Comparison of microanalytical methods for estimating H₂O contents of silicic volcanic glasses

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Abstract

Three methods of estimating H₂O contents of geologic glasses are compared: (1) ion microprobe analysis (secondary ion mass spectrometry), (2) Fourier-transform infrared spectroscopy (FTIR), and (3) electron microprobe analysis using the Na decay-curve method. Each analytical method has its own advantages under certain conditions, depending on the relative importance of analytical accuracy, precision, sensitivity, spatial resolution, and convenience, and each is capable of providing reasonably accurate estimates of the H₂O, or total volatile, content of geologic glasses. The accuracy of ion microprobe analyses depends critically on the availability of well-characterized hydrous standard glasses. Precision is often better than 0.2 wt% (1σ). The method provides good spatial resolution (~ 15 μm) and the capability to determine simultaneously the abundance of other volatile species of interest (e.g., F, B). FTIR spectroscopy provides excellent analytical sensitivity (~ 10 ppm), accuracy and precision (<0.1 wt%), and the capability to determine the abundance of H₂O and CO₂ species (H₂O, OH⁻, CO₂, CO₃²⁻) in analyzed glasses, although the spatial resolution (>25–35 μm) is not as good as that of the ion microprobe. The main advantages of the estimation of H₂O contents of hydrous glasses using the electron microprobe are excellent spatial resolution (~ 10 μm) and analytical convenience. The disadvantages are that accuracy and precision (>0.5 wt%) are not as good as those associated with the other methods, but, for certain applications, these uncertainties may be acceptable for the estimation of H₂O contents of H₂O-rich (>1 wt%) samples.

Introduction

The importance of volatile constituents (H₂O, CO₂, S, Cl) in magmatic processes is now well established. For example, it is the exsolution and expansion of volatile species, especially H₂O, that provides the mechanical energy of explosive volcanic eruptions. H₂O pressure also has an effect on crystal-melt phase relations and plays a role in determining the order of crystallization of minerals from silicate melts (e.g., Rutherford and Devine, 1988, 1995). Furthermore, the release of gaseous S species to the atmosphere by volcanic eruptions has been

shown to have a potential effect on global climate (Devine et al., 1984; Bluth et al., 1992).

One way of estimating the preeruption volatile content of natural silicate melts is to analyze glassy melt inclusions that were trapped by growing phenocrysts (e.g., Anderson, 1973). The presumption is that such glasses generally retain the volatile components dissolved in the silicate melt at the time of trapping. This assumption was called into question by Qin et al. (1992), who suggested that melt inclusions may reequilibrate with melt external to the host crystal after melt inclusion entrapment. The calculated time required for reequilibration, however, depends strongly on the diffusion rates of volatile species like H₂O in host crystal lattices, which are poorly known (see review in Qin et al., 1992). Tait (1992) calculated that the dilational stresses experienced by melt inclusions during eruption-related decompression could be sufficient to produce dilational cracks in host minerals that might allow some of the volatile content to be lost to the

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atmosphere, depending on the timing of fracture formation. In some cases it has also become apparent that significant quantities of some volatile species may be contained in phases other than the silicate melt prior to eruption (e.g., in a separate vapor phase or a volatile-bearing mineral such as anhydrite). Analyses of glassy melt inclusions in these cases provide only minimum estimates the of preeruption volatile content of the magma. In spite of these caveats, melt inclusion analysis has been demonstrated to be a useful method of estimating preeruption volatile contents of H_2O-rich magmas. Even if melt inclusions have reequilibrated after trapping, the usual goal of melt inclusion analysis is to infer conditions (i.e., P, T, P_{H_2O}, etc.) in magma chambers immediately prior to eruption.

In the course of an experimental petrological study of the 1991 eruption of Mount Pinatubo (Rutherford and Devine, 1991, 1995), both electron microprobe and ion microprobe analyses of Pinatubo melt inclusions were obtained. It became apparent that electron microprobe analyses of volatiles by difference in plagioclase melt inclusions (nearly entirely H_2O, as determined from FTIR analysis of the inclusions) were systematically higher (~6.4 wt%) than H_2O contents estimated from ion microprobe analyses (~5.2 wt%). One rationale for this study was to account for this discrepancy.

The typically small size of melt inclusions (~30 μm) requires that microanalytical techniques be used to estimate their volatile contents. This paper summarizes the results of tests of microanalytical methods for the estimation of H_2O contents of SiO_2-rich geologic glasses that make use of ion microprobe (secondary ion mass spectrometry), Fourier-transform infrared spectroscopy (FTIR), and electron microprobe methods. The focus is limited to SiO_2-rich glasses because the extinction coefficients that are required for quantitative FTIR analyses are well determined only for these compositions (Newman et al., 1986). Such glasses are also of great petrologic interest because the composition of the melt phase in many magmas that erupt explosively (e.g., Mount Saint Helens, 1980 eruption; Mount Pinatubo, 1991 eruption) is SiO_2-rich rhyolite.

ANALYTICAL AND EXPERIMENTAL METHODS

Choice of a microanalytical method for the estimation of H_2O contents of geologic glasses requires evaluation of the relative importance of analytical accuracy, precision, sensitivity, spatial resolution, convenience, and availability. For example, accuracy is of paramount importance if estimation of preeruption H_2O contents of volcanic glasses in explosive eruption products is the analytical objective. On the other hand, analytical sensitivity may be an additional important factor if the objective is to determine the H_2O content of H_2O-poor samples such as midocean ridge basalts. Finally, analytical convenience is of great importance in the analysis of the numerous charges that are typically required to construct experimentally determined phase diagrams for samples of in-

terest (e.g., Mount Saint Helens and Mount Pinatubo dacites: Rutherford and Devine, 1988, 1995).

A brief description of ion microprobe, FTIR, and electron microprobe methods for determining H_2O contents of geologic glasses used in this study is given below, followed by the rationale for the study. Results and discussion of test analyses of glassy standard reference materials and other H_2O-bearing glasses prepared for this study are presented in the following section.

Ion microprobe

The H_2O contents of several glass samples used in this study were determined using the Cameca IMS-3f ion microprobe at Woods Hole Oceanographic Institution. The glasses were mounted in a single Al ring mount 1 in. in diameter, which was polished, thoroughly cleaned, and sputter coated with 500 Å of Au. Analytical procedures were essentially similar to those described by Sisson and Layne (1993). H_2O contents of unknowns were quantified by comparison of the normalized ratio $1/R = (^1H^+/^{30}Si^+)\cdot SiO_2$ with a working calibration line constructed from analyses of standard glasses. The accuracy of the method depends on the accuracy of the estimates of H_2O and SiO_2 contents in standard glass. The sensitivity of the ion microprobe for H_2O is about 0.2 wt%, as is the analytical precision.

The main advantages of ion microprobe analysis for the determination of H_2O in SiO_2-rich glasses relative to other methods are (1) that the ion beam provides good spatial resolution (~15 μm), making it possible to analyze typically small melt inclusions (~30 μm), and (2) that the precision of the method should be better than 5% (relative) for samples containing >1 wt% H_2O, on the basis of replicate analyses of standard reference materials, and (3) that abundances of other elements of interest (e.g., F, B) may be determined simultaneously during H_2O spot analysis. The main disadvantages of the method are (1) that access to an ion microprobe may not be readily available to some workers, (2) that H_2O-bearing standard reference materials must be included along with unknown glasses in every sample mount to provide the most accurate results, and (3) that samples must be coated prior to analysis with an optically opaque layer of Au, requiring that sample mounts be mapped in some way (e.g., by photography) prior to analysis. Although the Au-coated samples must be observed in oblique reflected light for positioning during analysis, melt inclusions in phenocrysts are often readily visible because of polishing relief. Fine positioning, however, is achieved using the mass imaging capability of the ion microprobe to locate the boundaries of the inclusion. Mass imaging also readily reveals mineral inclusions and cracks or imperfections in the glass and host mineral.

FTIR

The application of FTIR spectroscopic methods to the analysis of H_2O and CO_2 in volcanic glasses was developed by E. M. Stolper and coworkers at the California

Institute of Technology. FTIR spectroscopic theory and practice have been thoroughly described in papers by Newman et al. (1986) and Silver et al. (1990), and so will not be repeated here. Fogel (1989) adapted these methods for use in the Department of Chemistry at Brown University.

The main advantages of FTIR spectroscopy are (1) excellent analytical sensitivity for H_2O ($\sim$10 ppm), accuracy and precision ($<$0.1 wt%), and (2) the ability to determine conveniently CO_2 as well as H_2O species (CO_2, CO_3^{2-}, H_2O, OH^-) in sample glasses. The main disadvantages of the FTIR method are (1) that sample preparation for melt inclusion analysis, which requires accurate measurement of the thickness of doubly polished thin sections of very small samples (say a crystal $\sim$350 μm in diameter that must be polished to less than the $<$100-μm thickness of a target melt inclusion), can be difficult due to sample fragility, (2) that the limited spatial resolution of the instrument ($>$25–35 μm; see below) requires that larger than normal melt inclusions ($>$30 μm) be analyzed, raising questions about how representative such melt inclusions are of more typical inclusions, and (3) that values of extinction coefficients for hydrous species (H_2O, OH^-) are functions of the bulk composition of the glass (e.g., Silver et al., 1990; Pandya et al., 1992).

Transmission FTIR spectra of the glass samples used in this study were obtained in the near-infrared (near-IR) and mid-infrared (mid-IR) regions using a Bruker A590 IR microscope attached to a Bruker IFS 113v FTIR spectrometer. The A590 microscope is equipped with a MCT detector cooled with liquid N_2. The mid-IR spectra were obtained using a SiC globar source and a Ge/KBr beam splitter. A W lamp and a quartz beam splitter were used in the near-IR. For the acquisition of all spectra, the optics bench was kept under vacuum and the microscope was purged with dry N_2 gas to minimize interference from atmospheric H_2O vapor and carbon dioxide. The spectral resolution of all measurements was $\sim$2 cm^{-1}. The number of scans collected for both the sample and reference spectra was 256. A correlation function was used to reject any bad scans having shifts of one point or greater in the centerburst position, although in general no bad scans were detected. A Happ-Genzel apodization function was used prior to Fourier transformation of the interferogram to the frequency-domain spectrum.

Because the extinction coefficients of the absorption bands in the mid-IR due to vibrational modes of molecular H_2O and OH^- are up to two orders of magnitude greater than those in the near-IR, it is generally necessary to measure spectra in these two different regions of the IR spectrum on polished glass plates of different thicknesses. Although the FTIR method gives quantitative results for even very small absorbance values, an attempt was made to polish glass plates to thicknesses that yielded absorbance values between 0.1 and 1.0 for the bands of interest. Mid-IR bands were used for samples with low H_2O contents, and near-IR bands for samples with high H_2O contents. Sample thicknesses were measured with a

digital dial indicator (543 Series Digimatic Indicator, Mitutoyo Manufacturing Company), which yields data to $\pm$1 μm, according to measurements on thickness standards.

Samples were placed on a brass sample holder over an aperture 300 μm in diameter. Selection of the 1.05-mm aperture on the A590 microscope then produced a 70-μm effective beam diameter for analysis. Although this beam diameter is large compared with the dimensions of the average melt inclusion ($\sim$30 μm), it was determined that smaller beam diameters produced unsatisfactory results unless an unacceptably large number of scans was collected. More modern instruments are capable of producing acceptable results using an aperture of 25–35 μm (Y. Zhang, 1994 personal communication). Defect-free regions of the analyzed samples were selected using the visible region optics of the microscope, and the focal point was moved through the entire sample thickness to ensure that clear optical paths were selected. Through means of a flip mirror, the FTIR optics were then focused onto the selected sample region.

Spectra were collected for at least three spatial regions for most samples. In order to minimize adverse effects of instrumental drift or changes in alignment, reference spectra were collected immediately prior to collection of each sample spectrum. All spectral data were processed by a Bruker Aspect 3000 computer. Peak heights for the spectral bands of interest were measured graphically relative to tangentially drawn linear or curved base lines, as appropriate (see Newman et al., 1986). Concentrations of molecular and OH-related H_2O were then calculated using Beer's Law and the extinction coefficients reported by Newman et al. (1986). More specifically, the 1630- and 3570-cm^{-1} absorption bands were used to determine molecular and OH-related H_2O concentrations in glasses with low H_2O content, whereas the 5200- and 4500-cm^{-1} absorption bands were used for glasses with higher H_2O content. The average standard deviation (1σ) of estimated total H_2O concentrations in samples we studied was 0.05 wt%.

Electron microprobe

The main advantages of electron microprobe analysis are (1) excellent spatial resolution ($\sim$10 μm) and (2) analytical availability and convenience. The main disadvantages are (1) that the method does not directly determine H_2O contents (total volatiles, mostly H_2O, are estimated by difference; i.e., total volatiles equal 100 wt% minus the measured major element analytical total), and (2) that analytical errors may be large ($>$0.5 wt%; poor precision) or systematic (poor accuracy). It is generally not feasible to estimate accurately the H_2O contents of hydrous glasses containing less than $\sim$1 wt% H_2O, but many geologic glasses of interest contain higher H_2O contents.

Errors in the estimation of total volatile content by difference reflect cumulative errors in determining abundances of the nine or more elements that are analyzed

TABLE 1. Electron microprobe analyses of geologic glasses used in this study

Sample	KN18 accepted	KN18 uncorr.	VNM50-15 corr.	PCD corr.	IF35-1 corr.	M3N corr.	M6N corr.
SiO_2 (wt%)	74.60	74.74(31)	76.60(27)	76.40(16)	74.39(4)	71.38(33)	69.47(48)
TiO_2	0.18	0.16(4)	0.08(4)	0.07(6)	0.03(3)	0.26(2)	0.30(4)
Al_2O_3	10.53	10.75(15)	12.32(10)	12.44(12)	13.65(8)	13.05(15)	12.84(12)
FeO*	3.45	3.52(14)	1.05(7)	1.02(5)	0.56(3)	1.56(5)	1.48(5)
MgO	0.01	0.01(1)	0.04(2)	0.02(2)	0.04(2)	0.29(2)	0.25(1)
CaO	0.15	0.16(12)	0.37(5)	0.53(4)	0.47(5)	1.19(5)	1.19(5)
Na_2O	5.68	5.45(26)	4.41(26)	4.21(20)	4.25(29)	4.06(16)	4.05(13)
K_2O	4.39	4.33(10)	4.64(14)	4.68(15)	4.21(10)	4.11(5)	4.02(13)
MnO	0.06	0.06(5)	0.05(5)	0.03(2)	0.13(4)	0.02(3)	0.05(5)
Total	99.05	99.18	99.56	99.41	97.72	95.92	93.65
No. analyses	—	44	8	3	3	6	3
H_2O, old**	0.10	—	—	0.15	1.05	2.94	5.10
H_2O, new†	—	—	0.16	0.17(8)	1.36(9)	3.95(13)	6.38(19)
No. analyses	—	—	1	1	2	2	2
Vols. by diff.‡	—	—	0.44	0.59	2.28	4.08	6.35
Cl (ppm)§	3700	—	1209(100)	671(124)	117(26)	804(35)	946(45)
F (ppm)	6400	—	859(185)	587(115)	822(110)	561(207)	616(174)

Note: numbers in parentheses are estimated standard deviations.
  * All Fe reported as FeO.
  ** Previously accepted H_2O analyses (weight percent; see text); samples KN18 and KE12 (see Table 3) were collected by D.K. Bailey, analyzed by S. Malik and D.A. Bungard, and kindly provided by H. Sigurdsson.
  † New H_2O analyses; FTIR analysis for VNM50-15 and ion microprobe analyses for PCD, IF35-1, M3N, and M6N (see text). Error propagation (1σ) estimated using the methods of York (1966) and Bevington (1969).
  ‡ Total volatile content estimated by the difference method (see text).
  § Cl and F contents estimated from electron microprobe analyses (15-kv accelerating voltage; 40-nA beam current; beam 20 μm in diameter); these values are not included in the analytical total cited above, and thus should be subtracted from estimated volatiles by difference values to provide a better estimate of H_2O content by difference.

directly. The greatest errors are usually associated with the estimation of Na abundances because of the phenomenon of alkali migration or Na loss during electron microprobe analysis of SiO_2-rich glasses (Na is driven away from the excited volume from which X-rays are generated). Nielsen and Sigurdsson (1981) showed, however, that errors in Na analyses could be greatly reduced using the decay-curve method.

The decay-curve method involves measurement of Na X-ray count rates for several consecutive counting intervals following initial exposure of the glass specimen to the electron beam (e.g., five 2-s counting intervals). The beam remains blanked until the beginning of the first counting interval. Extrapolation of the exponential decay curve so obtained to the time-zero intercept provides estimates of the true Na count rate and abundance. Experience in the analysis of hydrous, SiO_2-rich glasses has indicated that other methods that have been used to counteract alkali migration (specifically, using a broadly defocused beam or movement of the sample under the beam) do not adequately account for Na loss in hydrous, SiO_2-rich glasses. Na loss is generally not observed in basaltic glasses but may be observed in glasses of intermediate composition, depending especially on alkali content. Although a Na-loss decay-curve analytical routine is not presently available directly from electron microprobe manufacturers, it is possible to modify existing motor control software for some microprobe models (e.g., the Cameca Camebax model used in this laboratory) in order to accomplish this task.

An additional problem related to Na loss is that other elements, especially Si and Al, appear to increase or "grow in" as Na count rates decrease. In principle, it should be possible to monitor the grow-in of other elements using methods analogous to the Na decay-curve method. In practice, however, there are generally fewer spectrometers than the number of elements to be analyzed, so some elements must be analyzed after the first 10 s of analysis has elapsed; by this time, the effects of Na loss have already been manifested. The most convenient method of dealing with the grow-in of elements in electron microprobe analysis is to obtain test analyses of (SiO_2-rich) glass standard reference materials. The test analyses provide an estimate of the extent to which count rates for elements other than Na have grown in, and allow appropriate correction factors to be calculated. For example, test analyses of comenditic obsidian glass KN18 (Table 1) have revealed that estimates of the Si and Al contents of anhydrous SiO_2-rich glasses may be high by 0.3 wt% or more, compared with accepted values under normal operating conditions (15-kV accelerating voltage; 10-nA beam current; 10-μm beam diameter; elements analyzed in the order Na, Si, Al). Subsequent analyses of unknown glasses may be corrected accordingly (correction factor = accepted value divided by the analytical average for the standard reference glasses), and this is the practice that has been adopted in the laboratory at Brown University.

It is possible that systematic error may be introduced as a result of this method of accounting for the grow-in of Si, Al, and other elements. Experience has shown that the decay of Na count rates during electron microprobe analysis is more rapid and more extreme for hydrous SiO_2-rich glasses than it is for anhydrous glasses of the same major-element composition. The grow-in of elements other than Na may also be more rapid and extreme in the case of hydrous glasses. To some extent this effect

depends on operating conditions: the more focused the beam and the higher the beam current, the more extreme the effect. Therefore, if correction factors are developed on the basis of test analyses of anhydrous glasses such as KN18, there may be a tendency toward systematic errors unless operating conditions are fortuitously chosen to minimize differences in the responses of standard and unknown glasses to electron bombardment. If it is not possible to monitor directly the grow-in of elements such as Si and Al, however, the correction procedure outlined above seems preferable to the use of uncorrected analyses.

An additional refinement of the proposed method of analysis would be to determine directly the O contents of hydrous glasses, which account for the O associated with H_2O species (H_2O, OH^-) and also provide a check on the quality of the analysis (i.e., are analytical totals near 100 wt%?: Nash, 1992). As a practical matter, however, this requires that one spectrometer be dedicated to light-element analysis, and this is not always possible.

In order to minimize potential analytical error due to instrumental drift, it is highly advisable to obtain test analyses of standard reference glasses prior to, and following, analysis of unknown glasses.

It is often desirable to make grain mounts for separates of host minerals of interest so that a statistically sufficient number of melt inclusions suitable for analysis can be obtained. If the host mineral is plagioclase, magnetic separation may be conveniently used to produce clean feldspar separates from crushed tephra-fall samples (size fraction of 250–500 μm). As indicated above, stress patterns may be established in the vicinity of melt inclusions during eruption-related tephra decompression and cooling, which result in local microfracturing of the host mineral. This may potentially result in some leakage of volatiles from melt inclusions prior to eruption-related melt quenching (Tait, 1992). Such microfractures are not necessarily visible in normally prepared thin sections of mineral separates. This problem may be overcome, however, by immersing mineral separates in fluoboric acid (HBF_4) for several hours prior to mounting. The acid etches the microfractures so that they are readily visible; thus, melt inclusions intersected by microfractures may be avoided during analysis.

Experimental methods

A suite of hydrous SiO_2-rich glasses was produced for this study using standard hydrothermal experimental techniques and TZM and Rene pressure vessels (e.g., Rutherford and Devine, 1995). The aim was to produce glasses whose H_2O contents would span the geologically interesting range (0 to ~6 wt%). The starting material was a sample of Los Possos (New Mexico) rhyolitic obsidian glass (sample number VNM50-15; Table 1). H_2O was dissolved in the starting material by subjecting charges to H_2O vapor-excess conditions of P_{H_2O} (205–2200 bars) and T (950 °C) that were sufficient to produce the desired H_2O content ($f_{O_2} \approx$ NNO + 1 log unit). Initially, we attempted to use solid cores of the obsidian starting material ~0.3 cm in diameter in order to minimize vapor-filled bubble formation in the experimental glasses (Fogel, 1989). FTIR analyses of experimental charges produced in this manner revealed, however, that H_2O did not diffuse uniformly into the sample cores within a reasonable time interval (<1 week: Zhang et al., 1991). The starting material was therefore powdered for subsequent experiments. This produced uniform H_2O contents in the experimental glasses but also resulted in formation of some vapor-filled bubbles within the charges. The presence of bubbles in these experimental samples necessitated the use of the microscope attachment for FTIR analyses of the glasses, care being taken to ensure that the light path chosen for the analyses (~70-μm diameter) was bubble free.

POTENTIAL SOURCES OF ANALYTICAL ERROR

Because the estimation of volatile content by difference from electron microprobe analyses is an indirect method, it was decided that the investigation of sources of error should begin with electron microprobe analysis. One potential source of error that was investigated was the possibility that the correction procedure applied to raw electron microprobe data (the standard ZAF program supplied with the Cameca Camebax instrument) did not do an adequate job on hydrous SiO_2-rich glasses (ZAF refers to atomic number, absorption, and fluorescence). The reasoning was that the correction procedure might not adequately account for the absorption of X-rays by O atoms associated with dissolved H_2O species (H_2O, OH^-) in the analyzed glasses. In order to test this hypothesis, raw microprobe data were reduced using three correction procedures: (1) the empirical correction procedure of Bence and Albee (1968) and Albee and Ray (1970), (2) the ZAF correction procedure alluded to above, and (3) the $\phi(\rho,Z)$ correction procedure (Pouchou and Pichoir, 1991) supplied by Cameca Instruments with its latest software packages. In short, the three data reduction procedures produced essentially identical results and did not account for the magnitude of the discrepancy between electron microprobe and ion microprobe estimates of the H_2O content of Pinatubo melt inclusions.

Another possible source of error in electron microprobe analysis that was investigated was sample conductivity. The reasoning was that either the small size of the mineral fragments used to make grain mounts or the typically small size of the melt inclusions themselves (≤ 30 μm) might result in poor conduction of electrons away from the incident electron beam and consequently cause surface charging of the sample. This hypothesis was tested by mounting shards of glass standard reference materials of four size ranges (<30, 125–250, 250–500, and 500–1000 μm) in both normal epoxy and Ag-impregnated epoxy. Test analyses revealed that essentially identical results were obtained regardless of grain size or mounting medium.

In summary, investigation of possible sources of error in electron microprobe analysis did not reveal the cause

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TABLE 2. Electron microprobe analyses of H_2O-bearing glasses produced for this study

Sample	VNM50-15*	495	508	494	498	510
SiO_2 (wt%)	76.60(27)	75.62(33)	75.01(24)	73.72(22)	73.75(26)	71.82(32)
TiO_2	0.08(4)	0.10(5)	0.09(4)	0.11(4)	0.09(2)	0.10(5)
Al_2O_3	12.32(10)	12.22(14)	11.96(16)	11.79(13)	11.78(12)	11.62(15)
FeO**	1.05(7)	0.95(9)	0.93(10)	1.00(4)	0.65(16)	0.78(10)
MgO	0.04(2)	0.04(1)	0.04(2)	0.04(2)	0.04(2)	0.04(2)
CaO	0.37(5)	0.35(4)	0.34(5)	0.39(3)	0.33(6)	0.32(3)
Na_2O	4.41(26)	4.32(25)	4.19(22)	4.21(16)	4.31(13)	4.18(24)
K_2O	4.64(14)	4.51(10)	4.41(7)	4.38(11)	4.46(15)	4.17(11)
MnO	0.05(5)	0.06(4)	0.06(5)	0.06(3)	0.03(3)	0.06(4)
Total	99.56	98.17	97.03	95.70	95.44	93.09
No. analyses	8	12	8	6	6	10
Vols. by diff.†	0.44	1.83	2.97	4.30	4.56	6.91
H_2O by FTIR‡	0.16	1.42(3)	2.58(2)	4.09(4)	4.72(10)	6.23(9)
No. analyses	1	3	3	2	5	4
PH_2O (bars)§	—	205	500	1000	2000	2200

Note: numbers in parentheses are estimated standard deviations. Analyses are corrected.
* VNM50-15 was the starting material for the hydrothermal experiments.
** All Fe reported as FeO.
† Total volatile content estimated by the difference method (see text); these values are equal to 100 wt% minus the analytical total in the appropriate column and are not best-fit values derived from the regression shown in Fig. 3.
‡ H_2O content of experimental glasses estimated by FTIR spectroscopy.
§ H_2O pressure at which experimental glasses were produced (950 °C).

of the discrepancy between electron microprobe and ion microprobe estimates of the H_2O content of Pinatubo melt inclusions.

The next possibility that was investigated was that there were systematic errors in the ion microprobe analyses. Specifically, it was decided to investigate the possibility that the H_2O contents of the standard reference materials used to construct ion microprobe calibration curves were systematically underestimated. Natural (PCD) and synthetic (M3N, M6N) glass standards were originally provided by H. R. Westrich to G. D. Layne, with H_2O contents determined by Karl-Fischer titration (Westrich, 1987). An additional natural rhyolite glass (IF35-1) was provided by S. R. Hart (H_2O analysis by gas chromatography). In order to investigate the possibility that the H_2O contents of these glasses were not accurately determined, an attempt was made to obtain FTIR analyses of the ion microprobe H_2O standards. Two problems interfered with this approach. The first was that the two natural ion microprobe standards (PCD and IF35-1; Table 1) contained small, visible oxide and other inclusions, which made it difficult to choose inclusion-free light paths for analysis. The second problem was that the two synthetic ion microprobe H_2O standards (M3N and M6N; Table 1), though free of macroscopic inclusions, produced anomalous spectra in the near-infrared region that interfered with background subtraction procedures. It is possible that the anomalous spectra are produced by scattering due to the presence of cryptocrystalline inclusions in the glasses, but this conjecture has not been tested. (One qualitative difference between these two ion microprobe standard glasses and the H_2O-bearing glasses produced for this study is that the former are brown and the latter are gray.)

A suite of H_2O-bearing glasses was produced for use as new ion microprobe standards. The H_2O contents of the new ion microprobe standards were determined by FTIR, and they were used to analyze the old ion microprobe standard glasses.

RESULTS AND DISCUSSION

Estimated H_2O contents of the new H_2O-bearing standard glasses are presented in Table 2. The same glass plates that were used to obtain the FTIR analyses were placed in an ion microprobe mount along with samples of the old ion microprobe H_2O standards. The ion microprobe calibration curve constructed from multiple analyses of the new standard glasses is illustrated in Figure 1. The ratio $1/R$ in the figure is the product of the mass ratio $^1H^+/^{30}Si^+$ determined by ion microprobe and the SiO_2 content of the glass determined by electron microprobe.

The new calibration curve was used to determine the H_2O contents of the old ion microprobe standards. The revised estimated H_2O contents are also listed in Table 1. The revised estimated H_2O contents are compared with the previous estimates in Figure 2. The figure demonstrates that the old estimated H_2O contents of these glasses are systematically low by about 25% (relative) compared with the new estimates. It is concluded that this observed discrepancy accounts for the aforementioned differences in estimates of the H_2O contents of Pinatubo melt inclusions obtained by ion microprobe and electron microprobe analytical methods, respectively. Increasing the old ion microprobe estimates by ~25% brings the two estimates of the H_2O content of Pinatubo melt inclusions into general agreement. For plagioclase melt inclusions, the corrected ion microprobe results now yield estimated H_2O contents of 6.4–6.6 wt% ($n = 2$), which compares well with estimated volatiles by difference of 6.4 ± 0.5 wt% ($n = 15$).
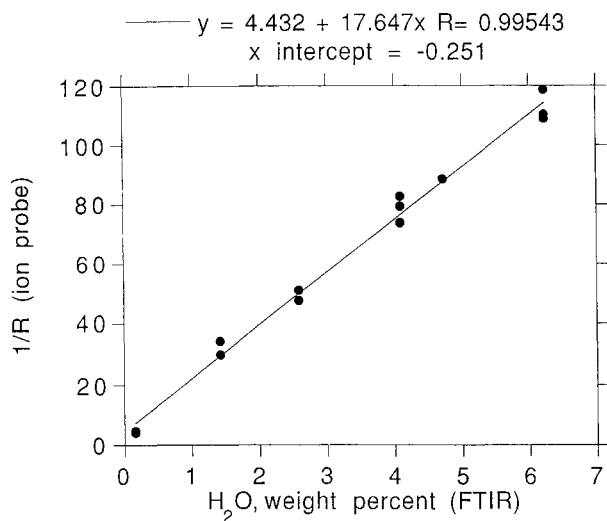
The new H_2O-bearing standard glasses were analyzed

y = 4.432 + 17.647x R= 0.99543
x intercept = -0.251

Fig. 1. Ratio $1/R = (^1H^+/^{30}Si^+) \cdot SiO_2$ vs. the FTIR-determined H_2O content (weight percent) of hydrous glasses produced for this study. The mass ratio $^1H^+/^{30}Si^+$ is determined by ion microprobe, and the SiO_2 content of the glass is determined by electron microprobe.

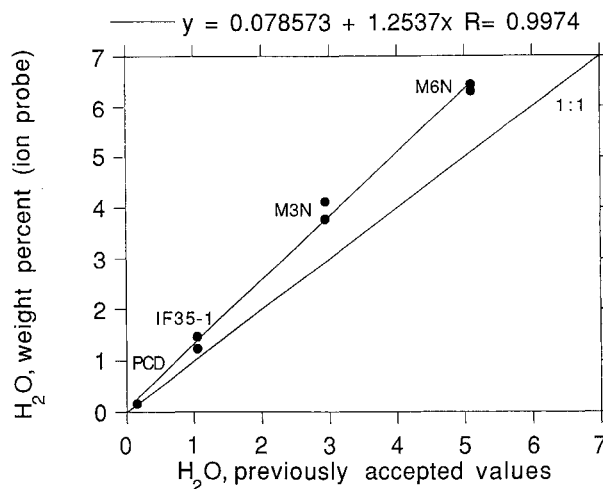y = 0.078573 + 1.2537x R= 0.9974

Fig. 2. H_2O contents determined by ion microprobe (weight percent) vs. previously accepted H_2O contents of old ion microprobe standard glasses.

by electron microprobe in order to test the accuracy of the decay-curve difference method for estimating total volatile content. Reported results, which are presented in Table 2 and Figure 3, were obtained in a single analytical session using the same sample mount that was prepared for ion microprobe analysis. None of the six or more analyses obtained for each sample was rejected. Six analyses of standard reference glass KN18 were obtained prior to and following analysis of the experimental glasses and were used to calculate Si and Al grow-in correction factors for analyses of the H_2O-bearing glasses, as indicated above.

The results (Fig. 3) indicate that estimates of total volatile content obtained by difference using the electron microprobe decay-curve method are well correlated with H_2O contents measured by FTIR ($R = 0.993$). Microprobe estimates of total volatile content are generally somewhat higher than FTIR-determined H_2O contents, however, and the difference is probably due to more than one factor. First, the total volatile content of the experimental glasses estimated by difference includes all those species that are not analyzed directly (CO_2, Cl, F, S, P, B, etc.), not just H_2O, and so total volatile contents should of course be higher than H_2O contents alone. But F, Cl (Table 1), S, and P analyses obtained by electron microprobe, B contents based on ion microprobe analyses, and estimated CO_2 contents based on FTIR analyses suggest that the combined weights of these other species should not exceed about 0.2 wt% in these samples. Furthermore, the discrepancy between total volatile contents estimated by difference and FTIR-measured H_2O contents should decrease with increasing H_2O in the experimental glasses, as the other volatile species become diluted. Yet, the dis-

crepancy between total volatiles estimated by difference and FTIR H_2O analyses is not observed to decrease with increasing H_2O (Fig. 3). Therefore, the results indicate that electron microprobe analyses may become less accurate with increasing H_2O content. As suggested above, the correction procedure adopted here, which relies on test analyses of KN18, implicitly assumes that the grow-in of count rates for Si, Al, etc. that attends Na loss is the same in hydrous glasses as it is in essentially dry KN18. This is not strictly the case, and it is likely that, the higher the H_2O content of an analyzed glass, the weaker the assumption. This is the second possible contribution to the errors observed in Figure 3. In contrast, estimates of
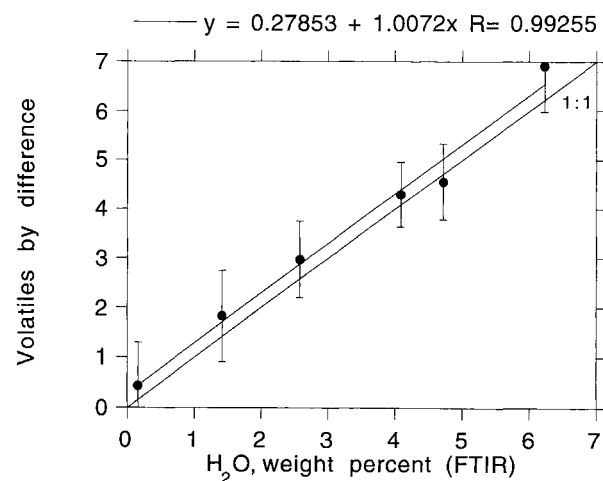
y = 0.27853 + 1.0072x R= 0.99255

Fig. 3. Total volatile content (weight percent) estimated by difference from electron microprobe analyses vs. FTIR-determined H_2O contents of new ion microprobe standard glasses. Error bars are conventionally calculated standard deviations (2σ).
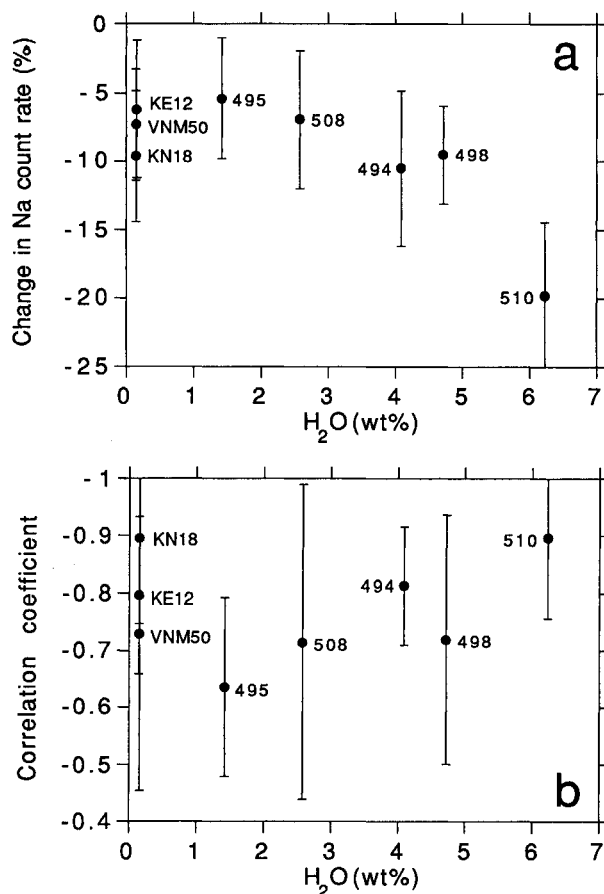
Fig. 4. (a) Change in Na count rate (percent) during the first 10 s of electron microprobe analysis vs. H_2O contents of glasses from Tables 1 and 2. Operating conditions: 15-kV accelerating voltage; 10-nA beam current; 10-μm beam diameter. (b) Correlation coefficients of regressions of the log of the Na count rate vs. time, plotted against the H_2O content of the respective glasses. Although the correlation coefficients are not high, the standard deviations for Na_2O analyses in Tables 1 and 2 indicate that this is mainly a result of the shallow slopes of the regressions rather than excessive scatter in measured count rates.

Na content may actually become more accurate with increasing glass H_2O content.

The evidence that supports these conclusions is illustrated in Figure 4 and Table 3. Figure 4a shows that Na loss increases with increasing H_2O content of glasses of similar major-element content (Table 2) under similar operating conditions. Figure 4b shows that average correlation coefficients for regressions of the log of the Na count rate vs. time improve with increasing H_2O content of these glasses. Although estimation of the Na content of hydrous glasses is adequately estimated using the decay-curve method, the estimation of Si and Al contents must rest on the assumption that the grow-in of count rates for these elements in hydrous glasses is essentially the same as the grow-in in anhydrous standard glass KN18. Inspection of Figure 4a shows that this assumption is probably valid for hydrous glasses containing less than about 5 wt% H_2O for the operating conditions chosen (15-kV accelerating voltage, 10-nA beam current, 10-μm beam diameter). The average grow-in of Al count rates, the third element analyzed in the routine, corresponds to an overestimation of Al_2O_3 content of ~0.3 wt%, or 3–4% (relative). The average overestimation of SiO_2 content is also ~0.3 wt%, or ~0.5% (relative).

It is also important to evaluate the effects of bulk composition and beam diameter on the analysis of hydrous glasses. Specifically, can the methods described here be applied directly to the analysis of strongly peralkaline glasses, as well as metaluminous (VNM50-15) or moderately peralkaline (KN18) glasses? Table 3 shows the results of test analyses of essentially anhydrous pantelleritic obsidian reference glass KE12. It is apparent that acceptable results can be obtained if beam diameters are greater than ~10 μm. If the beam is defocused to ~15 μm, Na loss is nearly eliminated. Use of a focused beam, however, results in decreases in the Na count rate of ~50% after 10 s of analysis, and the assumption that the Si and Al grow-in is analogous to the behavior of these elements in the KN18 standard glass breaks down. Analysis of strongly peralkaline hydrous glasses should be possible, however, if the beam is defocused enough to prevent ex-

TABLE 3. Electron microprobe analyses of peralkaline pantelleritic obsidian KE12

	Accepted values	15-μm beam	10-μm beam	Focused beam
SiO_2 (wt%)	70.30	70.56(26)	70.34(45)	71.35(33)
TiO_2	0.33	0.28(5)	0.31(2)	0.32(5)
Al_2O_3	7.62	7.67(11)	7.62(7)	7.75(10)
FeO*	8.36	8.48(23)	8.18(21)	8.30(23)
MgO	0.20	0.02(1)	0.03(2)	0.03(2)
CaO	0.35	0.36(5)	0.37(5)	0.40(4)
Na_2O	7.28	7.50(35)	7.22(16)	7.67(42)
K_2O	4.27	4.20(12)	4.31(8)	4.25(6)
MnO	0.26	0.24(7)	0.28(7)	0.26(7)
Total	98.79	99.31	98.66	100.33
No. analyses	—	7	7	7
Na corr. coeff.**	—	−0.102(781)	−0.796(137)	−0.992(7)
Δ count rate (%)†	—	−3.3(71)	−7.3(41)	−50.3(63)

Note: numbers in parentheses are estimated standard deviations.
 * All Fe calculated as FeO.
** Average correlation coefficient for regressions of the log of the Na count rate vs. time.
 † Change in Na count rate during the first 10 s of analysis.

cessive (>10%) Na loss in the first 10 s of analysis (the grow-in of other elements must still be accounted for). The tradeoff is that this method of analysis decreases the effective spatial resolution of the electron microprobe. If spatial resolution cannot be sacrificed, it may be necessary to use the ion microprobe for the analysis of hydrous, strongly peralkaline glasses.

Because of the probable systematic nature of errors in estimates of glass H_2O contents by the difference method, it is not meaningful to calculate conventional error statistics, which pertain to random, rather than systematic, errors. Nevertheless, Figure 3 suggests that the estimation of volatiles by difference can be within ~0.7 wt% (2σ) of H_2O contents determined by more accurate methods for glass H_2O contents up to about 6 wt%.

These results indicate that ion microprobe H_2O analysis combines the highly desirable features of spatial resolution, accuracy, precision, and sensitivity, so long as adequately characterized standard reference materials are available for the construction of calibration curves. FTIR spectrometry should provide superior results if the objective is to measure H_2O abundances of H_2O-poor samples, given the great sensitivity of the method for detection of H_2O. It is of course necessary that samples be large enough to accommodate a beam ~25–35 μm or larger in diameter (the practical limit depending on the instrument) and that appropriate extinction coefficients be available for the bulk composition of interest (e.g., Pandya et al., 1992). FTIR analysis has an added advantage over the other two methods in that CO_2, as well as H_2O, concentrations and speciation may be conveniently determined. Finally, electron microprobe analyses of volatiles by difference appear to be accurate enough, though imprecise, for some applications in which analytical convenience is desirable. For example, estimation of volatiles by difference is adequate for the purpose of determining if volatiles leaked from an experimental charge; it may also be the only method available for analysis of small experimental samples in which matrix glass contains microlite, making them unsuitable for FTIR analysis. The electron microprobe is inadequate for the estimation of H_2O contents of H_2O-poor samples. However, one might find it useful to be able to estimate rapidly the total volatile content of H_2O-rich melt inclusions in juvenile tephra produced by what may be precursor volcanic eruptions, for the purposes of volcanic hazard and risk assessment. In such a case, electron microprobe analysis can provide results in the shortest amount of time, conceivably within 24 h of receipt of the tephra at the laboratory. In conclusion, each of the analytical methods considered in this report has its own advantages under certain conditions, and each seems capable of providing reasonably accurate estimates of the H_2O or total volatile content of geologic glasses.

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