Methods

Sample preparation

In order to use the FTIR technique, the melt inclusions need to be quenched to glass. Olivine crystals were hand-picked under a binocular stereomicroscope. The crystal concentrate was put in refractive index oil (n = 1.67, close to that of olivine) in order to view the inclusions within the crystals. Crystals containing uncracked and fully enclosed inclusions were hand-picked under a binocular stereomicroscope and put in another oil-filled glass container to be described and photographed for documentation.

Crystals containing glass inclusions were mounted in acetone-soluble cement on microscope slides. Doubly polished crystal wafers (with inclusions exposed on both sides) were ground by hand using water-rinsed 600 grit paper and then polished with 6-μm and 1-μm diamond paste. Once the first side of the inclusion was polished the slide was warmed and the crystal was flipped. The grinding and polishing procedure was then repeated for the second side. The intersection of the inclusion on both sides needs to be parallel and well polished to ensure constant sample thickness. Uniform sample thickness was monitored during grinding and polishing by observing the distribution of interference colors in the crystal when viewed under crossed-polars. The doubly-polished crystal was then removed from the slide by dissolving the cement in acetone and cleaned with more acetone.

Infrared spectroscopy

A Thermo Nicolet Nexus 670 Fourier Transform Infrared (FTIR) spectrometer interfaced with a Continuum IR microscope was used to determine the concentrations of H_2O and CO_2 in the glass inclusions. The analyses were performed by placing a wafered olivine host crystal with an inclusion on an NaCl window. Then, depending on the size of the doubly intersected inclusion, the IR aperture was adjusted so it was totally contained within the inclusion and avoided the inclusion boundaries. Two individual spectra were taken on different areas of each inclusion.

Band assignments for dissolved H_2O and carbonate in basaltic glass are based on Dixon et al. (1995). Quantitative measurements of dissolved total H_2O, molecular H_2O, and carbonate (CO_3^{2-}) were obtained using Beer's Law:

$$C = \frac{MA}{\rho d \varepsilon}$$

where C is the concentration (weight fraction) of the absorbing species, M is the molecular weight of H_2O (18.02) or CO_2 (44.00), A is the absorbance intensity of the band of interest, ρ is room temperature density of the glass (calculated from a simple summation of partial molar volumes following Luhr, 2001), d is the thickness of the glass wafer, and ε is the molar absorption coefficient. The thickness of each inclusion was measured by mounting the edge of the doubly polished crystal wafer on the tip of a needle using crystal bond. The crystal wafer was then immersed into a cylindrical glass well filled with refractive index oil ($n = 1.67$). The crystal wafer could then be rotated and viewed parallel to its flat dimension under a microscope. Using a microscope with a calibrated eye piece, the thickness of the inclusion was measured with an accuracy of ± 1 to ± 5 μm depending on how close to the edge of the crystal the inclusion was.

Total dissolved H_2O was measured using the intensity of the band centered at 3550 cm^{-1}, which corresponds to the fundamental O-H stretching vibration. On a printed copy of the spectra the background was drawn as a smooth curve and graphically subtracted from the peak height to measure the absorbance intensity of the 3550 cm^{-1} band. The total dissolved water contents were calculated using a molar absorption coefficient of 63 ± 3 L/mol cm from Ihinger et al. (1994).

Dissolved carbonate was measured from the 1515 and 1430 cm^{-1} absorbance bands, which correspond to distorted asymmetric stretching of carbonate groups (Ihinger et al. 1994). Because the shape of the background in the region of the carbonate doublet is complex, it is necessary to subtract a carbonate-free reference spectrum to obtain a flat background (Dixon et al. 1995). We measured absorbance intensities of the 1515 and 1430 cm^{-1} bands using a peak-fitting program that fits the sample spectrum with a straight line, a spectrum for a CO_2-free basaltic glass, a pure 1630 cm^{-1} band for molecular H_2O, and a pure carbonate doublet (unpublished program by S. Newman). The molar absorption coefficient of carbonate in basaltic glass is compositionally dependent and was derived using the average composition of the inclusions and the linear equation reported in Dixon & Pan (1995). The dissolved carbonate content was calculated using a molar absorption coefficient of 370 L/mol cm.

Based on replicate analyses, precision (2σ) for total H_2O is <13% (relative) and <12% for CO_2. Accuracy for these techniques is estimated to be $\pm 10\%$ for total H_2O and $\pm 20\%$ for CO_2 (Dixon and Clague, 2001).

Electron microprobe analysis

The olivine-hosted melt inclusions were analyzed for major elements, S, F, and Cl using a Cameca SX-100 electron microprobe at the University of Oregon. An accelerating voltage of 15 kV, a 10 nA beam current, and a beam diameter of 10 μm were used along with a combination of glass and mineral standards. Between one and five separate spots were analyzed per inclusion depending on the inclusion size. The average and 1σ values for each inclusion are given in Appendix Table 1. A second run measured the composition of the olivine adjacent to the inclusions. These analyses were conducted on the JEOL JXA-8900R electron microprobe in the Laboratorio Universitario de Petrología at the Universidad Nacional Autónoma de México, using a focus beam, an accelerating voltage of 15 kV, and 20 nA beam current.

Correction for post-entrapment crystallization and Fe diffusive loss

Melt inclusion compositions were corrected for post-entrapment crystallization of olivine along the walls of the inclusion and Fe loss from the inclusion to the olivine host. Original microprobe and FTIR analytical values before any correction are given in Appendix Table 2. The correction for post-entrapment crystallization involved adding 0.1% increments of equilibrium olivine back into each melt inclusion until the inclusion composition was in equilibrium with the olivine host. A value of 0.3 was used for the Fe-Mg exchange coefficient ($K_D = (Mg/Fe^{2+})_{melt}/(Mg/Fe^{2+})_{olivine}$). Correction for Fe loss involved adding FeO back into each melt inclusion until the FeO^T of the inclusion was restored to the MgO vs. FeO^T trend of whole rock data (Witter et al., 2005) from Popocatépetl (see Danyushevsky et al., 2000). After correction for Fe loss, the calculated amounts of post-entrapment crystallization were 0.4 to 25.2 wt.%.

Volcanic gas compositions and fluxes

Mass ratios and fluxes of major gas components that have been measured for Popocatépetl are reported in Appendix Table 3.

Calculation of gas compositions in equilibrium with basaltic melts as a function of pressure

To construct Figure 3, we calculated the CO_2/SO_2 mass ratios of gases in equilibrium with basaltic melt as a function of pressure beneath Popocatépetl volcano using the vapor-melt partitioning model of Scaillet and Pichavant (2005). Input parameters for the calculation

are melt composition, temperature, pressure, dissolved H_2O and S contents, and oxygen fugacity. For composition, we used the average value for the melt inclusions reported in Table 1. We assumed a constant temperature of 1140 °C based on the average of the calculated melt inclusion temperatures in Table 1. We assumed that dissolved H_2O varied as a function of pressure according to a second order polynomial fit to the melt inclusion H_2O vs. pressure data, but we excluded from the regression the 3 inclusions shown in Fig. 2 that have low H_2O but relatively high CO_2. For the melt S contents, the melt inclusion data show evidence for only minor S loss by degassing until lower pressures (~150 MPa), as evidenced by relatively constant S/K_2O. This is similar to the conclusions of Spilliaert et al. (2006), who used melt inclusion data from Etna to show that degassing of S began at pressures below ~140 MPa. Thus, for simpicity, we assumed that the melts contained 2000 ppm S at pressures down to 150 MPa. Below that pressure, we varied S linearly with pressure such that S decreased to 700 ppm at 1 MPa pressure, based on the lower S contents of the melt inclusions trapped at ≤40 MPa. Although these simplifying assumptions about the behavior of S are a bit ad hoc, they are consistent with the melt inclusion S and pressure data, and small variations in the way that S varies with pressure will not substantially change the curves shown in Figure 3.

The oxygen fugacity of the basaltic endmember at Popocatépetl is estimated to be NNO+1 based on whole rock and mineral chemical data and thermodynamic modeling (Witter et al., 2005), and the uncertainty in this estimate is probably about ±0.5 log units in f_{O2}. Accordingly, we calculated gas compositions for a range of f_{O2} from NNO+0.5 to NNO+1.5. Because the f_{O2} has a strong effect on the mole fraction of SO_2 in the gas phase, the uncertainty in oxygen fugacity represents the largest uncertainty in our gas composition calculations. Thus the range in oxygen fugacities shown by the 3 curves in Figure 3 shows the uncertainty in our method.

Using these parameters, we varied the pressure and used the model of Scaillet and Pichavant (2005) to calculate the SO_2 fugacity in the gas phase and then converted that to SO_2 mole fractions using the Redlich-Kwong equation of state. Equilibrium thermodynamic calculations using standard state data for gas components show that over the range of temperature, pressure, H_2O content and oxygen fugacity, SO_2 is the dominant S species in the vapor phase, and thus we have ignored the contribution of H_2S to the total S contents of the vapor.

Using the H_2O+CO_2 solubility model of Papale et al. (2006), we computed the proportions of H_2O and CO_2 in the gas phase based on our melt inclusion data. The results

suggest that most inclusions were in equilibrium with vapor having 50 to 60 mol% CO_2, with an average of 56 mol% (this average again excludes one inclusion from Table 1 with low H_2O and high CO_2). Using this result together with the SO_2 mole fractions calculated as describe above, we renormalized the data such that the mole fractions of H_2O, CO_2, and SO_2 in the gas phase summed to 1.

To construct Figure 4, we used the methods (equations 1-4) described in Giggenbach (1997) based on Henry's law solubility constants, as follows. The effects of vapor exsolution on the concentration, c, of a magmatic volatile component, i, transferred to the vapor phase, v, or remaining in the melt, m, can be described in terms of the Henry's Law constant, $K_{i,T}$, in mg/kg bar, and the dimensionless mass/volume, Ostwald-type distribution coefficient, $Q_{i,T} = c_{i,v} / c_{i,m}$. The two are related through:

$$K_{i,T} = c_{i,m} / P_i = 10^6 MW_i / (\rho_m R T Q_{i,T})$$

Where $c_{i,m}$ is the concentration of volatile component i in the melt, P_i is the partial pressure of component i in the vapor phase, MW_i is the molecular weight of component i, ρ_m is the density of the melt, R is the gas constant (82.05 cm^3 bar/K mol), and T is the temperature. By use of mass balance and the assumptions that vapor-melt separation is a single-step, closed-system process and that the gases behave ideally, the total pressure, P_t, generated by the initial concentrations $c_{i,o}$ of the volatile components in the melt corresponds to:

$$P_t = \sum (c_{i,o} / (R_v Q_{i,T} + 1)\, K_{i,T})$$

Where R_v is the vapor/melt volume ratio. Because of the increasingly large non-ideal behavior of CO_2 with increasing pressure and the large contribution of CO_2 to the total pressure of the system, we accounted for the non-ideality of CO_2 using fugacity coefficients calculated with the Redlich-Kwong equation of state. For melt exsolution in a closed system (no loss of volatiles), R_v is related to the vesicularity, V_v, in %, through:

$$V_v = 100 R_v / (1 + R_v)$$

The fraction $x_{i,m}$ of the volatile component i remaining in the melt is given by:

$$x_{i,m} = c_{i,m} / c_{i,o} = 1 / (R_v Q_{i,T} + 1).$$

We used values of $K_{i,T}$ and $Q_{i,T}$ calculated with the model of Newman and Lowenstern (2002) for H_2O and CO_2, from experimental data of Webster et al. (1999) for Cl, and from experimental data of Jugo et al. (2005) for S.

REFERENCES

Danyushevsky, L. V., Della-Pasqua, F. N. & Sokolov, S. (2000). Re-equilibration of melt inclusions trapped by magnesian olivine phenocrysts from subduction-related magmas: petrological implications. Contributions to Mineralogy and Petrology 138, 68-83.

Dixon, J.E. and Clague, D.A., 2001. Volatiles in basaltic glasses from Loihi Seamount: evidence for a relatively dry plume source. Journal of Petrology, 42: 627-654.

Dixon, J.E. and Pan, V., 1995. Determination of the molar absortivity of dissolved carbonate in basanitic glass. American Mineralogist, 80: 1339-1342.

Dixon, J.E., Stolper, E.M. and Holloway, J.R., 1995. An experimental study of water and carbon dioxode solubilities in Mid-Ocean Ridge basaltic liquids. Part I: calibration and solubility models. Journal of Petrology, 36(6): 1607-1631.

Giggenbach, W. F., 1997, Chemical composition of volcanic gases. In: R. Scarpa and R. I. Tilling (Editors), Monitoring and Mitigation of Volcano Hazards. Springer-Verlag, Berlin, 221-255.

Ihinger, P.D., Hervig, R.V. and McMillan, P.F., 1994. Analytical methods for volatiles in glasses. In: M. Caroll (Editor), Volatiles in magmas. Review in Mineralogy. Mineralogical Society of America, Washington, DC, pp. 67-121.

Jugo, P. J., Luth, R. W. & Richards, J. P., 2005, An experimental study of the sulfur content in basaltic melts saturated with immiscible sulfide or sulfate liquids at 1300 degrees C and 1.0 GPa. Journal of Petrology 46, 783-798.

Luhr, J. F. Glass inclusions and melt volatile contents at Paricutin Volcano, Mexico. Contributions to Mineralogy and Petrology 142, 261-283 (2001).

Newman, S. & Lowenstern, J. B., 2002, VOLATILECALC: a silicate melt-H_2O-CO_2 solution model written in Visual Basic for Excel. Computers & Geosciences 28, 597-604.

Papale, P., Moretti, R., Barbato, D., 2006, The compositional dependence of the saturation surface of $H_2O + CO_2$ fluids in silicate melts. Chemical Geology 229, 78-95.

Scaillet, B. & Pichavant, M., 2005, A model of sulphur solubility for hydrous mafic melts; application to the determination of magmatic fluid compositions of Italian volcanoes. Annals of Geophysics 48, 671-698.

Spilliaert, N., Metrich, N., Allard,P., 2006, P. S-Cl-F degassing pattern of water-rich alkali basalt; modelling and relationship with eruption styles on Mount Etna Volcano. Earth and Planetary Science Letters 248, 772-786.

Webster, J. D., Kinzler, R. J. & Mathez, E. A., 1999, Chloride and water solubility in basalt and andesite melts and implications for magmatic degassing. Geochimica et Cosmochimica Acta 63, 729-738.

Witter, J. B., Kress, V. C. & Newhall, C. G., 2005, Volcan Popocatepetl, Mexico: Petrology, magma mixing, and immediate sources of volatiles for the 1994-present eruption. Journal of Petrology 46, 2237-2366.

Table DR1.

	n		SiO$_2$	Al$_2$O$_3$	FeO^T	MgO	CaO	Na$_2$O	K$_2$O	TiO$_2$	MnO	P$_2$O$_5$	F	S	Cl	TOTAL
M28-2 gr5	3	Average	51.92	18.11	4.81	4.52	8.76	4.47	1.02	1.24	0.08	0.25	0.03	0.19	0.09	95.48
		1 Std. Dev.	0.61	0.12	0.10	0.06	0.47	0.07	0.04	0.09	0.06	0.00	0.03	0.01	0.00	
M28-2 gr6	3	Average	51.48	19.10	3.86	4.23	9.07	5.31	1.10	1.43	0.08	0.31	0.12	0.22	0.10	96.41
		1 Std. Dev.	0.25	0.19	0.11	0.09	0.36	0.12	0.01	0.02	0.01	0.02	0.15	0.01	0.01	
M28-2 gr7	3	Average	50.96	20.03	3.69	3.99	9.30	5.20	1.13	1.32	0.07	0.28	0.33	0.20	0.09	96.60
		1 Std. Dev.	0.47	0.17	0.12	0.10	0.41	0.36	0.02	0.03	0.04	0.00	0.37	0.00	0.00	
M29-6	1		51.71	18.63	3.79	3.36	8.69	5.72	1.06	1.45	0.07	0.30	0.06	0.23	0.11	95.20
M48-5 gr1-2	3	Average	52.43	21.91	4.04	4.77	5.58	6.52	1.48	1.22	0.10	0.32	0.09	0.10	0.12	98.69
		1 Std. Dev.	0.21	0.11	0.02	0.03	0.58	0.07	0.05	0.06	0.02	0.02	0.06	0.00	0.00	
M48-5 gr2-1	1		52.46	18.95	3.91	2.74	9.03	5.53	1.20	1.38	0.05	0.26	0.20	0.20	0.09	96.02
M48-5 gr3old	3	Average	56.13	23.23	2.32	2.10	5.04	9.88	1.87	0.59	0.06	0.39	0.05	0.06	0.15	101.86
		1 Std. Dev.	0.29	0.22	0.01	0.01	0.50	0.21	0.02	0.02	0.04	0.01	0.05	0.00	0.01	
M48-5 gr5	5	Average	52.45	18.01	4.38	3.96	9.41	5.20	1.10	1.36	0.06	0.30	0.07	0.18	0.08	96.56
		1 Std. Dev.	0.35	0.29	0.10	0.23	0.22	0.29	0.03	0.08	0.03	0.03	0.06	0.01	0.00	
M53-51 gr1-1	4	Average	52.18	18.66	4.41	4.18	9.10	5.31	1.07	1.35	0.09	0.32	0.09	0.21	0.08	97.06
		1 Std. Dev.	0.48	0.17	0.07	0.12	0.22	0.29	0.03	0.06	0.02	0.04	0.01	0.00	0.00	

Table DR2

	M28-2 gr5	M28-2 gr6	M28-2 gr7	M29-6	M48-5 gr1-2	M48-5 gr2-1	M48-5 gr3old	M48-5 gr5	M53-51 gr1-1
SiO_2	51.9	51.5	51.0	51.7	52.4	52.5	56.1	52.4	52.2
Al_2O_3	18.1	19.1	20.0	18.6	21.9	19.0	23.2	18.0	18.7
FeO^T	4.81	3.86	3.69	3.79	4.04	3.91	2.32	4.38	4.41
MgO	4.52	4.23	3.99	3.36	4.77	2.74	2.10	3.96	4.18
CaO	8.76	9.07	9.30	8.69	5.58	9.03	5.04	9.41	9.10
Na_2O	4.47	5.31	5.20	5.72	6.52	5.53	9.88	5.20	5.31
K_2O	1.02	1.10	1.13	1.06	1.48	1.20	1.87	1.10	1.07
TiO_2	1.24	1.43	1.32	1.45	1.22	1.38	0.59	1.36	1.35
MnO	0.08	0.08	0.07	0.07	0.10	0.05	0.06	0.06	0.09
P_2O_5	0.25	0.31	0.28	0.30	0.32	0.26	0.39	0.30	0.32
F	0.03	0.12	0.33	0.06	0.09	0.20	0.05	0.07	0.09
S	0.19	0.22	0.20	0.23	0.10	0.20	0.06	0.18	0.21
Cl	0.09	0.10	0.09	0.11	0.12	0.09	0.15	0.08	0.08
H_2O	5.3	4.9	2.8	3.1	0.4	2.6	0.5	5.1	3.7
CO_2	2413	2128	1155	959	bdl	950	286	1708	1290
TOTAL	100.77	101.11	99.29	98.10	99.04	98.51	102.25	101.53	100.71

Table DR3

	SO2 (t/d)	CO2 (t/d)	CO2/SO2	HCl/SO2	SO2 emmission (Mt)	Ratio method	Reference
May 15, 1995	1300	≤10000	4-8			GASPEC	Goff et al., 2001
June 1995			1-2			LICOR	Gerlach et al., 1997
April 23, 1997	7200	33000	4.6			LICOR	Delgado-Granados unpublished data
June 19 1997	6150	37000	6			LICOR	Delgado-Granados unpublished data
1995 to 1998				0.12*		*	Goff et al., 2001
1995 to 1997					9 Mt	COSPEC	Delgado-Granados et al., 2001
1998	1350	190000	≤140			FTIR	Goff et al., 2001

* Average from 1995 to 1998 using different ratio methods (alkaline traps, leachate and FTIR)