

Water, CO₂, Cl, and F in melt inclusions in phenocrysts from three Holocene explosive eruptions, Crater Lake, Oregon

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ABSTRACT

Rare melt inclusions ~100 μm in diameter trapped near the boundaries of corroded patchy zones in plagioclase phenocrysts from Plinian pumice of three Holocene eruptions were analyzed by IR spectroscopy for molecular H₂O, OH groups, and CO₂ and by electron microprobe for Cl and F. The three rhyodacitic eruptions, each of which began with a Plinian phase, occurred over ~200 yr. The Llao Rock and Cleetwood eruptions ended with degassed lava flows and the subsequent climactic eruption with voluminous ignimbrite. Groundmass glass and melt inclusion compositions (anhydrous) are similar. Inclusions with total H₂O concentrations of 1.2–3.4 wt% are adjacent to fractures or are hour-glass inclusions, suggesting partial degassing caused by depressurization. Melt inclusions in phenocrysts in climactic ignimbrite may have vesiculated for the same reason. Intact inclusions in Plinian pumices have total H₂O concentrations believed to represent magmatic H₂O contents (wt%): Llao Rock, 5.3, 5.3; Cleetwood, 3.8, 4.7; climactic 3.9 ± 0.2 (1σ, n = 6). Ratios of OH/molecular H₂O indicate closure temperatures of 200–500 °C that reflect syn- or post-eruptive cooling. CO₂ concentrations are ≤25 ppm. H₂O and CO₂ concentrations indicate saturation pressures of 1.0–1.8 kbar or depths ≥5 km. Six inclusions from climactic pumice average 400 ± 40 (1σ) ppm F, 1880 ± 70 ppm Cl. F and Cl concentrations of the other samples are similar and not well correlated with each other or with total H₂O.

Location of melt inclusions near boundaries of patchy zones, which are mantled by oscillatory-zoned overgrowths, suggests that their H₂O concentrations represent magmatic values significantly before eruption. Although mean H₂O concentrations of analyzed melt inclusions decrease for the three successive eruptions, it is not certain that this indicates a corresponding change in magmatic H₂O content during the interval between eruptions.

INTRODUCTION

Melt inclusions in phenocrysts of volcanic rocks are believed in many instances to preserve magmatic concentrations of dissolved volatile components. In such cases, pre-eruptive processes, such as fractional crystallization and degassing, can be followed by studying the chemical compositions of melt inclusions. In addition, the minimum pressure of entrapment (therefore of crystallization) can be determined from the dissolved volatile compositions if the system was vapor saturated at the time of entrapment. However, it is essential to know the time of entrapment and the subsequent history of the liquid now preserved as glass in order to interpret data from melt inclusions correctly.

The primary goal of most studies of dissolved volatiles in melt inclusions has been to quantify pre-eruptive magmatic volatile contents. Dissolved volatile concentrations in melt inclusions in bulk samples of quartz phenocrysts from the Bandelier Tuff were determined by Sommer (1977); see also Sommer and Schramm (1983). Data for

individual melt inclusions were first reported by Harris and Anderson (1983, 1984). Recently, use of infrared spectroscopy and the ion microprobe has facilitated measurements on individual inclusions (Anderson et al., 1989; Dunbar et al., 1989; Hervig et al., 1989; Newman and Chesner, 1989; Vogel et al., 1989; Webster and Duffield, 1991; Lowenstern and Mahood, 1991). A common conclusion of modern studies is that pre-eruptive magmatic volatile concentrations have less influence on eruptive style (i.e., explosive eruption vs. quiet effusion) than decompression history, which controls subsurface degassing behavior. Data for melt inclusions have also allowed estimates of minimum depths to reservoirs, assuming gas saturation, and in some cases have led to the conclusion that magmas were vapor saturated during phenocryst growth (Anderson et al., 1989). Our study attempts to document pre-eruptive magmatic volatile contents based on analysis of melt inclusions in plagioclase phenocrysts.

In this study we report infrared spectroscopic and electron probe microanalyses of melt inclusions in plagioclase

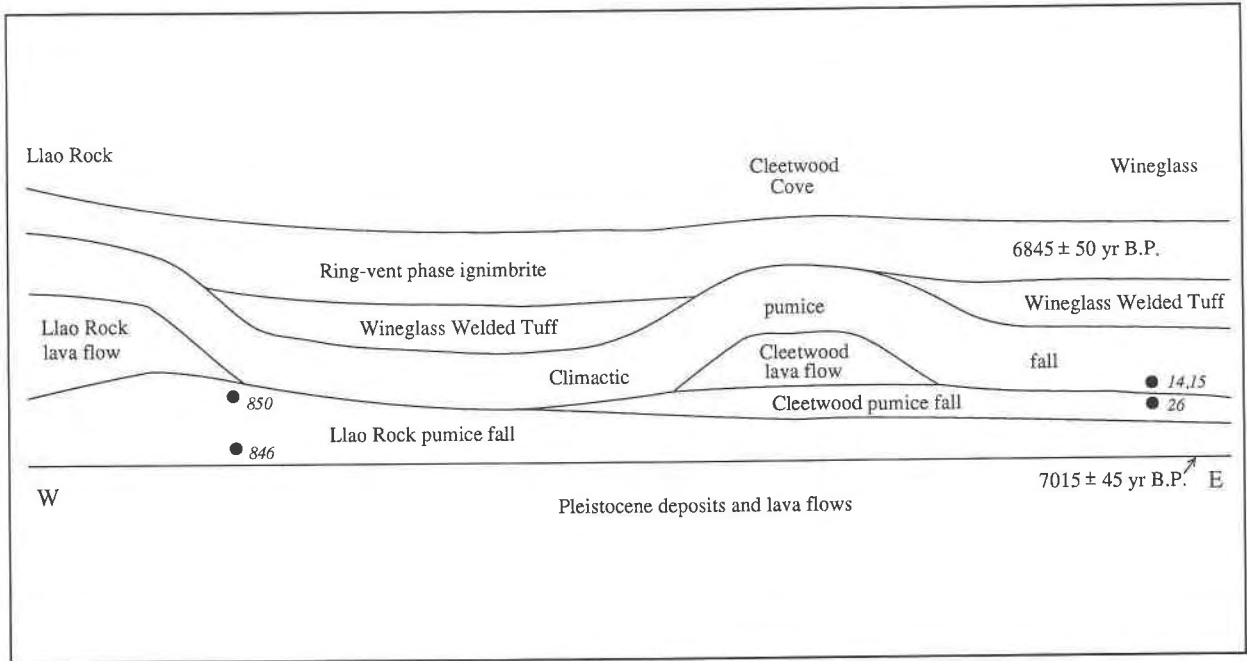


Fig. 1. Schematic stratigraphic relations between Holocene preclimactic and climactic eruption pyroclastic deposits and lava flows along the north rim of Crater Lake caldera. Numbers indicate localities for pumice samples from which melt inclusions were analyzed. Not to scale.

clase from pumices of three Holocene eruptions at Mount Mazama (Crater Lake), Oregon. Much volcanological and petrological information exists for these eruptions (Bacon and Druitt, 1988; Druitt and Bacon, 1986, 1989; Young, 1990), and their timing is relatively well known (Bacon, 1983). All began with an explosive Plinian phase. The first two ended with degassed lava flows, the third with collapse of Crater Lake caldera during the climactic eruption, which ejected $\sim 50 \text{ km}^3$ of magma. Our study focuses on Plinian pumices with melt inclusions whose dissolved volatile concentrations are believed to represent magmatic values at times significantly before each Plinian eruption began. The melt inclusion data provide information about points in the magmas' history and constrain minimum depths for magma reservoirs. We also discuss volatile concentrations in glass in vitrophyres from one of the late-stage lava flows and some implications of the vesiculation of melt inclusions in phenocrysts from the climactic eruption.

GEOLOGY

Mount Mazama is one of the major Quaternary volcanic centers of the High Cascades. It consists of a complex of basaltic andesitic to dacitic shields and stratovolcanoes constructed between $\sim 420,000$ and $\sim 40,000$ years ago (Bacon, 1983; Bacon and Lanphere, 1990). Rhyodacitic volcanism related to growth of the climactic magma chamber began $\sim 30,000$ years ago, producing several preclimactic lava flows and domes, at least some of which were preceded by small Plinian eruptions. The samples

we have studied are from the Lloa Rock and Cleetwood preclimactic eruptions and the climactic eruption itself.

Products of the Lloa Rock event consist of two dikes in the caldera wall, a mildly zoned Plinian deposit, and a thick lava flow (Fig. 1). Charcoal fragments from beneath the Plinian deposit gave a ^{14}C age of 7015 ± 45 yr B.P. (Bacon, 1983). The Cleetwood eruption is represented by a Plinian deposit and an overlying lava flow. The Cleetwood lava flow was still hot, and plastic in its interior, at the time of the climactic eruption. The climactic eruption began with a Plinian column that collapsed to form the Wineglass Welded Tuff (Williams, 1942) ignimbrite that is found on the north and east flanks of Mazama; the Plinian deposit and the Wineglass originated from a single vent and are nearly entirely rhyodacite. Eruption of the Wineglass ended when the caldera began to collapse. Caldera formation was accompanied by emplacement of zoned ignimbrite, dominantly rhyodacite that was followed by andesite and mafic cumulate material, from highly mobile pyroclastic flows that were fed by multiple vents around the perimeter of the subsiding block (Bacon, 1983; Druitt and Bacon, 1986). Bacon (1983) reported a weighted mean ^{14}C age of 6845 ± 50 yr B.P. for charcoal associated with primary deposits of the climactic eruption.

PETROLOGY

Compositions of rocks, glasses, and phenocrysts are known for all products of the climactic magma chamber (Bacon and Druitt, 1988; Druitt and Bacon, 1989). The

Llao Rock Plinian deposit is zoned from relatively differentiated rhyodacite at its base to rhyodacite similar to that of the climactic eruption at its top (except for slightly higher Ba and lower Mg and Sr concentrations); Fe-Ti oxide microphenocryst equilibration temperatures are ~ 860 °C at the base and ~ 890 °C at the top of the deposit. The overlying lava flow apparently consists of a mixture of these two rhyodacite compositions. Cleetwood pumice and lava are compositionally (anhydrous basis) and mineralogically identical to rhyodacite pumice of the climactic eruption, which is remarkably homogeneous; all glassy samples from these units have Fe-Ti oxide temperatures of ~ 880 °C, regardless of mode of eruption or vesicularity. We were successful in analyzing intact melt inclusions in plagioclase from late Llao Rock, Cleetwood, and early climactic pumice, all of which have Fe-Ti oxide temperatures of ~ 880 – 890 °C.

The rhyodacites studied contain approximately 10 vol% phenocrysts of plagioclase, orthopyroxene, clinopyroxene, hornblende, magnetite, and ilmenite (Druitt and Bacon, 1989). Consistency of phenocryst rim compositions indicates preeruptive equilibrium with melt now represented by groundmass glass. Here we focus on plagioclase because it is the host phase for analyzed melt inclusions. Anorthite and Sr contents of plagioclase can be used to fingerprint individual crystals in terms of their sources in the zoned chamber (Druitt and Bacon, 1989), which contained crystallization products of parent magmas with different Sr concentrations (Bacon and Druitt, 1988). Reverse zoning of Sr concentrations accompanying normal Ab-An zoning of plagioclase is common, reflecting hybridization of magmas. Patchy zoning with little compositional range is present in many phenocrysts, either in cores or in thick zones, which are overgrown by thick, oscillatory zoned rims (Figs. 2a, 2b). The patchy zoning may have resulted from cellular growth of plagioclase (Anderson, 1984) or from resorption. Margins of patchy zones are irregular and rounded suggesting resorption, as is also indicated by truncated oscillatory zones (Fig. 2c) attending magma mixing or temperature increase.

Melt inclusions in plagioclase phenocrysts are most common near the irregular margins of patchy-zoned cores (Figs. 2a, 2b). Inclusions are composed of brown glass, have negative crystal shapes, and are up to ~ 130 μm in maximum dimension. Intact inclusions yielded what we consider to be magmatic volatile concentrations. In these, a single or small number of 10–20- μm bubbles that are commonly present are attributed to shrinkage (ca. 1–2 vol% of an inclusion). No daughter crystals were observed, and there is no evidence for postentrapment crystallization (e.g. no inverse correlation between Ca or Al and Cl or Mg).

Many inclusions, some of which were analyzed, display petrographic evidence for leakage and volatile loss during or after entrapment. For example, very thin (≤ 2 μm) capillary tubes connect some inclusions with groundmass glass (Fig. 2d), as in "hourglass" inclusions described by Anderson (1991) in quartz of the Bishop Tuff. In addition,

many inclusions have vesiculated and show evidence of having leaked melt, either through capillaries or fractures (cf. St. Seymour and Vlassopoulos, 1989, their Fig. 6; Anderson et al., 1989). Inclusions in all phenocrysts examined from the Wineglass Welded Tuff and the ring-vent phase ignimbrite are of this type. Some inclusions are partially devitrified, and this may have affected the volatile concentrations in their glass.

ANALYTICAL METHODS

Fresh pumice clasts were selected from deposits of known stratigraphic position. Plagioclase phenocrysts containing melt inclusions large enough for analysis were picked from crystal concentrates made by gently crushing fragments of single pumice clasts and washing away the glass with H_2O . Crystals were mounted on glass slides, ground, and polished to expose melt inclusions. Major element compositions of plagioclase and melt inclusions were determined on an automated, five-crystal spectrometer JEOL 733 electron microprobe; in addition, Sr was measured in plagioclase (a correction was made for interference of $\text{SiK}\beta$ on $\text{SrL}\alpha$; precision of concentration measurements is $\pm 10\%$ or better) and F and Cl in glass. Microprobe operating conditions were 15 kV accelerating voltage, 12–30-nA beam current, and 20- μm diameter electron beam. Corrections were calculated using the Citza program (Armstrong, 1988) employing the absorption correction of Armstrong (1982), the atomic number correction of Love et al. (1978), and the fluorescence correction of Reed (1965) as modified by Armstrong (1988). Doubly polished wafers were then made from the plagioclase phenocrysts so that individual melt inclusions were exposed on both sides of the crystal. Infrared spectroscopic measurements were made on these inclusions using a Nicolet 60SX Fourier transform (FTIR) spectrophotometer following procedures modified after Newman et al. (1986). The modifications consisted of the use of the microbeam chamber as opposed to the main sample chamber of the 60SX spectrophotometer. Using this chamber increases the signal-to-noise ratio up to 36 times relative to the same conditions in the main chamber because of a 6X condensing lens. The melt inclusions were mounted over 35–50- μm apertures during the FTIR measurements. Molecular H_2O concentration was determined from the band at ~ 5200 cm^{-1} and OH at ~ 4500 cm^{-1} ; the sum of molecular H_2O + OH calculated as H_2O was checked against total H_2O determined from the band at ~ 3550 cm^{-1} (Newman et al., 1986). Five vitrophyre samples from the Cleetwood lava flow were also analyzed for total H_2O using the ~ 3550 - cm^{-1} band. The molar absorptivity used for the 3550- cm^{-1} band, the fundamental OH-stretching vibration, was 88 ± 2 (Dobson et al., 1989). Dissolved molecular CO_2 concentration in melt inclusions was obtained from the ~ 2350 - cm^{-1} band. The molar absorptivity used was 1078 (Blank et al., 1989). We assumed that the density of the glasses was 2.3 $\text{g}\cdot\text{cm}^{-3}$. Two to five analyses were made of each inclusion.

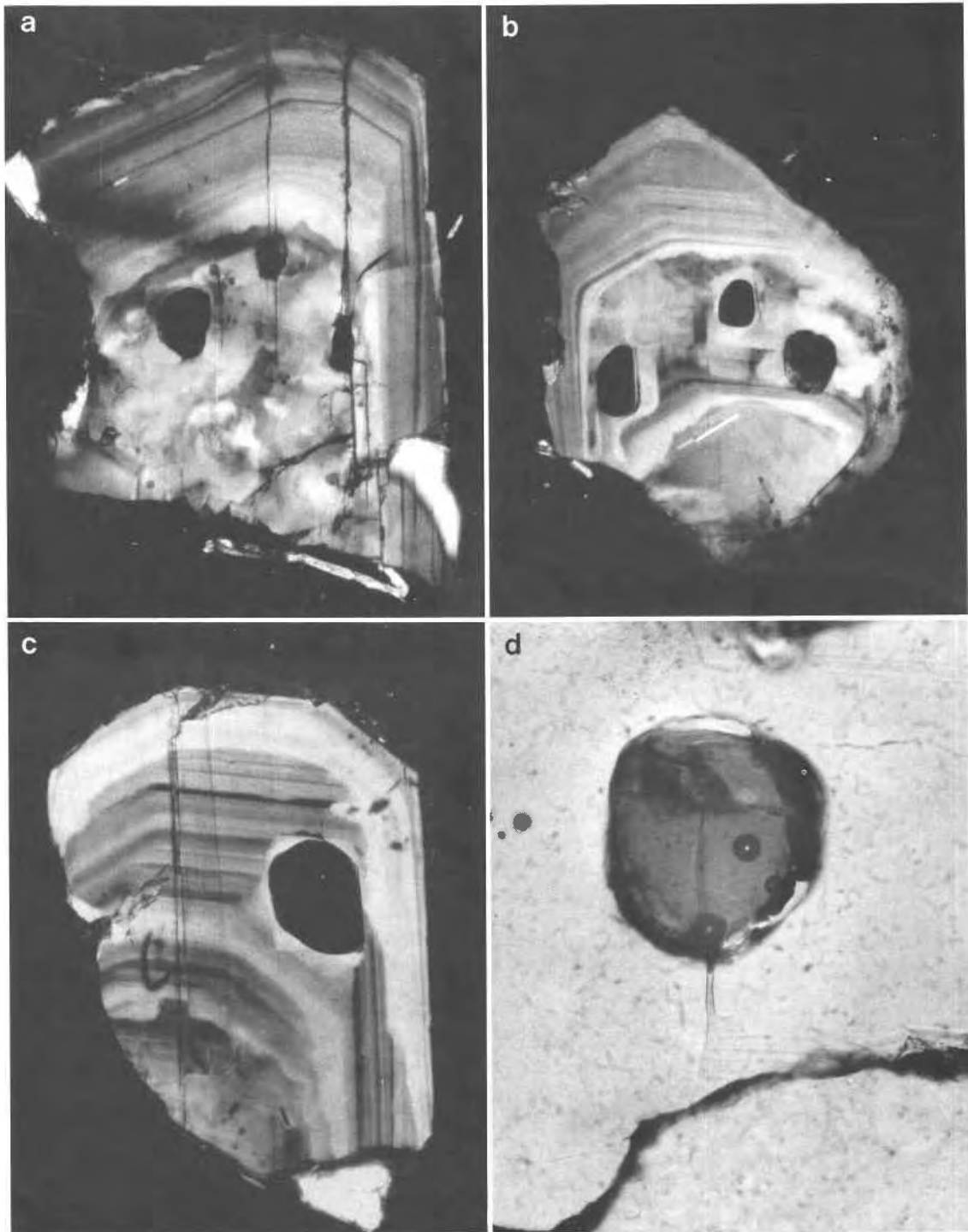


Fig. 2. Photomicrographs of plagioclase phenocryst fragments and melt inclusions from sample 14 from the Plinian deposit of the climactic eruption. (a) Patchy-zoned core with melt inclusions near outer edge (crystal 7), overgrown by oscillatory zoned rim. Large melt inclusion is $100 \times 130 \mu\text{m}$. (b) Patchy zone containing melt inclusions between core and oscillatory zoned rim (crystal 5). Elongate melt inclusion is $70 \times 130 \mu\text{m}$. (c) Complex oscillatory zoned crystal showing three unconformities representing resorption followed by renewed growth; melt inclusion is $90 \times 120 \mu\text{m}$ (crystal 6). (d) Hourglass melt inclusion (crystal 1). Inclusion is $100 \mu\text{m}$ across, capillary $\sim 2 \mu\text{m}$.

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TABLE 1. Plagioclase phenocryst compositions

Unit	Sample	Xtl	An (mol%)	Ab (mol%)	Or (mol%)	Sr (ppm)	Comments
Climactic	14	1	37.8	60.5	1.7	1080	by mi
			39.2	59.3	1.4	1250	by mi
			37.2	61.2	1.7	1360	rim
Climactic	14	2	38.5	59.9	1.6	1100	by mi
			39.5	59.1	1.4	1160	inner rim
Climactic	14	3	47.9	51.1	1.0	890	core
			47.9	51.0	1.1	1170	by mi
			45.1	53.7	1.2	1150	by mi
			40.6	57.9	1.5	1140	inner rim
			36.9	61.5	1.6	940	mid rim
			37.4	60.9	1.6	1150	rim
Climactic	14	5	38.7	59.9	1.5	1220	core
			40.3	58.2	1.5	1100	by mi
			42.0	56.7	1.4	970	by mi
			38.3	60.2	1.5	1500	rim
Climactic	14	6	36.2	62.1	1.6	1010	core
			37.3	61.1	1.7	1160	by mi
			39.2	59.2	1.6	1600	rim
Climactic	14	7	42.9	55.8	1.2	1080	core
			40.8	57.8	1.4	960	by mi
			33.9	64.2	1.9	980	rim
Climactic	15	8	38.9	59.6	1.5	1050	by mi
			38.6	59.9	1.5	1090	inner rim
			34.4	61.7	3.8	1300	rim
Cleewood	26	3	38.8	59.8	1.4	1110	core
			35.6	62.7	1.7	1070	inner rim
Cleewood	26	4	40.7	57.9	1.3	1040	core
			41.7	57.1	1.2	1280	rim
Llao Rock	850	1	39.1	59.5	1.4	990	core
			46.8	52.1	1.1	1190	rim
Llao Rock	846	3	38.7	60.0	1.4	1000	by mi
			38.6	60.0	1.4	1100	core
			45.3	53.6	1.1	1470	rim

Note: Sr concentrations corrected for interference of $\text{SiK}\beta$ on $\text{SrL}\alpha$. The abbreviation mi = melt inclusion.

The average standard deviation of the replicate analyses for H_2O was 5% and for CO_2 was 35%.

RESULTS

Inclusion and host compositions

A necessary, but not sufficient, condition for volatile concentrations in melt inclusions to reflect magmatic conditions in the host magma just prior to eruption is that host crystals must be representative of the phenocryst population and glass compositions must be similar to that of the groundmass glass. Plagioclase compositions adjacent to analyzed melt inclusions are An_{37-48} , most being $\sim\text{An}_{39}$ (Table 1). Sr concentrations at the same points are 960–1250 ppm but are not directly correlated with An. Rim compositions range from An_{39} , 1600 ppm Sr to An_{34} , 980 ppm Sr. Comparison of these data with those of Druitt and Bacon (1989) shows that the host crystals for the studied melt inclusions are indeed compositionally representative of phenocrysts in their respective eruptive units.

Major element compositions of melt inclusions determined by electron microprobe are similar to X-ray fluorescence analyses of glass separates from pumices when both are recalculated to total 100 wt% on an anhydrous basis. Mean compositions of melt inclusions (23 spot analyses) in climactic pumice are compared with the mean

of five analyses of groundmass glass separates from climactic rhyodacite in Table 2. In general, differences between specific melt inclusion analyses and typical groundmass compositions are small and similar to the reproducibility of the microprobe data. Although we cannot prove that a particular melt inclusion is identical in composition to nearby groundmass glass, the analyzed melt inclusions are representative of liquids in the remarkably homogeneous (Bacon and Druitt, 1988) rhyodacitic part of the magma chamber.

H_2O concentrations in melt inclusions

Results of FTIR measurements of molecular H_2O , OH, and total H_2O concentrations are presented in Table 3. The sum of molecular H_2O and OH calculated as H_2O is believed to be a more accurate value than total H_2O determined from the $\sim 3550\text{-cm}^{-1}$ band at the observed concentrations in melt inclusions; we refer to this sum as total H_2O concentration in what follows, except for the Cleewood lava flow samples, which contain very little H_2O .

A total of three melt inclusions were analyzed in two samples from the Llao Rock pumice fall beneath the east edge of the Llao Rock lava flow, one from the base (846) and one from the top (850). The inclusion in the basal sample gave a low total H_2O concentration (2.1 wt%),

TABLE 2. Mean glass compositions, climactic rhyodacite

	Climactic				Cleetwood		
	Melt incl	1 σ	Pumice glass	1 σ	Melt incl	1 σ	Vitrophyre glass
	Wt%						
SiO ₂	73.0	0.4	73.2	0.8	73.6	0.4	73.8
Al ₂ O ₃	14.7	0.26	14.4	0.46	14.3	0.18	14.2
FeO*	1.93	0.08	1.66	0.17	1.87	0.08	1.65
MgO	0.41	0.05	0.49	0.09	0.41	0.05	0.34
CaO	1.50	0.12	1.63	0.15	1.41	0.11	1.41
Na ₂ O	5.11	0.17	5.13	0.21	5.30**	—	5.26
K ₂ O	2.84	0.07	2.85	0.11	2.55	0.20	2.82
TiO ₂	0.36	0.06	0.42	0.02	0.39	0.03	0.40
P ₂ O ₅	0.06	0.02	0.09	0.01	0.04	0.03	0.08
MnO	0.05	0.01	0.05	0.01	0.05	0.01	0.06
	ppm						
Sr	320	150	307	7	—	—	298

Note: Analyses recalculated to total 100% volatile free. Climactic melt inclusions, average of 23 electron probe analyses from samples 14 and 15 (Caltch JEOL 733); climactic pumice glass, average of five X-ray fluorescence analyses of glass separates from pumice (Bruggman et al., 1987); Cleetwood melt inclusions, average of six electron probe analyses from sample 26 (Caltch JEOL 733); Cleetwood vitrophyre glass, electron probe analysis of groundmass glass in lava sample 160 (USGS ARL SEMQ), Sr by X-ray fluorescence on glass separate (Bruggman et al., 1987).

* Total Fe as FeO.

** Na₂O fixed at 5.30% for recalculation.

apparently owing to visible connection with the outside of the plagioclase. Inclusions from two phenocrysts in the late-erupted sample each gave 5.3 wt% total H₂O. The latter values are thought to represent magmatic conditions.

Analyses of melt inclusions in two phenocrysts from a pumice clast (26) from near the top of the Cleetwood pumice fall in the caldera wall at Wineglass yielded total H₂O concentrations of 3.8 and 4.7 wt%. This difference appears to be well outside the precision of measurement.

Two pumice clasts from <1 m above the base of the climactic pumice fall were studied (14, 15; Wineglass locality). Two melt inclusions in sample 15 and one in sam-

ple 14 have low total H₂O concentrations (2.4, 3.1, 1.2 wt%, respectively). The two higher values are for inclusions that appear to have leaked into glass-filled cracks in plagioclase that connect the inclusions to the outside of the crystals. The lowest value is for an inclusion that is in communication with groundmass glass by a capillary (Fig. 2d). Another six inclusions from sample 14 range from 3.6 to 4.3 wt% total H₂O. We take the mean value of 3.9 ± 0.2 (1 σ) wt% for these six to be representative of magmatic H₂O content, since the standard deviation about this value is approximately equivalent to our analytical precision. Note that two nearby inclusions in one phenocryst, where the thickness of the analyzed glass is

TABLE 3. Volatile concentrations in melt inclusions in plagioclase phenocrysts from Mount Mazama and in vitrophyre glass from the Cleetwood lava flow

Unit	Sample	Xtl*	Incl**	H ₂ O mol wt% (5200 cm ⁻¹)	H ₂ O OH wt% (4500 cm ⁻¹)	H ₂ O† tot wt%	H ₂ O tot wt% (3550 cm ⁻¹)	CO ₂ ppm	F ppm	Cl ppm	Comments
Climactic	14	1	1	0.62	0.62	1.2			400	2100	
Climactic	14	2	1	2.7	1.1	3.8		11	350	1850	hourglass
Climactic	14	3	1	3.3	0.99	4.3			350	2000	
Climactic	14	5	1	2.9	0.95	3.8			400	1900	
	14	5	2	3.1	0.93	4.0			450	1800	
Climactic	14	6	1	2.7	1.0	3.6			400	1800	
Climactic	14	7	1	2.8	0.99	3.8			450	1850	hourglass
Climactic	15	8	1	1.8	0.62	2.4			300	1900	cracked
	15	8	2	2.1	1.0	3.1			500	2050	cracked
Cleetwood	26	3	1	2.5	1.3	3.8	4.0	17	500	1600	
Cleetwood	26	4	1	3.6	1.0	4.7		10	300	1750	cracked?
Liao Rock	850	3	1	4.3	0.97	5.3	6.0		650	1800	
Liao Rock	850	4	1	4.1	1.2	5.3	5.4		250	1850	
Liao Rock	846	3	1	0.95	1.1	2.1	2.0	25	300	2150	cracked
Cleetwood	160	—	—	—	—	—	0.13	—	—	1400	vitrophyre
Cleetwood	770	—	—	—	—	—	0.095	—	250	1100	vitrophyre
Cleetwood	771	—	—	—	—	—	0.077	—	500	900	vitrophyre
Cleetwood	779	—	—	—	—	—	0.11	—	400	1150	vitrophyre

Note: H₂O, OH, and CO₂ by infrared spectroscopy; F and Cl by electron microprobe (see text).

* Crystal number.

** Inclusion number.

† H₂O_{mol} + OH as H₂O.

comparable and thus is not a factor in relative analytical precision, gave 3.8 and 4.0 wt% total H₂O.

CO₂ in melt inclusions

It was difficult to obtain molecular CO₂ data for the Crater Lake melt inclusions because of the low concentration of this species. We detected CO₂ in four inclusions, with values ranging from 10 to 25 ppm. The data are not sufficiently precise or abundant to allow discrimination of any differences that might be present between melt inclusions in pumice from the three eruptive units.

Cl and F in melt inclusions

There is little variation in Cl among melt inclusions. Ranges for inclusions from preclimactic and climactic pumices are similar: 1750–2150 and 1850–2100 ppm, respectively. Mean values are virtually identical. Cl concentration can be determined with good precision (ca. ± 100 ppm, or better, here) with the electron microprobe, suggesting that extreme values, at least, represent true differences in Cl concentration. Cl concentration is not correlated with F, total H₂O, or eruptive sequence.

Microprobe analyses for F vary between 270 and 630 ppm. The variation in F appears to be random, and we suspect that most, if not all, can be ascribed to poor analytical precision, largely as a result of determination of background intensities in the presence of overlaps with multiple order Fe and Mg peaks. Like Cl, mean values for F in climactic and preclimactic samples are similar (~400 ppm). Interestingly, Cl and F concentrations in low-H₂O melt inclusions are not significantly lower than those of melt inclusions that appear to have retained magmatic levels of H₂O. In contrast, Anderson et al. (1989) reported decreased Cl concentrations in hourglass and cracked inclusions in the Bishop Tuff. Retention of Cl in the Crater Lake inclusions may be a result of shorter duration of the Crater Lake Plinian eruptions and the fact that some of the Bishop Tuff inclusions were from late-erupted ignimbrite.

Volatile concentrations in Cleetwood vitrophyre glass

Glass in four porphyritic vitrophyre samples from widely separated localities on the surface of the Cleetwood lava flow was analyzed for total H₂O, F, and Cl (Table 3). Results are typical of nonhydrated, degassed glassy rhyolitic lava. The range of values is 770–1280 ppm H₂O, with a mean of 1000 ± 180 (1 σ) ppm. The average concentrations of Cl and F are 1100 ppm, lower than those of the inclusions, and 320 ppm, similar to those of the inclusions, respectively.

The identical mineral content and anhydrous composition of Cleetwood samples and climactic pumice, their vent locations, and the timing of eruptions suggest that the two eruptions tapped the same rhyodacitic magma. The Cleetwood vitrophyre is part of a lava flow that presumably degassed through loss of a dominantly aqueous vapor phase during ascent and eruption. Cleetwood vitrophyre glass and melt inclusions in Cleetwood and cli-

matic pumices have indistinguishable F concentrations, but the melt inclusions have $\sim 1.5\times$ the Cl and $40\times$ the H₂O. The different behavior of F and Cl is qualitatively consistent with experimental studies of F and Cl partitioning between silicate melt and aqueous fluid (Webster and Holloway, 1990). The H₂O concentration in the vitrophyre glass is a result of open-system degassing, as described by Newman et al. (1988).

DISCUSSION

Magmatic dissolved volatile concentrations

The general consistency of total H₂O concentrations for intact melt inclusions from a particular eruptive unit suggests these represent preeruptive magmatic H₂O contents. There is some question, however, as to the point in a magma's history when melt inclusions were trapped. Herein lies an advantage of the plagioclase host, where zonation is observable, over the more readily prepared quartz of most other studies of inclusions in silicic magmas: The location of inclusions near the margins of patchy zoned cores of plagioclase phenocrysts (Fig. 2) suggests entrapment was associated with at least one major contamination, mixing, or heating event. Sr concentrations in plagioclase rims (Table 1) are generally higher than in cores, suggesting that resorption of the patchy zones occurred during early Holocene introduction of a new batch of parent magma relatively rich in Sr (Druitt and Bacon, 1989). The uniformity of major element glass compositions among inclusions and groundmasses and the mineral content of the samples imply little change in conditions between entrapment and eruption, regardless of the elapsed time. There is a suggestion of secular decrease in magmatic H₂O content in the order of decreasing age of the samples, spanning what is believed to have been ~ 200 yr (Bacon, 1983). Given the similar phenocryst content and mineral content of the studied pumices, however, it seems unlikely that melt inclusions record the evolving H₂O concentrations in melt during this period. On the other hand, if intracrystalline diffusion of H₂O in plagioclase is as rapid as H₂O diffusion in quartz may be (so that melt inclusions reequilibrate with external magma in a period measured in years), inclusion H₂O concentrations may indeed reflect magmatic H₂O values effectively at the times of eruption (Qin et al., 1992). In this case, the inclusions in plagioclase phenocrysts in climactic pumice may have adjusted their H₂O concentration by intracrystalline diffusion in the ~ 200 yr between the Lloa Rock and climactic eruptions. We might speculate that the small variation in melt inclusion H₂O concentration in Cleetwood and climactic phenocrysts may be due to different diffusion path lengths for inclusions, reflecting incomplete reequilibration, but we have found no correlation between H₂O concentration and apparent minimum distance from inclusion to crystal margin as measured in photomicrographs of doubly polished wafers (accurate measurement of minimum diffusion path would require determination before polishing). In any case, be-

TABLE 4. Calculated saturation pressures and minimum depths

H ₂ O (wt%)	P _{sat} (bars) (CO ₂ = 0 ppm)	Depth (km)	P _{sat} (bars) (CO ₂ = 50 ppm)	Depth (km)
3.8	988	4.6	1095	5.1
3.9	1036	4.8	1143	5.3
4.7	1446	6.7	1557	7.2
5.3	1788	8.3	1900	8.8

Note: Assumptions for calculations include rhyolite speciation for H₂O, rhyolite solubilities for H₂O and CO₂, 880 °C, density of overburden = 2.2 g·cm⁻³. See Newman et al. (1988) for details.

cause all of our samples have analytically indistinguishable Fe-Ti oxide equilibration temperatures that must reflect conditions shortly before eruption, we suspect that the different H₂O concentrations in intact melt inclusions resulted from entrapment, or possibly reequilibration, at different times or depths in the magma reservoir.

We accept 3.9–5.3 wt% H₂O, <25 ppm CO₂, ~400 ppm F, and 1800–2100 ppm Cl as typical of volatile compositions represented by climactic, Cleetwood, and late Llao Rock rhyodacitic magmas. The lower limit of 3.9 wt% H₂O is probably most representative, at least of climactic and Cleetwood magma, because it is based on several measurements from samples typical of the greatest erupted volume of magma and is in agreement with the ~4 wt% estimated by Bacon and Druitt (1988) on the basis of glass composition (Merzbacher and Eggler, 1984). Dacite from Mount St. Helens contains the same phenocryst assemblage as the Mazama rhyodacites, and both have broadly similar glass compositions (the dacite from Mount St. Helens has a greater phenocryst content and its glass is more calcic and less potassic than the Mazama examples). Electron microprobe analysis of melt inclusions in Mount St. Helens phenocrysts and experimental duplication of phase relations indicate 5.0 ± 0.5 wt% H₂O in the liquid (Rutherford et al., 1985; Rutherford and Devine, 1988), which is within the range of measured H₂O concentrations in melt inclusions from Crater Lake.

The preeruptive volatile concentrations in rhyodacitic magma at Crater Lake are similar to the electron (Cl) and ion microprobe results of Dunbar et al. (1989) for H₂O, F, and Cl in melt inclusions in phenocrysts of the Taupo and Hatepe Plinian tephra from the Taupo Volcanic Zone, New Zealand. Hervig et al. (1989) presented the same type of data for air-fall tephra from Obsidian Dome near Long Valley, California, in which volatile concentrations are variable but average 4.1 wt% H₂O; many F values are notably higher, and Cl lower, than those for Plinian pumices from Crater Lake and the Taupo Volcanic Zone. Anderson et al. (1989) studied melt inclusions in Plinian and ash-flow pumice from the Bishop Tuff, finding typically higher H₂O (5–6 and 4–5 wt%, respectively) and CO₂ but lower Cl concentrations than present in the Mazama samples. Melt inclusions in phenocrysts from the Bandelier Tuff (Hervig and Dunbar, 1989) have mean H₂O ≤ 4.7 wt%, Cl somewhat higher

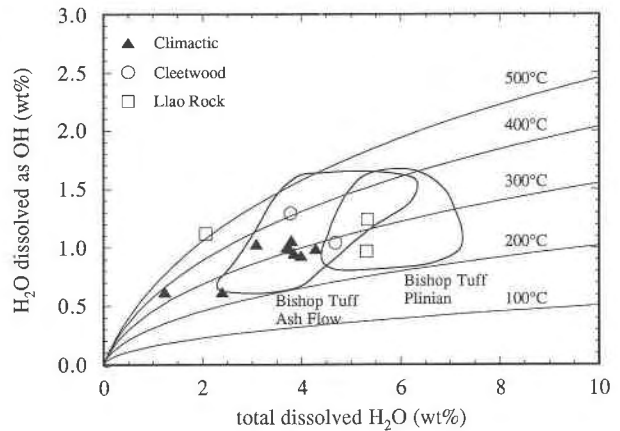


Fig. 3. Molecular H₂O concentrations in melt inclusions plotted against total H₂O concentration and showing H₂O speciation equilibration temperature from Zhang et al. (1991). Fields for the Bishop Tuff from data given by Anderson et al. (1989) and Skirius (1990).

(up to 2900 ppm) than Crater Lake and F much higher (maximum 2400 ppm). On the basis of melt inclusion analyses Webster and Duffield (1991) reported preeruptive volatile concentrations of ≤2.7 wt% H₂O, 2500 ppm Cl, and 2600 ppm F in the 28 Ma highly differentiated Taylor Creek Rhyolite of New Mexico. The relatively high Cl/F of the Crater Lake and Taupo melt inclusions in comparison with Obsidian Dome, Bandelier, and Taylor Creek samples is consistent with dominance of Cl over F in arc environments and the importance of F in continental settings (Christiansen et al., 1983).

Pressure and depth

Minimum pressures implied by H₂O and CO₂ concentrations can be estimated from solubility relations for rhyolitic liquids (Blank et al., 1989; Silver et al., 1990). If we assume saturation with a H₂O-CO₂ vapor at 880 °C, equilibrium pressures for 3.9–5.3 wt% H₂O in the liquid are 1.0–1.8 kbar for CO₂^{elt} = 0 and 1.1–1.9 kbar for CO₂^{elt} = 50 ppm (Table 4). These pressures correspond to depths of 5–9 km for a bulk density of upper crustal volcanic rocks of 2.2 g·cm⁻³ (Williams et al., 1987). Thus, the top of the climactic magma chamber was ≥5 km below the ground surface.

H₂O speciation in melt inclusions

The ratio of molecular H₂O to OH groups dissolved in glass is temperature dependent (Zhang et al., 1991). Speciation data are plotted in Figure 3. The speciation results indicate the final cooling history of the inclusions whether or not inclusions leaked before cooling. The melt inclusions indicate closure temperatures for H₂O speciation of 200–500 °C. The inclusions studied by Anderson et al. (1989) in quartz phenocrysts in Plinian pumice of the Bishop Tuff overlap this temperature range. The fall deposits from which pumice samples were collected at Crater Lake are nonwelded, although the climactic pumice

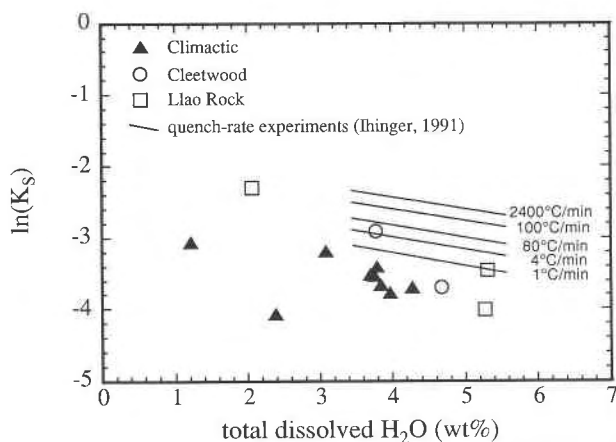


Fig. 4. Comparison of the speciation of H₂O in Crater Lake melt inclusions with that of glassy products of quench-rate experiments by Ihinger (1991).

$$\ln K_s = \ln \frac{(X_{\text{OH}_{\text{melt}}})^2}{(X_{\text{O}_{\text{melt}}}) \times (X_{\text{H}_2\text{O}_{\text{melt}}})}$$

where $X_{i,\text{melt}}$ is the mole fraction of species i in the melt. The shapes of the lines drawn for the constant quench rates are schematic.

fall, particularly near its base, tends to be slightly pinkish in color and forms steeper slopes than the Cleetwood or Llao Rock deposits as though it was hotter when deposited (recall that sample localities are near vent sites). The highest closure temperatures shown in Figure 3 are for an inclusion in early pumice from the Llao Rock deposit and for one of two inclusions in a single pumice lump from the Cleetwood deposit. The generally lower temperatures recorded by climactic pumice may result from slower postdepositional cooling. Indeed, a comparison of these results with quench-rate data from Ihinger (1991) suggests that cooling rates for the inclusions from the climactic eruption were slower than 1 °C/min, whereas those for some pumice clasts of the Cleetwood and Llao Rock eruptions were much faster (as fast as ~100 °C/min) (Fig. 4). Cooling of climactic inclusions through closure temperatures therefore must have occurred predominantly after deposition.

Degassing during the climactic eruption

It was noted above that melt inclusions in all clasts examined from nonwelded exposures of the Wineglass Welded Tuff and the ignimbrite of the ring-vent phase of the climactic eruption are vesiculated. The majority can be seen to have leaked to the outsides of fractured crystals. This is particularly spectacular in late-erupted crystal-rich scoriae (Druitt and Bacon, 1989) in which melt inclusions are larger and more common than in phenocrysts in rhyodacitic pumices (although resorption of crystals results in some ambiguities in interpretation of textures in thin sections of scoriae). A plausible explanation for the vesiculation and fracturing is that of differential vapor pressure between melt trapped as inclu-

sions and that outside of the crystals (Tait, 1992): depressurization of the magma allowed melt inclusions literally to blow apart their host crystals. Because this process affected all ignimbrite inclusions examined but only affected some of the inclusions in phenocrysts in Plinian pumices, it seems possible that vesiculation and leaking of melt inclusions in later erupted materials took place in the chamber because of degassing and depressurization of the magma during the Plinian phase of the climactic eruption.

The amount of Cl lost to the atmosphere during the climactic eruption may be estimated from the difference between Cl concentrations in melt inclusions and degassed Cleetwood vitrophyre. This value is ~1000 ppm. If all ~50 km³ of erupted magma degassed to this degree, ~10⁸ tons of Cl entered the atmosphere.

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