R.S. (Eds.), *Fire and Mud—Eruptions and Lahars of Mount Pinatubo, Philippines*. *PHIVOLCS and Univ. Washington Press*, Seattle, pp. 751–766.
- Sato, H., 1996. A model of the 1991 eruption of Unzen volcano inferred from petrographic textures of the ejecta. *Mem. Geol. Soc. Jpn.* 46, 115–125, (in Japanese).
- Sato, H., Fujii, T., Nakada, S., 1992. Crumbling of dacite dome lava and generation of pyroclastic flows at Unzen volcano. *Nature* 360, 664–666.
- Scott, G.L., Kusakabe, M., Hirabayashi, J., Ohba, T., Nagao, K., Kita, I., 1994. Geochemical evolution and origin of volcanic gases and springs in Japan. *J. Geol. Soc. Philippines* 59, 89–110.
- Seino, M., Hashimoto, T., Uhira, K., Yamasato, H., 1991. Viscosity of lava flows from three eruptions of Unzen volcano. *Volcanol. Soc. Jpn., Annu. Mtg. Abstr.* 2, 39, (in Japanese).
- Shen, A., Keppeler, H., 1995. Infrared spectroscopy of hydrous silicate melts to 1000°C and 10 kbar: direct observation of H₂O speciation in a diamond–anvil cell. *Am. Mineral.* 80, 1335–1338.

- Silver, L.A., Ihinger, P.D., Stolper, E., 1990. The influence of bulk composition on the speciation of water in silicate glasses. *Contrib. Mineral. Petrol.* 104, 142–162.
- Stolper, E., 1982. The speciation of water in silicate melts. *Geochim. Cosmochim. Acta* 46, 2609–2620.
- Suzuoki, T., Epstein, S., 1976. Hydrogen isotope fractionation between OH-bearing minerals and water. *Geochim. Cosmochim. Acta* 40, 1229–1240.
- Takahashi, E., Miyagi, I., Tomiya, A., Caprarelli, G., Nakamura, M., 1993. Experimental simulation studies of magma reservoir. Technical report on the project 'Eruption mechanisms and volcanic disasters', No. A-4-8, Okayama University, pp. 26–48 (in Japanese).
- Taylor, B.E., 1991. Degassing of Obsidian Dome rhyolite, Inyo volcanic chain, California. In: Taylor, H.P., O'Neil, J.R., Kaplan, I.R. (Eds.), *The Geochemical Society, Spec. Publ.* 3, pp. 339–353.
- Taylor, B.E., Westrich, H.R., 1985. Hydrogen isotope exchange and water solubility in experiments using natural rhyolite obsidian. *EOS* 66, 387.
- Taylor, B.E., Eichelberger, J.C., Westrich, H.R., 1983. Hydrogen isotopic evidence of rhyolitic magma degassing during shallow intrusion and eruption. *Nature* 306, 541–545.
- Wilding, M.C., Macdonald, R., Davies, J.E., Fallick, A.E., 1993. Volatile characteristics of peralkaline rhyolites from Kenya: an ion microprobe, infrared spectroscopic and hydrogen isotopic study. *Contrib. Mineral. Petrol.* 114, 264–275.
- Woods, A.W., Koyaguchi, T., 1994. Transitions between explosive and effusive eruptions of silicic magmas. *Nature* 370, 641–644.