

## Degassing of Obsidian Dome rhyolite, Inyo volcanic chain, California

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**Abstract**—Research drilling of Obsidian Dome and a nearby feeder dike in Inyo volcanic chain, California, has provided a set of samples that gives us an opportunity to characterize the isotopic signature of rhyolite magma degassing in several near-surface igneous environments. A positive correlation between  $\delta D$  and wt.%  $H_2O$  is observed for  $H_2O$ -rich obsidian clasts from tephra deposits and  $H_2O$ -poor samples of the flow erupted from Obsidian Dome; these samples record progressive degassing of the magma. The initial water content and  $\delta D$  of the magma are estimated to be, respectively, 4.1 wt.%  $H_2O$  (based on analyses of melt inclusions, HERVIG *et al.*, 1989) and  $-40$  (assuming closed-system degassing prior to the first eruption). Subsequent to the first eruption, variations in  $\delta D$  and wt.%  $H_2O$  indicate that degassing became effectively more open-system in character as multiple stages of dominantly closed-system degassing were periodically interrupted by removal of water and melt during successive tephra eruptions. Quantitative modelling of the isotopic effects of vapor loss, including fractionation of hydrogen involving the melt species OH and  $H_2O$ , according to a multi-step scheme, reproduces the observed  $\delta D$  vs. wt.%  $H_2O$  trend of the obsidian data. Final-stage, dominantly open-system degassing resulted in  $\delta D$  values of the obsidian flow as low as  $-120$ .

Crystallization (devitrification) of the vitreous dome flow and conduit magma yielded no large differences in  $\delta D$  and  $\delta^{18}O$  relative to flow obsidian. Water-loss upon crystallization was virtually complete, except for that retained in biotite, and thus no degassing signature was recorded. Low-Ba and high-Ba varieties of rhyolite (VOGEL *et al.*, 1989) have similar  $\delta^{18}O$  values, but a larger variation in  $\delta D$  is found for the low-Ba rhyolite. Crystalline rhyolite and, in particular, the glassy margin of the feeder dike record interaction with hydrothermal meteoric waters, as does the hydrogen isotopic composition of basement granitic rocks. Glassy pyroclasts from tephra-filled, sub-horizontal fractures suggest only minor interaction with meteoric water, and much of the hydrothermal alteration probably occurred after emplacement of the dike.

### INTRODUCTION

SEVERAL RECENT FIELD and experimental studies have demonstrated that exsolution of water from vapor-saturated rhyolite magma results in a change in the D/H ratio of the silicate liquid. Obsidian fragments in tephra units, and glassy zones in subsequent dome-building flows, represent quenched melt from which the degassing history of the magma may be surmised. Isotopic studies by TAYLOR *et al.* (1983) first suggested that obsidian flows from the Inyo volcanic chain and from Medicine Lake Highlands with  $\delta D$  values as low as  $-130$  were the products of open-system magmatic degassing of  $H_2O$ . NEWMAN *et al.* (1988) refined this model to include the effects of  $H_2O$ -OH speciation on bulk melt- $H_2O$  hydrogen isotope fractionation during degassing. Experimental determination of deuterium partitioning between  $H_2O$  and hydrous rhyolite melts (TAYLOR and WESTRICH, 1985; DOBSON *et al.*, 1989) permits us to construct quantitative models of the degassing of such rhyolite magmatic systems.

A Department of Energy-funded drilling program at Obsidian Dome in the Inyo volcanic chain, California (EICHELBERGER *et al.*, 1984, 1985; Fig. 1) provides a unique opportunity to sample a young, 600–525 year-old (MILLER, 1985) rhyolitic flow, its

conduit and near-by feeder dike, and its wallrocks. I report here hydrogen and oxygen isotope data for glassy and crystalline samples collected from these drill holes, and for obsidian and pumice clasts from two sections through related tephra deposits. I use these data to constrain a degassing model for the Obsidian Dome magma which includes both first-boiling (*i.e.*, depressurization-driven degassing) and second-boiling (*i.e.*, crystallization-driven degassing) phenomena. The proposed degassing scenario for Obsidian Dome magma more accurately describes observed isotopic changes than do previous models. In this model, first-boiling is a multi-step degassing process that evolves from an essentially closed-system to an open-system during tephra eruption and doming.

### GEOLOGICAL AND PETROLOGICAL BACKGROUND

Obsidian Dome represents one of seven centers in the 11-km long Inyo volcanic chain from which rhyolite to rhyodacite tephra and lava flows erupted 650–550 years ago (MILLER, 1985; SAMPSON, 1987; Fig. 1). The eruptions are from a dike intrusion localized along one of several en echelon north-northeast-trending fractures (FINK, 1985) within a major north-south trending fracture zone (MILLER,

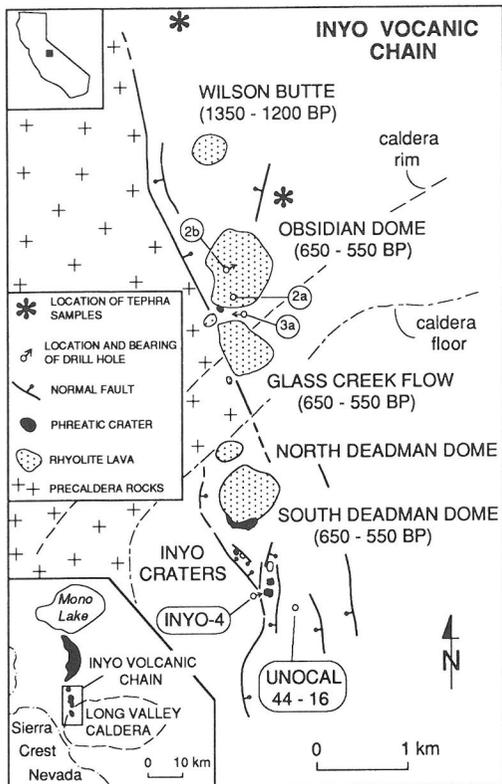


FIG. 1. Location map showing location of drill holes (RDO-) 2a, 2b, and 3a through and adjacent to Obsidian Dome in the Inyo volcanic chain (modified after EICHELBERGER *et al.*, 1988; SUEMNICHT and VARGA, 1988; MILLER, 1985). Locations of two sampled sections of Obsidian Dome tephra are also indicated (C. D. MILLER, pers. comm.).

1985). FINK (1985) interprets the location of the vents and orientation of the local fracture geometry to reflect near-surface rotation of segments of the dike. SUEMNICHT and VARGA (1988) suggest that the vent locations were controlled by the intersection of regional fault trends, both within and north-west of Long Valley caldera. Numerous explosion craters, including Inyo Craters within the caldera (Fig. 1), formed in places along the N-S fracture zone above the dike. This occurred after explosive eruption of tephra from the vents, but prior to emplacement of the lava domes (MILLER, 1985; MARTIN and POLLARD, 1988; EICHELBERGER *et al.*, 1988).

Petrologic and petrochemical studies, including those by BAILEY *et al.* (1976, 1983), SAMPSON (1987), SAMPSON and CAMERON (1987), and VOGEL *et al.* (1989) recognize two chemically distinct types of rhyolitic lava: (1) a finely-porphyrific variety (*ca.* 70–74 wt.% SiO<sub>2</sub>), which comprises Obsidian

Dome, and (2) a coarsely porphyritic rhyolite found intermingled with the finely porphyritic rhyolite in the Glass Creek flow and at South Deadman Dome. The finely and coarsely porphyritic rhyolites appear to be derived from separate magma chambers (SAMPSON and CAMERON, 1987; HIGGINS, 1988; VOGEL *et al.*, 1989). The finely porphyritic rhyolite of Obsidian Dome can be further classified as a high-SiO<sub>2</sub> (73.40 ± 0.22 wt.%), low-Ba (<475 ppm) variety and a low-SiO<sub>2</sub> (71.48 ± 0.90), high-Ba (>475 ppm) variety (VOGEL *et al.*, 1989). The low-Ba variety occupies the lower portion of the dome and outer part of the conduit, whereas the high-Ba variety occurs in the center of the conduit and in the upper portion of the dome (VOGEL *et al.*, 1989). The high-Ba rhyolite constituted was the last magma to be emplaced.

Various kinds of evidence suggest a complex thermal and degassing history for Obsidian Dome magma. Estimates of crystallization temperature based on Fe-Ti oxides in rhyolite from the conduit margin and center (hole RDO-2b; VOGEL *et al.*, 1989) are similar (912 to 927°C), whether for quickly cooled conduit margins, or for the more slowly cooled conduit interior; these must therefore represent pre-eruption temperatures which were effectively quenched. Higher temperatures are estimated utilizing the phase equilibria for the observed mineral assemblages, and combined with the measured water contents of the glasses (SWANSON *et al.*, 1989). SWANSON *et al.* (1989) suggest that the quenching of Fe-Ti oxide equilibria was the result of vapor loss from the magma (*i.e.*, constitutional supercooling) rather than thermal undercooling. The Fe-Ti oxide temperatures are, however, higher than the 600°C formation temperature suggested by STOLPER (1989) for the conduit margins at Mono Craters (Fig. 1) based on IR-measured H<sub>2</sub>O/OH ratios in obsidian tephra clasts. NEWMAN *et al.* (1988) and STOLPER (1989) suggest that, in fact, the obsidian clasts found in tephra represent rapidly-cooled melt (to *ca.* 600°C) originating at glassy dike margins, but subsequently eroded during eruption.

The initial water content, initial δD value, and pressure of the Obsidian Dome magma are required to formulate a quantitative degassing model using hydrogen isotope and water contents of obsidian. HERVIG *et al.* (1989) found a mean value of 4.1 ± 1.2 wt.% H<sub>2</sub>O in glass inclusions in feldspar phenocrysts from tephra, in marked contrast to the 0.4 to 1.5 wt.% H<sub>2</sub>O in matrix glass. The higher water content is in general agreement with the presence of hornblende, which indicates >4.0 wt.% H<sub>2</sub>O at a vapor-saturated pressure of 200 MPa (NANEY, 1983); this compares with the minimum water con-

tent of 2.04 wt.% estimated for nearby Glass Creek rhyolite (TAYLOR *et al.*, 1983). Two inclusions in biotite analyzed by HERVIG *et al.* (1989) give lower values (1.0 and 1.3 wt.%), indicating lower pressure crystallization, and/or that interface kinetics may result in non-representative water contents in the glass inclusions.

The degassing of rhyolitic magma may be considered in terms of two end-member processes: single or multi-step closed-system (batch equilibrium) degassing on the one hand, and open-system (equilibrium or Rayleigh) degassing on the other. The complete degassing process may involve aspects of both processes. At magmatic temperatures, the magnitude and sign of the H<sub>2</sub>O-melt hydrogen isotope fractionation factor are sufficient to cause distinctly different  $\delta D$  signatures for open-system and closed-system degassing. Thus, there should be a correlation between the style of volcanism and the nature of the degassing process, as indicated by its isotopic signature.

#### SAMPLE SELECTION AND ANALYTICAL PROCEDURES

Samples were analyzed from both extrusive tephra and dome deposits, and from intrusive glass, partially vesicular glass, pumice, crystalline rhyolite, and wall rocks sampled by drill core. Comparison of results for rhyolite of varying texture and depths with those for tephra from both distal and proximal sections (Fig. 1) permits investigation of the effect of degassing during first- and second-boiling in three different magmatic environments. The extrusive tephra and dome flow and the intrusive rhyolite conduit and feeder dike are generally similar in chemical composition (except for distinction of the low- and high-Ba members; C. D. MILLER, pers. comm.; VOGEL *et al.*, 1989). All of these are believed to have originated from the same, or a closely related, magma system.

#### Tephra

Obsidian and pumice clasts were analyzed from a proximal, ca. 1.5 m-thick, 7-layer section, and from a distal, 85 cm-thick, 5-layer section of tephra erupted from Obsidian Dome (C. D. MILLER, pers. comm.; see locations in Fig. 1). Obsidian clasts are generally dark gray, with frosted exteriors and slightly rounded edges, are typically <1 cm in diameter, and comprise less than about 25% of each sample. Pumice and lithic fragments make up the rest. The least vesicular obsidian clasts were selected for analysis. Several clasts of associated pumice >1 cm in diameter were also selected for analysis.

#### Dome flow, intrusive rhyolite, and wall rocks

Three drill holes (RDO-2a, -2b, and -3a; Fig. 1) cored different portions of the dome and conduit complex. Hole RDO-2a (Fig. 2) cored the distal portion of the Obsidian Dome flow, hole RDO-2b the proximal portion of the flow, and hole RDO-3a, immediately south of the dome, cored a dike not exposed at the surface. This dike is in-

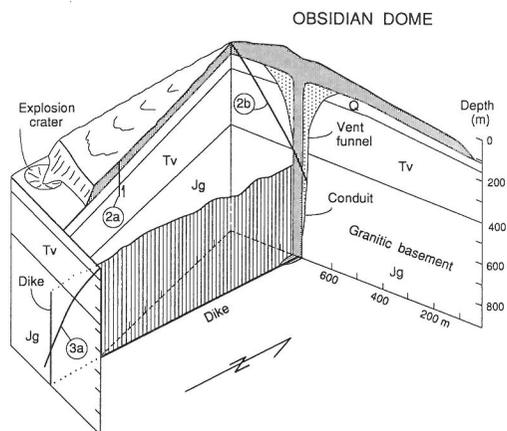


FIG. 2. Block diagram of Obsidian Dome showing location of the distal drill hole (RDO-) 2a, through the dome flow; proximal hole 2b, through the near-vent flow and flow conduit; and dike hole 3a, which intersects the feeder dike just south of the dome. Abbreviations are: Jg, Jurassic granitic rocks (basement); Tv, Tertiary basalt and rhyolite, and fluvial sediments; and Q, Quaternary gravels (modified after WESTRICH *et al.*, 1988).

terpreted to be part of the feeder dike which supplied magma to the Obsidian Dome conduit.

In the drill core samples RDO-2a and -2b, the uppermost part of the flow is characterized by finely vesicular pumice, underlain by coarsely vesicular glass, an obsidian zone (only in hole RDO-2a), a zone of devitrified, crystalline rhyolite, and (only in hole RDO-2a) a lower zone of obsidian. A breccia zone was intersected in each hole at the base of the flow. Hole RDO-2b also penetrated the crystalline rhyolite of the conduit beneath the dome; this material has a microporphyritic texture (SWANSON *et al.*, 1989).

To the south, the intrusive rhyolite dike of hole RDO-3a is generally similar to the conduit rhyolite, except for a water-rich glassy margin along one wall. Other distinctive samples of glass are from the drill core fragments of glass comprising "intrusive pyroclasts" (HEIKEN *et al.*, 1988). These samples, together with the water-rich glassy margin of the dike, are particularly important in interpreting the origin of the obsidian and in understanding the isotopic variations.

Several samples of flow basalt and pre-caldera basement (Jurassic quartz monzonite) were obtained from core of holes RDO-2b and -3a.

#### Sample preparation and isotopic analysis

Samples from drill core were generally prepared in one of two ways: either by washing of ground material (to -100 mesh) with distilled H<sub>2</sub>O and "high purity" acetone, or ultrasonically rinsing alternately with distilled water and dilute HCl. Tephra clasts were ultrasonically washed in dilute HCl and acetic acid, followed by rinsing in distilled water and acetone. Obsidian selected from splits of tephra samples was washed in distilled H<sub>2</sub>O. Fresh glass was hand-picked from individual, coarsely crushed clasts in order to exclude any exterior surfaces. Pumice was treated similarly, and interior portions of clasts were hand-picked for

analysis. Obsidian and pumice were also analyzed from samples collected from the dome flow. Crystalline granodiorite was coarsely crushed and a pulverized sample prepared from washed interior ("fresh"-sided) fragments.

Hydrogen isotope extraction procedures used were similar to those described in TAYLOR *et al.* (1983), except that all samples described in this paper were, upon conversion to H<sub>2</sub>, Toepler-pumped into a 12" length of 3/8" O.D. pyrex tubing, and sealed with a torch for later mass spectrometric analysis. No leakage from the stored tubes was detected. Data are reported in the usual  $\delta$ -notation relative to V-SMOW, and duplicate analyses indicate an uncertainty of the average  $\delta$ D values of replicate analyses in the same laboratory on the order of 1.0 per mil. Data were collected at the Geological Survey of Canada (Ottawa) and at the U.S. Geological Survey (Menlo Park, California).

Water contents determined by H<sub>2</sub> manometry are precise to better than 5% of the reported values. The total water contents determined by H<sub>2</sub> manometry reported here can be as much as 0.1 wt.% larger than water contents determined by Karl Fischer titration (WESTRICH, 1987; WESTRICH *et al.*, 1988), for samples containing less than 0.6 wt.% H<sub>2</sub>O. Oxygen isotope extraction was accomplished using ClF<sub>3</sub>, and followed procedures noted in TAYLOR *et al.* (1983). The average difference in  $\delta^{18}$ O of 12 replicate analyses of rhyolite was 0.17 per mil; a mean  $\delta$ -value of +9.6 was measured for NBS-28.

## RESULTS

### Tephra

As shown in Fig. 6 virtually bubble-free obsidian clasts in tephra contain 0.51 to 1.27 wt.% H<sub>2</sub>O and  $\delta$ D = -82 to -57 in the distal section, and 0.42 to 1.21 wt.% H<sub>2</sub>O and  $\delta$ D = -61 to -88 in the proximal section. Pumice clasts vary from 0.30 to 1.88 wt.% H<sub>2</sub>O and in  $\delta$ D from -115 to -80 in the distal section, whereas pumice in the proximal section has from 0.54 to 1.16 (one clast has 2.22) wt.% H<sub>2</sub>O and  $\delta$ D values of -124 to -96. Although pumice can alter readily owing to its high surface area, the glass comprising most of these young pumice clasts is not extensively hydrated by secondary water, owing to the very recent age of eruption and to the relatively arid climate.

### Dome flow

Two outcrop samples of obsidian from the distal edge of the Obsidian Dome have water contents and  $\delta$ D values of 0.19 and 0.14, and -89 and -104, respectively. These are similar to other bubble-free glasses from the distal drill hole RDO-2a, which contain 0.07 to 0.23 wt.% H<sub>2</sub>O, and  $\delta$ D values of -104 to -114. Except for one sample with 0.13 wt.% H<sub>2</sub>O, obsidian from the proximal hole RDO-2b exhibits much higher water contents, 0.50 to 0.93, and a slightly lower range of  $\delta$ D values, -95 to -122. Coarsely vesicular glass and pumiceous samples in the proximal portion of the flow have

similar ranges of  $\delta$ D as the obsidian, but occasionally slightly higher water contents (to 0.93). In comparison to pumice from the tephra sections, pumiceous samples from the dome flow have the lowest water contents and most negative  $\delta$ D values of any of the tephra samples. The basal breccia zone contains welded glass with  $\delta$ D of -92 to -94 and 0.34 to 0.49 wt.% H<sub>2</sub>O (Fig. 3).

Crystalline rhyolite in the lower portion of the flow in both distal and proximal portions (Fig. 3) has 0.07 to 0.34 wt.% H<sub>2</sub>O, similar to the associated flow obsidian which contains  $\leq$ 0.6 wt.% H<sub>2</sub>O (most samples have  $\leq$ 0.40 wt.%). The  $\delta$ D of the rhyolite (-113 to -119) is also broadly similar to that of the obsidian. Water in the crystalline rhyolites is primarily sequestered in biotite. The data for both the glassy and the crystalline rocks are plotted for comparison in Fig. 4.

The above-described data are plotted in Fig. 5 and indicate the following: (1) slightly lower  $\delta$ D values of obsidian occur higher in the flow; (2) the  $\delta$ D values of the two analyzed pumice samples span the entire range exhibited by all of the other samples; (3) crystalline rhyolite from the lower portion of the flow has a comparatively uniform  $\delta$ D, distinctly lower than the obsidian; (4) glassy samples exhibit a larger range and extend to much higher values of  $\delta$ D than the crystalline rhyolite; and (5) rhyolite samples have a lower mean  $\delta$ D value (-118) than do the samples of obsidian (-107; including two samples from the edge of the flow not plotted in

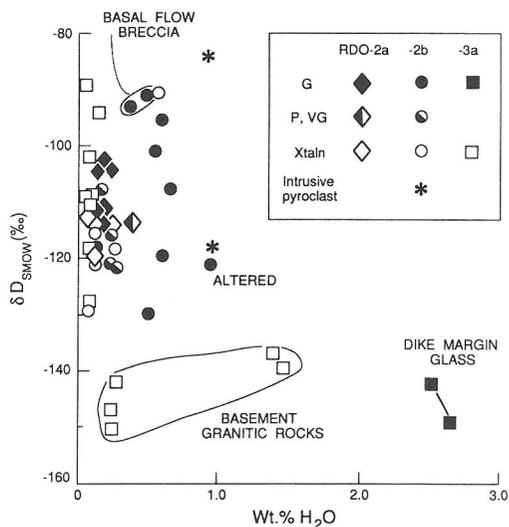


FIG. 3. Plot of  $\delta$ D vs. wt.% H<sub>2</sub>O for whole-rock samples of crystal-line (Xtaln) rhyolite, granitic basement rocks, vitreous rhyolite (G, obsidian; VG, coarsely vesicular glass; and P, pumice), and glass from tuff-breccia dikes (\*).

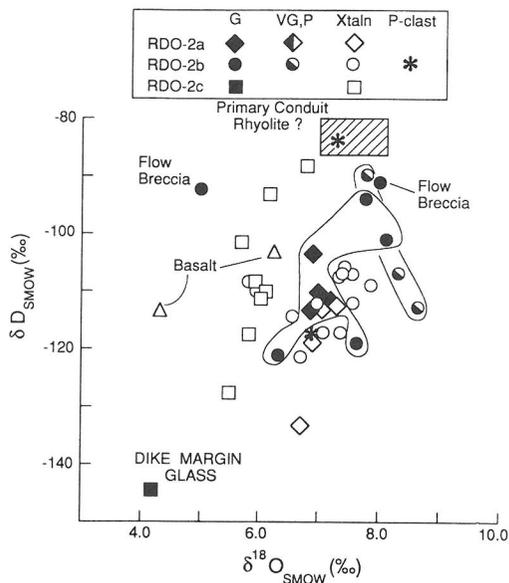


FIG. 4. Plot of  $\delta D$  vs.  $\delta^{18}O$  for whole-rock samples of obsidian (G), coarsely vesicular glass (VG), pumice (P), and crystalline rhyolite (Xtaln). The compositions of two glass fragments from tuff-breccia dikes (\*) are shown for comparison. The field of "primary rhyolite" represents the approximate composition of the Obsidian Dome rhyolite degassed to a pressure equivalent to about 400–600 m depth.

Fig. 5). In addition, obsidian from the distal part of the flow (hole RDO-2a) has a smaller range of  $\delta D$  than the near-vent obsidian (hole RDO-2b).

Oxygen isotope compositions of the proximal flow are similar to those reported previously for the Glass Creek flow (TAYLOR *et al.*, 1983), with  $\delta^{18}O$  of 6.3 to 8.1 for obsidian and 7.9 to 8.7 for coarsely vesicular glass and pumice. Most crystallized rhyolite and glass from the basal breccia zone typically have  $\delta^{18}O$  values of 6.0 to 8.0, although rare samples are as low as 5.0.

*Intrusive rhyolite of the conduit and feeder dike*

Microcrystalline rhyolite in the conduit, at an approximate vertical depth of 410 to 490 m, contains 0.08 to 0.39 wt.%  $H_2O$ , which is considerably less than the equilibrium values (of the order of 1.2 to 1.4 wt.%  $H_2O$ ) expected for confining pressures on vapor-saturated rhyolite magma at this depth (*cf.* WESTRICH *et al.*, 1988). The  $\delta D$  values of the conduit rhyolites vary from  $-128$  to  $-89$ , similar to the dome flow, whereas the  $\delta^{18}O$  values of the rhyolite (6.5 to 7.9) and, especially, of the conduit-margin breccia (4.3 to 6.0; not plotted in Fig. 4) are

slightly lower than those measured for obsidian (see Fig. 4).

*Glassy dike margin and intrusive pyroclasts*

Two samples of gray, finely porphyritic glass with a waxy luster were analyzed from "tuff breccia dikes" intersected by hole RDO-3a at vertical depths of approximately 329 and 413 m, giving, respectively,  $\delta D$  values of  $-85$  and  $-119$ . The dikes and their tuffaceous contents are described by HEIKEN *et al.* (1988). The water contents of the obsidian (0.92 and 0.97 wt.%  $H_2O$ ) are close to those expected for equilibrium (see also WESTRICH *et al.*, 1988). The higher  $\delta D$  value in the shallower samples is consistent with open system degassing as discussed below, and is consistent with a near primary composition, whereas the lower  $\delta$ -value clearly suggests interaction with meteoric water.

Analyses of glass from the margin of the dike intersected in RDO-3a at *ca.* 650 m vertical depth yielded variable water contents dependent upon the length of time of high-vacuum degassing in our laboratories at 150–200°C, prior to water extraction. For example, after *ca.* four hrs. degassing at 150°C the total water content was as high as 2.65 wt.% (O'NEIL and TAYLOR, 1985). Other experiments showed that up to 2.6 wt.% (B. TAYLOR, unpubl. data) of water can be released during such pretreat-

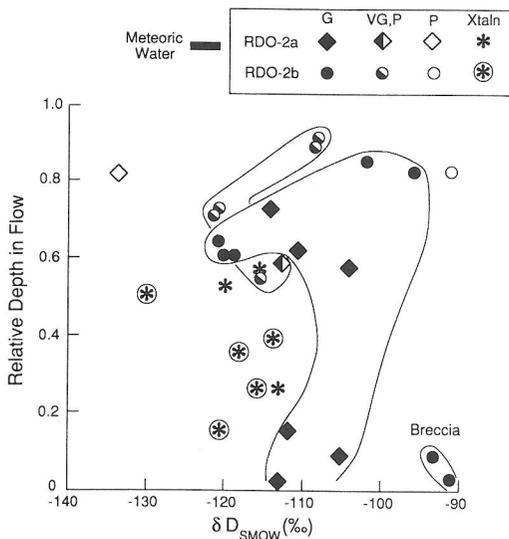


FIG. 5. Plot of  $\delta D$  vs. relative position in the dome flow for the principal textural varieties of rhyolite (G, obsidian; VG, coarsely vesicular glass; P, pumiceous; and Xtln, crystalline). The composition of local meteoric water (from Glass Creek; TAYLOR *et al.*, 1983) is plotted for comparison.

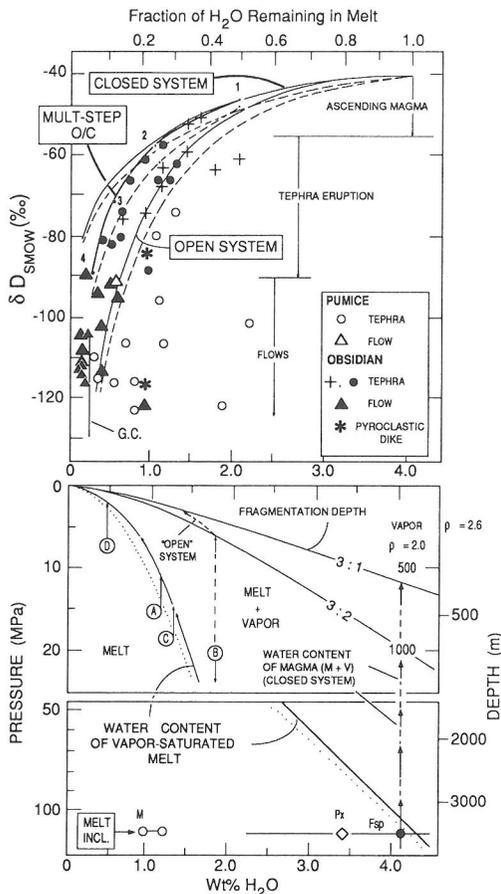


FIG. 6. Plot of  $\delta D$  (top) and pressure (bottom) versus water content of rhyolite melt, illustrating hydrogen isotope fractionations and variations in water content of melt during magma ascent, Plinian eruption of tephra, and emplacement of dome flows under open and closed systems. Data are plotted for obsidian and pumice from both tephra and dome flows. Hydrogen isotope fractionation models were calculated for: (1) an initial water content of 4.1 wt.%, based on analyses of glass (melt) inclusions in feldspar (HERVIG *et al.*, 1989; mean values are plotted for inclusions in feldspar (Fsp), and individual analyses of glass inclusions in pyroxene (Px), and biotite (M)); (2) a  $H_2O/OH$  distribution for dissolved water based on quick-quench experiments in SILVER *et al.* (1990); and (3)  $H_2O$ -melt fractionation factors from DOBSON *et al.* (1989; dashed lines) and as discussed in the text (solid lines). The initial  $\delta D$  of the magma is assumed to be  $-40$  (see text). Solubility curves (solid curves, lower two portions of the diagram) are based on BURNHAM (1979), at  $950^\circ C$ , and on quick-quench experiments of SILVER *et al.* (1990) at  $850^\circ C$ , and equivalent depths are indicated for melt densities of 2.6 and 2.0. Point (A) represents the highest water content of tephra obsidian reported by WESTRICH *et al.* (1988), and point (C) the most water-rich tephra obsidian in this study. Point (B) is the water content of the melt upon eruption (fragmentation) of a closed-system magma (see text) with initial water content of 4.1 wt.%, and point (D) is the approximate low-water limit of melt erupted as tephra. Curves in the melt + vapor field are drawn for bubble:

ment at 150 to  $200^\circ C$ ; this is more than usually retained by surface adsorption (*cf.* WESTRICH, 1987). Water contents of 1.48–1.58 wt.% were determined after extended (12–14 hrs.) high-vacuum pretreatment at  $150$ – $200^\circ C$ , and these are interpreted to represent the primary water content of the glass. These values are close to a probable equilibrium value for the depth of sampling.

A low  $\delta D$  value of  $-148$  and a  $\delta^{18}O$  value of 4.2 were reported for the water-rich glass by O'NEIL and TAYLOR (1985). These data indicate high-temperature contamination of the glassy dike margin by meteoric water.

#### Wall rocks and basement

A basalt flow and breccia, and granitic rocks, also brecciated where near the margin of the conduit have  $\delta D$  values of  $-104$  to  $-151$ , presumably reflect some hydrothermal alteration. Whereas the  $\delta^{18}O$  of the basalt (6.2) has not been greatly affected by any hydrothermal alteration, the granitic rocks have  $\delta^{18}O$  values of 6.7–7.3, slightly lower than most other orogenic granites (TAYLOR and SHEPPARD, 1986), and also possibly indicative of minor isotopic exchange with meteoric waters.

## DISCUSSION

#### First boiling: magmatic degassing during tephra eruption and dome emplacement

The positive correlation found between  $\delta D$  and total water content for obsidian from Obsidian Dome's tephra and flow units (Fig. 6) is broadly similar to that found for the Glass Creek tephra and dome rhyolite by TAYLOR *et al.* (1983) and for the tephra and dome obsidian from Mono Craters (NEWMAN *et al.*, 1988). A general characteristic of rhyolitic Plinian eruptions appears to be a general decrease in both the average value and the range of wt.%  $H_2O$  in obsidian fragments with increasing stratigraphic height in tephra sequences (*e.g.*, Medicine Lake Highlands: Fig. 2 in TAYLOR *et al.*, 1983; Mono Craters: NEWMAN *et al.*, 1988). The magnitude of the variation in water content of obsidian clasts is broadly similar in both the distal and prox-

melt ratios of 3:2 and 3:1 (fragmentation) based on EICHELBERGER *et al.* (1986) and SPARKS (1978). The "open" system curve illustrates the decrease in water content of vapor-saturated magma (*i.e.*, bubbles + melt) upon diffusive loss of water from a magmatic foam. Data for tephra obsidians from the near-by eruption site of the Glass Creek flow (crosses (+); TAYLOR *et al.*, 1983) are shown for comparison.

imal sections of Obsidian Dome tephra. A marked bottom-to-top variation in total water content is not apparent, but the sample population is probably too small at this stage to characterize any stratigraphic trend. As found in other studies, the tephra obsidian clasts contain up to ten times more water than the obsidian in the subsequently erupted Obsidian Dome flow. Inasmuch as equilibration of magma at successively lower pressures (*i.e.*, at shallower depths) can explain the decrease in water content of the obsidian with progress of eruption (EICHELBERGER and WESTRICH, 1981; EICHELBERGER *et al.*, 1986; WESTRICH *et al.*, 1988), I will presume that the variations in wt.% H<sub>2</sub>O (and also  $\delta D$ ) reflect a common degassing process, and proceed by comparison of the measured  $\delta D$  vs. wt.% H<sub>2</sub>O relationship for the Obsidian Dome tephra with calculated degassing trends.

Figure 6 compares  $\delta D$  and water content data for obsidian from tephra clasts, dome flow, and tephra dikes to several calculated degassing trends, in conjunction with pressure-solubility relationships (calculated and experimental) for a rhyolite melt at 850°C. In addition, the water content of the melt is shown as a function of pressure for two bubble:melt volume ratios: 3:2 and 3:1. The 75% bubble volume represents the bubble content beyond which the melt would fragment and erupt, although SPARKS (1978) suggests that bubbles could comprise as much as 83 vol.% before eruption. In any case, three principal stages of magmatism can be described using with the water content and  $\delta D$  data: ascent of a magma to the point of rupture, Plinian eruptions producing tephra, and quiescent dome emplacement. The boundaries for each are approximate and correspond to the  $\delta D$  ranges of the samples analyzed.

A melt with initially 4.1 wt.% H<sub>2</sub>O may fragment and erupt from a depth as shallow as perhaps 400 m, when the equilibrium water content of the melt (silicate liquid) is 1.15 wt.% H<sub>2</sub>O (*i.e.*, melt with composition of point (A)). Removal of some of the H<sub>2</sub>O-saturated magma (due to draw-down in the magma column) will result in residual melt with a water content higher than at point (A). Bubble growth in response to depressurization during eruption may lead to additional degassing of entrained melt (SPARKS, 1978). Point (B) represents the highest water content (1.8 wt.% H<sub>2</sub>O) found to date for the Obsidian Dome tephra obsidian (WESTRICH *et al.*, 1988). Point (C) represents the water content of the most water-rich obsidian (1.21%; proximal section) analyzed in this study.

NEWMAN *et al.* (1988) demonstrated the marked effect of varying hydrogen speciation on the bulk

H<sub>2</sub>O-melt hydrogen isotope fractionation factor. Accurate modelling of the isotopic effect of water loss from a rhyolitic melt requires the hydrogen isotope fractionation factors between the exsolved H<sub>2</sub>O and the hydrogen species dissolved in the melt (*i.e.*, OH and H<sub>2</sub>O). DOBSON *et al.* (1989) determined the H<sub>2</sub>O-(OH<sub>melt</sub>) fractionation factor ( $\alpha = 1.0415$ ) by equilibration between water and rhyolite at low pressures, for which OH is virtually the sole species (STOLPER, 1982; SILVER *et al.*, 1990). The bulk fractionation between H<sub>2</sub>O gas and coexisting melt can be expressed as follows:

$$1000 \ln \alpha_{(H_2O-melt)} = X_{H_2O} 10^3 \ln \alpha_{H_2O-(H_2O_{melt})} + (1 - X)_{OH} \ln \alpha_{H_2O-(OH_{melt})} \quad (1)$$

where  $X$  and  $1 - X$  are, respectively, the atom fractions of hydrogen present in the melt as H<sub>2</sub>O and as OH.

In a manner analogous to that of DOBSON *et al.*, I estimate the fractionation factor for H<sub>2</sub>O-(H<sub>2</sub>O<sub>melt</sub>) using (1) DOBSON *et al.*'s H<sub>2</sub>O-(OH<sub>melt</sub>) fractionation factor at 750°C ( $\alpha = 1.0415$ ); (2) the relationship between total water content, dissolved H<sub>2</sub>O, and dissolved OH determined spectroscopically for rapidly quenched rhyolite by SILVER *et al.* (1990); and (3) the preliminary bulk H<sub>2</sub>O-melt fractionation at 950°C ( $\alpha = 1.0239$ ) for rhyolite melt with 3.1 wt.% H<sub>2</sub>O (TAYLOR and WESTRICH, 1985; see TAYLOR, 1986). The estimated value of  $\alpha_{H_2O-(H_2O_{melt})}$  is 0.9896, which is comparable to a value of 1.000 estimated by DOBSON *et al.* (1989). DOBSON *et al.*'s choice of 1.000 avoids the problematical cross-over in the fractionation factor implied by a value of less than 1.000.

The closed-system and open-system degassing trends were each calculated step-wise, for small increments of water loss, by recalculation of the effective vapor-melt fractionation at each step. In this way the continual variation in the bulk H<sub>2</sub>O-melt fractionation factor was approximated. In terms of the bulk fractionation factor (derived from Eq. 1), the closed-system trend was calculated by

$$\delta D_{final} = \delta D_{initial} - (1 - F) 1000 \ln \alpha_{(H_2O-melt)}. \quad (2)$$

Similarly, the open-system trend was calculated with the step-wise recalculated bulk fractionation using

$$\delta D_{final} = \delta D_{initial} - 1000 (1 - F^{\alpha_{(H_2O-melt)}-1}). \quad (3)$$

The mean value of 4.1 wt.% H<sub>2</sub>O determined by HERVIG *et al.* (1989) for glass inclusions in plagioclase and potassium feldspar phenocrysts in Obsidian Dome tephra provides the best estimate for the wt.% H<sub>2</sub>O<sub>initial</sub>, presuming that this was not elevated

beyond the bulk water content of the melt due to rapid growth of the feldspar. The  $\delta D_{\text{initial}}$  cannot be directly measured, but should be at least as high as the value of  $-57$  measured in an obsidian clast with 1.09 wt.%  $\text{H}_2\text{O}$  from the distal section. If the magma is presumed to have approximated a closed system prior to eruption of the first tephra deposit, then  $\delta D_{\text{initial}}$  was  $-40$  (derived from Eq. 2 for  $\text{H}_2\text{O}_{\text{initial}} = 4.1$  wt.%, and  $\delta D = -57$  for a melt with 1.0 wt.%  $\text{H}_2\text{O}$ ). This is a reasonable estimate, since for this same  $\delta D_{\text{initial}}$  value, both open- and closed-system model  $\delta D$  values at 1 wt.%  $\text{H}_2\text{O}$  differ by only 3.1 per mil.

Complete degassing of magma with  $\delta D_{\text{initial}} = -40$  and  $\text{H}_2\text{O}_{\text{initial}} = 4.1$  wt.% results in  $\delta D$  values of ca.  $-80$  (closed-system) and  $-120$  (open-system; Fig. 6). A marked increase in the bulk  $\text{H}_2\text{O}$ -melt fractionation factor accentuates the depletion in deuterium during degassing, calculated for either open- or closed-systems in Fig. 6. The increase in the bulk fractionation factor is primarily due to the rising proportion of OH relative to  $\text{H}_2\text{O}$  in the melt.

Neither the open-system nor the closed-system trend in Fig. 6 exactly mimics the  $\delta D$  vs. wt.%  $\text{H}_2\text{O}$  variation of the tephra and flow obsidian. The small difference in values estimated for  $\alpha_{\text{H}_2\text{O}-(\text{H}_2\text{O}_{\text{melt}})}$  by DOBSON *et al.* (1989) and by the present author does not affect the calculation (as also noted by DOBSON *et al.*, 1989). Thus, none of the open-system scenarios of TAYLOR *et al.* (1983) and NEWMAN *et al.* (1988), nor the two-stage, closed- followed by open-system degassing scenarios of NEWMAN *et al.* (1988) and DOBSON *et al.* (1989), completely describe the first-boiling process for Obsidian Dome. Rather, the present data seem to require a degassing process that becomes *in effect* progressively more open from initiation of the tephra eruptions to emplacement of the dome flow.

Open-system behavior via a magma-foam model has been called upon to explain the marked depletion of deuterium in the flow obsidian (TAYLOR *et al.*, 1983; TAYLOR, 1986), as well as to explain the variation in water content of tephra obsidian and the non-explosive emplacement of co-magmatic flows (EICHELBERGER *et al.*, 1986). The shortening of the diffusion path length due to a greater volume of bubbles facilitates gas flow through the melt, which is otherwise severely restricted by the slowness of water diffusion in the melt (SHAW, 1974; SPARKS, 1978; summary in TAYLOR, 1986). EICHELBERGER *et al.* (1986) measured a marked increase in apparent  $\text{N}_2$  permeability of pumice with 60 vol.% of bubbles under a pressure differential of 1.2–50 bars, at Earth-surface temperatures. Although not directly applicable to the diffusion of  $\text{H}_2\text{O}$  through rhyolite

melt at  $850^\circ\text{C}$ , the pumice measurements demonstrate an increasing permeability with bubble content, analogous to that envisioned to explain vapor loss from a saturated melt during ascent.

The distance  $\text{H}_2\text{O}$  may migrate is limited, even with the foam-diffusion model. EICHELBERGER *et al.* (1986) show that an exponential increase in degassing time is required with a linear increase in width of the magma conduit (or magma body; *cf.* SPARKS, 1978). They suggest that significant water loss could have occurred through the Obsidian Dome feeder dike's walls, but that larger magma bodies would tend to behave as closed-systems and erupt more catastrophically. The diffusive loss of water from the magma (melt + vapor) with a total water content given by point (B) is indicated schematically in Fig. 6 by the dashed curve line labeled "Open System." As a consequence, magmas following such a path may more closely approach the surface before erupting than those characterized by large, catastrophic eruptions that follow strictly closed-system degassing. Indeed, a purely open-system magma would obviously not erupt explosively (*i.e.*, would not fragment).

Two facts suggest that the Obsidian Dome magma did not behave as a purely open system: (1) the very existence of multiple tephra beds from the same source, and (2) a  $\delta D$  vs. wt.%  $\text{H}_2\text{O}$  trend for the data in Fig. 6 that lies between the end-member open- and closed-system cases. At some point, the magma must have been effectively closed (*i.e.*, the rate of bubble growth exceeded the rate of vapor loss), although the progressively lower  $\delta D$  values measured for tephra obsidian and for dome flow obsidian require some "open" character to the degassing process.

A quasi-open degassing process, which I term here "multi-step open/closed," may consist of several closed or nearly closed stages. Each "stage" represents bubble growth during ascent of vapor-saturated magma, and vapor loss at each successive eruption. This is described schematically in Fig. 7(I–IV). Consider a magma in Fig. 7(II) that is virtually closed to water loss up to the point of first eruption at (A), at which point the lowest equilibrium water content is that of (A). Draw-down during eruption (which could be as much as 200–300 m: SPARKS, 1978; see Fig. 7(III)) may remove some, *but not all* of the vapor-saturated magma. The erupted magma might have a water content (at initiation of the eruption) as high as, say (A"). If the magma remains a closed system, it can erupt (at point (B")) when the lowest equilibrium water content is that of (B), and extract magma with a range of wt.%  $\text{H}_2\text{O}$ . The range of water contents of glass which survives the

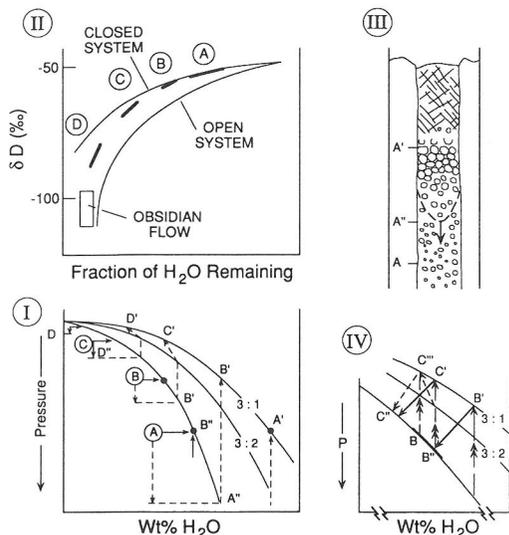


FIG. 7. Schematic diagrams illustrating the change in  $\delta D$  of rhyolitic melt by open-system and multi-step open/closed (eruption) degassing for a magma with initial water content equal to  $A'$ : (I) Points  $A$  and  $A'$  are, respectively, the water contents of the melt and melt + vapor at the point of rupture. Draw-down to point  $A''$  during eruption marks the water content of the ascending magma which erupts at point  $B'$ ; similarly for points  $C$  and  $C'$ . The saturation curve  $A''-B''-C''$  may not be reached (*i.e.*, probably not all vapor-saturated magma is erupted). Open-system degassing of a portion of the upper-most melt prior to eruption causes a decrease in the water content of the melt + vapor. (II) Points  $A-B-C$  record the continuous variation in water content and  $\delta D$  of the melt during magma ascent and  $H_2O$  exsolution. Points  $A'-B'-C'-D'$  record the discontinuous variation in water content of the magma (melt + bubbles) during ascent and eruption: (III) Upward increase in bubble density and volume is shown in a dike (conduit) intrusion. The draw-down and extraction of melt with fewer bubbles during eruption is represented by the heavy dashed line. (IV) This illustrates lowering of the water content of the magma by episodic eruption following closed-system degassing. Upon eruption at  $B'$ , pressure and water content might change along path  $B'-B''$  (or some similar path). Generally,  $B'$  is not reached, and only a portion of the vapor-saturated magma may be extracted. Continued ascent results in further bubble growth until eruption at  $C'$ , and so on.

rapid unroofing of the magma column is likely to be more restricted than is consistent with the range of the depths from which magma is excavated, because much of the upper portion of the magma column will be lost as ash. Changes in water content upon eruption are schematically illustrated in Fig. 7(IV) by the paths  $(B')-(B'')$  and  $(C')-(C'')$ . Figure 7(III) implies the existence of gradients in  $\delta D$  and wt.%  $H_2O$  in the melt column (*i.e.*, in the dike). The principal point is that the water content of the magma is reduced with each eruption, and this pro-

duces a quasi-open system isotopic shift which cannot be modelled as a single-step batch equilibrium.

This multi-step degassing scenario can be modelled to fit the isotopic relationships, and it is at the same time consistent with both the measured water contents of glass found at depth (*i.e.*, the pressure-dependent solubility constraint) and the multiple-layer tephra deposits (*i.e.*, evidence for some degree of closure to water loss). It also provides a mechanism (*i.e.*, sudden vapor loss) to produce the constitutional super cooling consistent with textural and phase relationships (*cf.* SWANSON *et al.*, 1989). An infinite number of similar closed-system degassing stages would approach the open-system end-member, Rayleigh fractionation.

With closer approach to the surface, the pressure difference between intervals of fragmentation and vapor undersaturation decreases, as does the water content of the magma. Although pressure is not likely to be a strictly linear function of depth (due to changing magma density), the foregoing implies that the volume of successively erupted tephra layers should generally decrease with time. This is broadly consistent with the relative order of layer thickness in the Obsidian Dome tephra (C. D. MILLER, pers. comm.).

The Obsidian Dome tephra comprise three thick layers in the 5-layer distal section and five thick layers in the proximal section of ten beds (C. D. MILLER, pers. comm.). Therefore, I chose a simple 4-step degassing model for the tephra series to illustrate the isotopic effects of major water loss during eruption. Each stage is presumed to extract 50% of the water contained in the vapor-saturated magma column at chemical and hydrogen isotope equilibrium. Closed-system degassing (Eq. 2) describes the isotopic variation of each stage. Two such degassing paths are shown in Fig. 6, the dashed curves for  $\alpha_{H_2O-(H_2O_{melt})} = 0.9896$ , and the solid curve for  $\alpha_{H_2O-(H_2O_{melt})} = 1.000$  (see discussion above). Although only approximations, both curves more closely mimic the trend of the data than do either of the single-step closed- or continuously open-system trends. A more accurate model would require constraints for the number of stages and for the resultant change in water content of the magma. Nevertheless, the cumulative effect resembles an open system (*cf.* B. TAYLOR, 1986).

Some continuously open-system vapor loss probably also occurs through the magma foam, prior to eruption, and this is shown schematically by the shift in magma water content from point  $(C')$  to  $(C'')$  in Fig. 7(IV). Quantitative evaluation of the isotopic effect is difficult, however, because the relative amount of water lost via diffusion through the

bubble walls is unknown. EICHELBERGER *et al.* (1986) suggest that eruptions fed by thin dikes may be more open than eruptions fed by larger conduits. However, multi-step, *Rayleigh-dominated* degassing is precluded. Such a process would produce extreme deuterium depletions, and few samples of either tephra or flow obsidian indicate greater deuterium depletion than the simple open-system model path.

The markedly low  $\delta D$  values attained by obsidian comprising the dome flow are consistent with the cumulative effect of multi-step open/closed-system degassing. Rayleigh degassing of magma in the shallow (<100 m) portions of the conduit with water contents on the order of 0.5 wt.% and  $\delta D$  values of ca.  $-90$  (similar to residual magma at step no. 4 in Fig. 6) is also consistent with the low  $\delta D$  values and, in particular, large variation in both  $\delta D$  of the dome obsidian and the water content of 0.1 to 0.2 wt.% (*e.g.*, WESTRICH *et al.*, 1988). Diffusion of exsolved water through a foam, perhaps aided by local rupture of bubble walls, provides a mechanism to decrease (1) internal pressure (approaching equilibrium at one bar), and (2) deuterium in the magma. This eventually ceases due to loss of permeability, collapse, and re-welding to form the obsidian zones (TAYLOR *et al.*, 1983; EICHELBERGER *et al.*, 1986; WESTRICH *et al.*, 1988). The effect of increasing deuterium fractionation between  $H_2O$  and  $OH_{melt}$  with decreasing temperature could be on the order of 10 per mil, or so (DOBSON *et al.*, 1989), but this is minor in comparison to Rayleigh effects. The softening point of the obsidian is in the vicinity of  $650^\circ C$  (WESTRICH *et al.*, 1988; STOLPER, 1989), which limits any large variations due to temperature.

#### *Pumice: the open system?*

Despite the potential for hydrous alteration, owing to the high surface area of the frothy glass, a case can be made that most of the  $H_2O$  in pumices from tephra units and dome flow tops is primary. If one excludes the two samples on Fig. 6 with more than 1.9 wt.%  $H_2O$ , there is a generally positive correlation between water content and  $\delta D$  value; this correlation is broadly similar to that illustrated in Fig. 6 for obsidian, but the pumices show more scatter and are shifted toward high water contents and lower  $\delta D$  values. This could indicate that *all* of the pumices are slightly contaminated by meteoric water. However, a number of pumice clasts have water contents greater than the one bar equilibrium value (*e.g.*, WESTRICH *et al.*, 1988) yet still display high  $\delta D$  values. Also, hydration of pumice by local meteoric water ( $\delta D \approx -122$ ; *e.g.*, TAYLOR

*et al.*, 1983) would cause a negative correlation between  $\delta D$  and wt.%  $H_2O$  on Fig. 6.

Although not apparent from Fig. 6, many pumice clasts have water contents only about 0.5 wt.% higher, and 20–40 per mil lower in  $\delta D$ , than obsidian clasts from the same layer. The  $\delta^{18}O$  values of the pumice (6.3 to 7.9) are in the same range of  $\delta^{18}O$  as the obsidian, and clearly do not display the type of  $^{18}O$  enrichment that is indicative of low-temperature surface weathering (*e.g.*, H. P. TAYLOR, 1968). This is mainly due to the extremely young age of the pumice but in part may also be attributed to the relatively arid conditions and to the protective insulation of the outer pumiceous portions of the clasts (only the interiors were sampled; see above).

If any sample of quenched hydrous melt approaches Rayleigh-type degassing, it probably should be pumice, especially those pumices that formed or continued to degas during eruption. Interestingly, none of the pumice samples plots above the Rayleigh model path. The generally positive correlation of the pumice data on Fig. 6 is probably indicative of a degassing signature, despite the fact that some absorption of meteoric water has occurred. Four samples of flow pumice are either isotopically similar or slightly heavier to coexisting obsidian. This is consistent with both the suggested origin of flow obsidian (*i.e.*, from collapse of magmatic foam) and some additional degassing of tephra pumice relative to the obsidian. Flow pumice may have absorbed minor quantities of magmatic water.

#### *Interaction between magma and meteoric water*

Some evidence for direct magma-water interaction is found in the physical characteristics of pyroclastic particles and bed forms of explosively erupted products (*e.g.*, WOHLTZ, 1986, 1987). Lowered  $\delta^{18}O$  values of unaltered igneous rocks also provide evidence of incorporation of meteoric water by magmas (probably most commonly via assimilation of altered rocks; FRIEDMAN *et al.*, 1974; HILDRETH *et al.*, 1984; H. P. TAYLOR, 1986). The latter occurrences are not necessarily closely associated with an explosive eruption.

The low  $\delta^{18}O$  (+4.2) of the glassy dike margin in hole RDO-3a suggests high-temperature contamination by, or isotopic exchange with, meteoric water, because low-temperature hydration is known to increase the  $\delta^{18}O$  of silicic glasses (H. P. TAYLOR, 1968). The glass has a distinct reddish color, indicative of oxidation, consistent with post-quench meteoric-hydrothermal alteration. However, if water was present in the fractured wall rocks, why did the

glass survive and not crystallize? Perhaps the rapid undercooling experienced by magma at the dike margins was sufficient to prevent crystallization.

One obsidian clast from a tephra dike (329 m depth; 0.92 wt.% H<sub>2</sub>O; hole RDO-3a) with a  $\delta D$  value of  $-119$  further suggests isotopic exchange with meteoric water without loss of the sample's glassy character. The water content of the clast is appropriate for equilibrium at the depth of sampling, and, like the glassy dike margin, may have acquired its low  $\delta D$  value via vapor-saturated exchange with local meteoric ground waters. This could have occurred prior to the quenching and collapse of vesicular melt to form obsidian (see below). Granitic rocks in and adjacent to the tuff-filled fractures have  $\delta D = -147$ , which further document alteration by heated meteoric waters.

The tephra-dike glass sampled in RDO-3a at 413 m vertical depth (0.92 wt.% H<sub>2</sub>O;  $\delta D = -85$ ;  $\delta^{18}O = 7.3$ ) from thin (7 to 40 cm-thick) sub-horizontal pyroclast-filled fractures (see HEIKEN *et al.*, 1988) is consistent with open-system degassing (see Fig. 6). The  $\delta^{18}O$  values and water contents of the glassy tephra clasts permit only minor high-temperature absorption of meteoric water. HEIKEN *et al.* (1988) concluded that the glassy clasts were injected into subhorizontal fractures during phreatomagmatic hydrofracturing late in the eruptive sequence, prior to the emplacement of the dome. MILLER (1985) suggested a similar chronology for "phreatic vents" along the Inyo chain.

#### *Origin of obsidian*

The difference between the measured water contents for flow, conduit, and dike glass with that expected for equilibrium in a silicic melt at the depths of emplacement (*e.g.*, WESTRICH *et al.*, 1988) suggests that obsidian is derived from an originally vapor-saturated melt. Two somewhat different quench histories have been suggested: (1) The obsidian may have originated by collapse of magmatic foam associated with loss of internal vapor pressure due to outward diffusion of water, followed by collapse and annealing of vesicles along conduit walls, probably assisted by ascending magma (TAYLOR *et al.*, 1983; EICHELBERGER *et al.*, 1986; DUNBAR and KYLE, 1989). (2) On the other hand, NEWMAN *et al.* (1988) and STOLPER (1989) suggest that the obsidian forms by thermal quenching of magma on the roof and walls of the conduit, and is subsequently eroded during eruption. Having cooled below its softening point (*ca.* 670°C; WESTRICH *et al.*, 1988), the glass would not vesiculate upon eruption. The mean temperature for all obsidian with  $>0.8$  wt.% H<sub>2</sub>O

is *ca.* 600°C (STOLPER, 1989; compare NEWMAN *et al.*, 1988). Inasmuch as apparent equilibration temperatures of H<sub>2</sub>O/OH ratios in rhyolite glasses on the order of 600°C result from quenching 850°C melts at 3–4°C s<sup>-1</sup> (SILVER *et al.*, 1990), a glassy margin on a conduit a few centimeters thick could form in minutes.

The above two hypotheses are not mutually exclusive, because thermal quenching could readily occur against the walls of ascending and degassing magma. Both hypotheses are consistent with the variation in water content with depth, according to the eruption scenario discussed above. Magma that was thermally quenched to form glass on the conduit margins must have at one time been vesicular (*i.e.*, vapor-saturated) in order to explain the variation in water content with eruption (and degassing) progress.

For how long could the glassy walls of the conduits survive unaltered? Experiments at 400°C reported by STOLPER (1989) indicate that rhyolite glass can coexist with water at 400°C for at least 15½ days without crystallizing. Obsidian dome probably took much longer to cool, and thick obsidian zones survived. Chemical and isotopic equilibration between water and rhyolitic melts at 850–950°C can occur within four hours over a scale of 1–2 mm (TAYLOR and WESTRICH, 1985; STOLPER, 1989). Isotopic data for the 10 cm-thick glass conduit (dike) margin suggest that glass held in high temperature hydrothermal environments will either isotopically exchange or exhibit other alteration signatures. However, neither isotopic nor textural evidence for alteration are evident in the tephra obsidians analyzed in this study or those of TAYLOR *et al.* (1983) and NEWMAN *et al.* (1988). Therefore, the dike margins must have been relatively dry, or the time between glass formation and eruption was relatively short. Hydrothermal alteration of the still-glassy dike margin (hole RDO-3a) would have occurred after, rather than during, tephra eruptions.

#### *Second boiling, or subsolidus reactions?— Evidence from Ba, Cl, and S*

Comparison of the texture of crystalline rhyolite in the dome (sampled by drill holes RDO-2a and RDO-2b) with that of the holocrystalline rhyolite in the conduit and feeder dike (penetrated by hole RDO-2b and 3a, respectively) provides evidence for distinct crystallization histories (SWANSON *et al.*, 1989). These studies indicate (1) growth of phenocrysts prior to extrusion, (2) probable growth of microlites in response to degassing, and (3) devitrification of the slower cooling portion of the dome

flow and crystallization of the conduit magma. The water contents of microcrystalline rhyolite sampled in the conduit and dike (average: 0.22 wt.% H<sub>2</sub>O in RDO-2b; 0.1 in RDO-3a) are considerably lower than expected for equilibrium (as much as 1.5 wt.%) and lower than the values measured in the intrusive glassy pyroclast from the tuff-breccia dikes (Fig. 6). Indeed, two samples from the glassy margin of the feeder dike have an average of 1.53 wt.% H<sub>2</sub>O and are within several centimeters of rhyolite with <0.25 wt.% H<sub>2</sub>O.

Loss of water (degassing) upon cooling and crystallization (so-called second boiling) may be contrasted between the environments of the dome flow and the conduit. Comparison of the water contents of the glassy intrusive pyroclast and rhyolite (Fig. 3) indicates that crystallization of the conduit magma was accompanied by a loss of about 1.3 wt.% H<sub>2</sub>O. The final water content of the rhyolite would be controlled by phase equilibria primarily involving biotite. Devitrification of the dome flow, on the other hand, did not result in a substantial loss of water, as the melt had already degassed to its present water content (*i.e.*, that of equilibrium at *ca.* one bar; WESTRICH *et al.*, 1988). However, based on deformed flow banding about spherulites, SWANSON *et al.* (1989) suggest that the devitrification proceeded at or above the softening point of the glass.

The fact that the  $\delta D$  values of crystalline rhyolite and glassy samples (obsidian and coarse vesicular glass) from the flow are generally similar (Fig. 5) is, in part, because devitrification followed degassing. Figure 4 illustrates that crystalline rhyolite is typically characterized by  $\delta^{18}O$  values 0.5 to 2.0 per mil lower than adjacent obsidian. The field of "primary conduit rhyolite" denotes the approximate compositional range expected for rhyolitic magma that had achieved internal equilibrium at approximately 400 to 600 m. In contrast, both the hydrogen and oxygen isotope compositions of the basalt and granitic basement indicate exchange with hydrothermal meteoric water, and samples of crystalline rhyolite from the thin dike (hole RDO-3a) are relatively more depleted in D and <sup>18</sup>O than the conduit rhyolite, also suggesting some exchange with local meteoric water. Nevertheless, it is puzzling that the dike margin glass, which bears evidence of the largest isotopic and chemical changes (see below) also remains today a glass and has not crystallized (because hydrothermal activity was very short-lived?).

The correspondence between state of crystallization and  $\delta^{18}O$  is particularly well-shown for the high-Ba and low-Ba magmas (Fig. 8). None of the  $\delta$ -values of the rhyolite is so low (especially in view

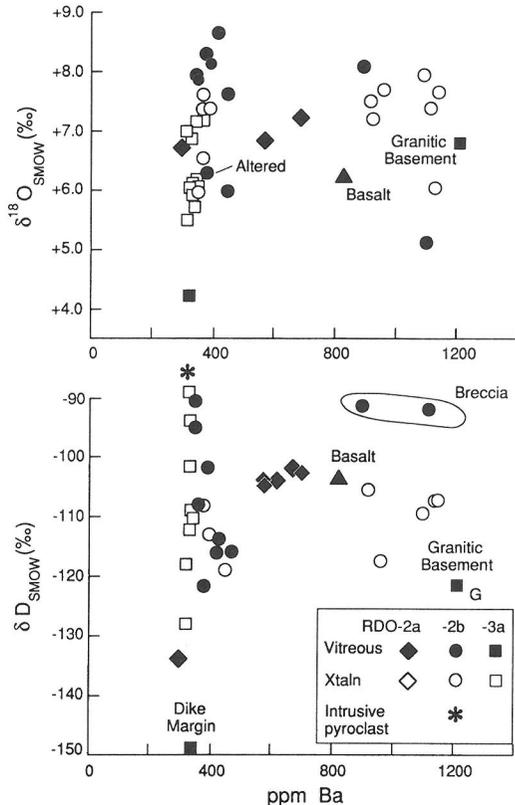


FIG. 8. Plot of  $\delta^{18}O$  and  $\delta D$  vs. Ba for vitreous and crystalline (Xtaln) rhyolite, and an obsidian clast from a tuff-breccia dike. The two "Breccia" samples represent the basal flow breccia beneath the dome flow. The high-Ba type rhyolite (see VOGEL *et al.*, 1989) appears to have a more restricted range of  $\delta^{18}O$  and  $\delta D$  than the low-Ba rhyolite. Barium analyses are from WESTRICH *et al.* (1988) and H. STOCKMAN (pers. comm.).

of the degassing effect on  $\delta D$ ) as to unequivocally indicate meteoric-hydrothermal alteration, although the  $\delta^{18}O$  values <6.0 are strongly suggestive. Typically, variation in  $\delta^{18}O$  (and <sup>18</sup>O-depletion) of feldspar-bearing rocks due to meteoric-hydrothermal exchange will increase with increasing water/rock ratio (*e.g.*, CRISS and TAYLOR, 1986). Presumably, the Ba resides with the feldspar or with the glass, yet there is no apparent variation with decreasing  $\delta^{18}O$ , such as might be due to leaching at a higher water/rock ratio. Barium has evidently remained largely immobile.

The variations of  $\delta^{18}O$  and  $\delta D$  with Cl and S are illustrated in Figs. 9 and 10. Second boiling is thought to generate a Cl-rich fluid (*e.g.*, BURNHAM, 1979; WESTRICH *et al.*, 1988), and, indeed, the vitreous rhyolite has a higher concentration of Cl than crystalline rhyolite with a similar range in  $\delta^{18}O$  and

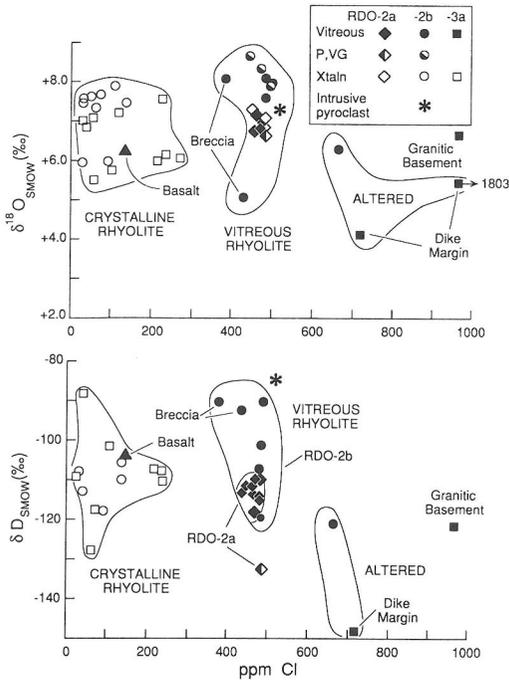


FIG. 9. Plot of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  vs. Cl for vitreous and crystalline (Xtaln) rhyolite, an obsidian clast (\*) from a tuff-breccia dike, and for samples of basaltic and granitic wall rocks. Chlorine analyses are from WESTRICH *et al.* (1988) and H. STOCKMAN (pers. comm.).

$\delta\text{D}$ . Dike margin glass and one sample of apparently exchanged or "altered" flow obsidian have markedly higher Cl contents. The trend shown for Cl could be considered consistent with progressive degassing of Cl (the dike margin glass would then represent quenched higher, primary contents). However, the low  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values of the dike margin glass most likely imply that Cl released by crystallization of the vitreous rhyolite may have been added to the dike margin during meteoric-hydrothermal alteration (via a brine?).

Slightly lower S contents are also apparent for the crystalline rhyolite (WESTRICH *et al.*, 1988), although the distinction from vitreous rhyolite is less clear than for Cl. Either sulfur was not particularly mobile, or most samples have suffered approximately equal sulfur loss.

CONCLUSIONS

The hydrogen isotopic compositions and water contents measured for tephra and dome obsidian (and, to some degree, pumice clasts) are consistent with calculated isotopic degassing trends which quantitatively account for D/H fractionation of  $\text{H}_2\text{O}$  and OH in the melt. Degassing and eruption

of vesicular magma from Obsidian Dome vent became a progressively more open process with time because of the removal of magmatic water with melt after successive stages of essentially closed-system degassing (with each stage punctuated by eruption of a tephra layer). Completely open-system degassing would result in no eruption at all, and this may have been the fate of the magma in the feeder dike.

Devitrification of glassy rhyolite was not accompanied by any major shifts in either  $\delta\text{D}$  or  $\delta^{18}\text{O}$ , probably because of virtually complete water loss from the hydrous melt. Only biotite remained behind as a hydrous component.

Isotopic evidence of magma-water interaction is recorded in the glassy margin of the feeder dike. Glassy pyroclasts in sub-horizontal, tuff-breccia-filled fractures related to emplacement of the dike record some (minor) hydrogen isotopic exchange with meteoric water.

The  $\delta\text{D}$  value of water in the Obsidian Dome magma prior to degassing is estimated to have been

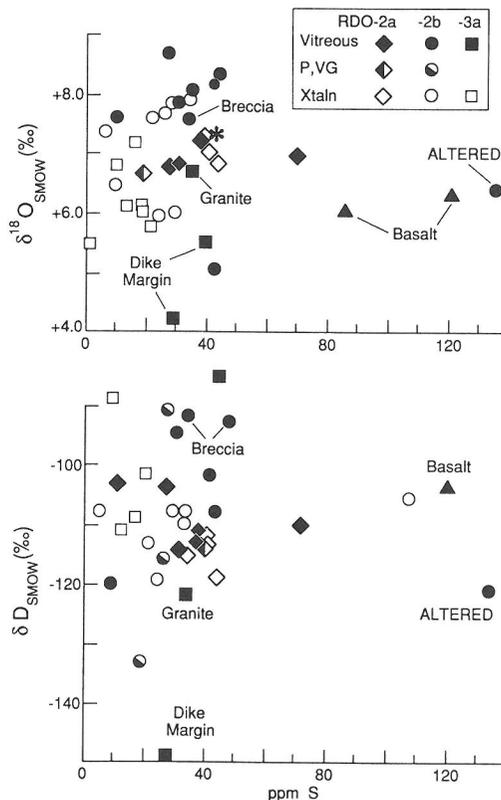


FIG. 10. Plot of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  vs. S for vitreous and crystalline (Xtaln) rhyolite, an obsidian clast (\*) from a tuff-breccia dike and samples of basaltic and granitic wall rocks. Sulfur analyses are from WESTRICH *et al.* (1988) and H. STOCKMAN (pers. comm.).

approximately  $-40$ . This is in stark contrast to the  $\delta D$  of local meteoric water (ca.  $-122$ ), and somewhat higher than usually considered for magmatic water (cf. B. TAYLOR, 1986; H. P. TAYLOR and SHEPPARD, 1986). The large variation in  $\delta D$  of the obsidian, to final values of  $-120$ , represents fractionation dominated by OH species in the melt as it progressively degassed. Exsolved magmatic water was not nearly so deuterium-depleted; the bulk of it had a  $\delta D$  value  $-50$  or higher. Final-stage degassing during emplacement of the dome was dominantly open-system in nature, with distal portions of the flow more degassed than either the basal breccia or the later-extruded proximal portion.

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