

LETTER

Analysis of oxygen with the electron microprobe: Applications to hydrated glass and minerals

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ABSTRACT

The development of layered synthetic dispersion elements makes it possible to analyze routinely for O with the electron microprobe. The precision for O in silicate glass is 0.6% of the amount present, comparable to that for Si. Optimum results occur when standards similar in composition to unknowns are used and care is taken in standard and sample preparation. The procedure is particularly advantageous in the analysis of hydrous glass and minerals in which conventional microprobe analyses yield totals of less than 100% because O attached to H remains unmeasured. The direct determination of O provides a measure of the quality of the analysis and yields an indirect estimate of the H₂O content of the sample by comparison of measured with stoichiometric O concentrations.

INTRODUCTION

The analysis by electron microprobe of light elements ($Z < 9$) such as O presents numerous problems resulting from the low cross sections for ionization, high absorption of the low-energy X-rays, and spectral interferences by higher order X-ray lines of heavier elements. O has rarely been analyzed directly despite its abundance, and its concentration is traditionally calculated by stoichiometry with measured cations. This method neglects O associated with cations not measured, notably H in H₂O-bearing materials, and other light elements such as Li, Be, B, C, and N. Because O that may be associated with these elements is not determined, analytical totals are less than 100%. Uncertainties in valence may also result in inaccurate totals when O is calculated by stoichiometry. Under these circumstances, it is difficult to assess the quality of an analysis, although the calculation of the structural formula for a mineral may confirm whether or not the analysis is acceptable. In the case of natural glass, no such recourse exists, and low totals are generally accepted and attributed to the presence of H₂O or the loss of Na caused by interaction of the electron beam with the sample.

The recent development of layered synthetic dispersion elements (LSDE), often referred to as multilayer diffracting crystals, has made O and other light elements measurable, even in minor concentrations. Although it is now possible to analyze for O routinely in minerals, the determination of O is particularly advantageous in the analysis of hydrous minerals and glasses because, first, the analytical total provides a direct measure of the quality of the analysis, and, second, H₂O contents can be estimated from the difference in measured and stoichiometrically calculated O contents.

OBSTACLES TO THE ANALYSIS OF LIGHT ELEMENTS

The problems encountered in the analysis of light elements are of two varieties: those resulting from the physics of X-ray generation and detection, and those associated with preparation of the sample and standard. Light elements have very low cross sections for ionization that result in a low yield of X-rays, and these low-energy X-rays are readily absorbed in the sample. Mass absorption coefficients are often large, and if there are significant differences in composition between standards and unknowns, the mass absorption coefficients must be known with high accuracy. Moreover, although O X-rays may be generated at considerable depth (micrometers) in the sample, the emission volume is much shallower because of high absorption. Thus, the O signal may be strongly influenced by surficial and near-surface conditions.

In the past, the problem of low X-ray yield was exacerbated by inefficient diffraction of characteristic X-rays to the detector. The situation has been significantly improved by the development of layered synthetic dispersion elements. These X-ray reflectors consist of alternating layers of heavy and light elements that act as diffracting crystals, with d values determined by the thickness of the light element layer. The advantage of these X-ray reflectors in the analysis of light elements has been described by several authors (Nicolosi et al., 1986; Love and Scott, 1987; Armstrong, 1988; Kawabe et al., 1988; Bastin and Heijligers, 1991; McGee et al., 1991). Not only do these reflectors provide greater peak intensities, they also suppress higher order interfering X-ray lines, such as AlK α (III) on the OK α peak and AlK α (IV) on the N peak, which are present if a lead stearate diffracting crystal is used. Counting rates with the LSDE crystals are sufficiently high that the statistical precision for O is similar to heavier ele-

ments conventionally analyzed with the electron microprobe. Minor shifts in position and shape of the $OK\alpha$ line occur with LSDE, as described by Armstrong (1988) and Bastin and Heijligers (1989). In the application described here, the problems of mass absorption and shifts in peak position and shape are minimized by the traditional method of using standards similar in composition to the unknowns.

In order to obtain accurate and reproducible microprobe results, care must also be taken with sample preparation. The standards and unknowns must be well polished and clean, have the same thickness of C coating, and have surfaces perpendicular to the electron beam. These procedures are particularly critical for O because the signal is derived from very near the surface, and C has a high mass absorption coefficient for $OK\alpha$ radiation. Goldstein et al. (1991) describe the effects of surficial oxidation of metallic samples. Although this is not a problem for silicate glasses and minerals, it could be a serious problem in the analysis of low concentrations of O in metals, sulfides, etc. In addition, adsorption of H_2O by the samples could be problematic and should be evaluated. Finally, errors of up to 1% per degree of inclination are produced by samples that are inclined to the primary electron beam.

ANALYTICAL CONDITIONS

Analyses were performed on a Cameca SX-50 electron microprobe equipped with four wavelength-dispersive spectrometers. The X-ray reflector, manufactured by Ovonic Synthetic Materials Company (OVONYX OV-060a) is a 60-Å W/Si multilayer deposited on a single-crystal substrate of Si (100). O and F were measured on a spectrometer with this crystal. The remaining spectrometers were equipped with TAP, PET, and LiF analyzing crystals. Gas-flow proportional counters using P-10 gas (90% Ar, 10% methane) were used on all spectrometers. Analyses were made at 15 keV accelerating voltage, a beam current of 25 nA, and a beam diameter varying from 5 to 25 μm . O was measured at the beginning of each analysis; counting time was 20 s. A similar counting time was used for standardization so that any effects of C contamination in the sample chamber would be similar for the standard and the unknowns. Background intensities were measured on both sides of the analytical peaks. Concentrations were calculated from relative peak intensities using the $\phi(\rho z)$ algorithm of Pouchou and Pichoir (1991), utilizing mass absorption coefficients from Henke et al. (1982). On the natural glass standard containing 49.8 wt% O, these conditions yielded a peak to background ratio of 41, comparable to that for Al (50).

Synthetic Al_2O_3 was used as a standard for reconnaissance measurements of O in a variety of mineral standards. A natural obsidian (MM3) was used for analyses of silicic glass. The O content of MM3 was calculated by stoichiometry, with 41 cations analyzed by wet chemical, X-ray fluorescence, instrumental neutron activation, and atomic absorption methods. O, Si, Al, and K were calibrated with this standard; natural mineral standards were

used for the remaining elements. Kaersutite was used as the O, Si, and Al standard for the analysis of hornblende, and muscovite was used as the O standard for illite. Samples and unknowns were coated with C simultaneously to assure an equivalent thickness of the C coat. During analysis, repetitive measurements were made on synthetic Al_2O_3 to determine if O were present in amounts greater than stoichiometric because of adsorbed H_2O on the samples; no excess O was detected.

H concentrations in melt inclusions were determined by secondary ion mass spectroscopy with a Cameca IMS 4f ion microprobe at the University of Edinburgh (cf. Hervig et al., 1989, for discussion of SIMS measurements of H_2O in melt inclusions). H_2O concentrations of glass separates were determined manometrically on the H extraction line at the University of Utah.

RESULTS

The O contents of 18 mineral standards, determined using synthetic Al_2O_3 for O calibration, are illustrated in Figure 1. Nominal O contents were calculated assuming stoichiometry of the mineral standards. The correlation between measured and nominal O contents is generally good. However, hematite and magnetite have measured O contents that are low by 1% absolute; these are the two data points at lowest O contents in Figure 1. This discrepancy is attributed to reduced peak intensities due to peak broadening associated with differential energetics of the bonding of Fe oxides compared with that of alumina or silicates. This emphasizes the need to correct for changes in peak shape, if present (cf. Bastin and Heijligers, 1989), or, alternatively, to utilize standards similar to unknowns in composition.

Conventional analyses of hydrated silicic glasses yield low analytical totals, which are attributed to H_2O and alkali mobility under the electron beam. Table 1 presents data for four silicic glasses. The first is the average of 130 analyses performed over a period of 2 yr on MM3, the high-silica obsidian standard. The standard deviation for O represents a reproducibility of 0.6% of the amount present, slightly better in this case than the error on Si (0.8%, relative). The conventional analysis in terms of oxides is shown for comparison.

The second data set is for glass shards from the Lava Creek B tuff, erupted from the region of Yellowstone National Park 0.6 Ma. A common practice is to assume that the difference between the analytical total and 100% is caused by the presence of unanalyzed H_2O and to normalize the data to 100%, producing an analysis of the "anhydrous" glass. The procedure has merit only if the analysis is of good quality, Na has not been lost during analysis, and there has not been an exchange of H_2O for other elements such as alkalis during hydration. The latter is best addressed isotopically (Cerling et al., 1985). However, the two former concerns are resolved by analysis for O, whereupon a good analysis results in an analytical total approaching 100%. A conventional analysis of glass shards from this same tephra unit by Sarna-Wojcicki et al. (1987) is presented for comparison. Al-

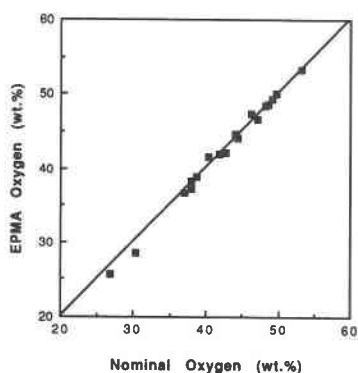


Fig. 1. Comparison of O determined with the electron microprobe (EPMA) vs. nominal O contents (assuming stoichiometry) in a variety of mineral standards. The analytical error is less than the size of the data point.

though it is not possible a priori, to assess the quality of the latter, comparison of the two analyses confirms its quality.

The third data set is the average of 12 analyses on a single silicate melt inclusion, 120 μm in diameter, in a quartz phenocryst from rhyolitic pumice. The elemental analytical total is 100.1% compared to the stoichiometric oxide total of 93.8%.

The fourth data set is for melt inclusions, 30–50 μm in diameter, from quartz phenocrysts in the Fire Clay unit of Carboniferous age (Lyons et al., in preparation). Conventional analyses yielded, as expected, low analytical totals. However, the question remained as to whether the totals were low due to H_2O content or Na loss during analysis. Subsequent analysis for O in our laboratory yielded analytical totals approaching 100%, with only slightly elevated Na concentrations, supporting the assumption that the major deficit in the oxide total is H_2O .

ESTIMATION OF H_2O CONTENTS OF NATURAL GLASS

In hydrous materials, the concentration of O measured by electron microprobe exceeds the stoichiometrically calculated content because H, as well as He, Li, Be, B, C, and N, have not been measured. Assuming that the latter elements are in low concentration and that all other elements present and their valence states have been accounted for properly, the difference between measured and stoichiometric O can be attributed to the presence of H_2O or OH. The abundance of H_2O determined by this method is, of course, an estimate because there has not been a direct determination of H_2O or the H concentration, and the method relies upon the accurate determination of all other elements present. In this respect, the method is similar to that of assuming that the difference between the oxide total and 100% is the H_2O content. Other than measuring O directly, it has the additional advantage of monitoring the quality of the analysis. The method does not have the precision of infrared spectroscopy (e.g., Newman et al., 1986) nor the desirability of direct measurement of H, as in secondary ion mass spectrometry; however it is simple, and the result emerges from any

TABLE 1. Analyses of hydrated natural glasses

Sample	MM-3 <i>n</i> = 130	LCB <i>n</i> = 11	LCB(S)	HH <i>n</i> = 12	FC <i>n</i> = 4	FC(L) <i>n</i> = 17
Si	35.89(0.32)	34.45	—	33.2	34.64	—
Ti	0.08(0.02)	0.06	—	0.00	0.12	—
Al	6.59(0.07)	6.15	—	8.25	6.39	—
Fe	0.51(0.04)	1.02	—	0.36	0.83	—
Mn	0.04(0.02)	0.02	—	0.08	0.03	—
Mg	0.04(0.01)	0.02	—	0.00	0.06	—
Ca	0.38(0.02)	0.36	—	0.21	0.40	—
Na	2.59(0.09)	2.59	—	2.30	1.73	—
K	4.33(0.05)	4.04	—	3.24	5.14	—
Cl	0.07(0.01)	0.15	—	0.13	0.03	—
F	0.14(0.03)	0.01	—	2.23	0.24	—
O	49.41(0.30)	50.90	—	49.9	49.50	—
Total	100.07(0.42)	99.73	—	100.1	99.09	—
SiO_2	76.8	73.7	72.2	71.1	74.1	73.5
TiO_2	0.14	0.10	0.10	0.00	0.20	0.22
Al_2O_3	12.4	11.61	11.7	15.6	12.1	12.3
FeO^*	0.65	1.31	1.33	0.46	1.06	1.16
MnO	0.05	0.03	0.03	0.10	0.04	0.01
MgO	0.06	0.03	0.02	0.00	0.10	0.14
CaO	0.53	0.50	0.51	0.29	0.55	0.62
Na_2O	3.49	3.49	3.37	3.09	2.33	2.1
K_2O	5.21	4.87	4.86	3.91	6.20	6.04
Cl	0.07	0.17	—	0.13	0.03	0.02
F	0.14	0.01	—	2.23	0.24	0.2
Sum	99.5	95.7	94.3	94.8	96.9	96.4
–O**	0.08	0.04	—	0.97	0.11	0.08
Total	99.5	95.7	94.3	93.8	96.8	96.4
$\text{H}_2\text{O}^\dagger$	0.6	4.5	—	4.5	2.6	—
Total	100.1	100.2	—	98.3	99.4	—

Note: Numbers in parentheses are standard deviations. MM-3 = Mineral Mountains obsidian. LCB = Lava Creek B ash, Promontory Point, Utah. LCB(S) = Lava Creek B ash; average of six localities; analysis recast as original EPMA data from Sarna-Wojcicki et al. (1987, Table 1). HH = melt inclusion in quartz phenocryst, Honeycomb Hills rhyolite, Utah. FC = average of melt inclusions in Fire Clay tonstein (Lyons et al., in preparation), University of Utah. FC(L) = average of melt inclusions in Fire Clay tonstein (Lyons et al., in preparation), U.S. Geological Survey.

* Total Fe as FeO.

** –O = F, Cl.

† H_2O estimated from difference between measured and stoichiometric O.

analysis in which O is measured. For materials with moderate to high Fe contents, the estimate requires a knowledge of the valence state of Fe. The method is well suited for rhyolitic glasses because of their low Fe content (Table 1).

In Figure 2 estimates of H_2O contents of silicic glasses determined by electron microprobe are compared to measurements of H_2O content by manometry and secondary ion mass spectrometry in natural glasses. EPMA results agree well with manometry and less well with SIMS, perhaps because of the lower precision of the latter. For moderate H_2O contents in glasses, the method yields values within about 1% absolute of the amount present. H_2O contents estimated for silicate glasses are given in Table 1.

HYDROUS MINERALS

The analysis of O is advantageous in hydrous minerals insofar as the analytical total serves as a measure of the quality of the analysis. Furthermore, if the valence state of the cations is known, H_2O contents can be estimated.

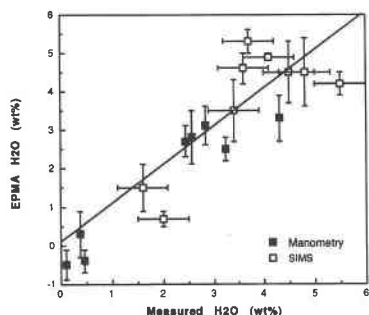


Fig. 2. H₂O content of hydrated glass estimated by EPMA vs. H₂O determined by secondary ion mass spectrometry (SIMS) on melt inclusions (open squares) and manometry on obsidian glass separates (solid squares). The line is the linear least squares fit to the data. The error bars on EPMA values are standard deviations for ten analyses on each sample. SIMS error estimates are 0.5%; manometry uncertainties are less than the size of the data points.

An example of an analysis of a hornblende is given in Table 2. The analytical total by conventional microprobe analysis is 97.5%. Also presented in Table 2 is the analysis of an ammonium-bearing, tobelitic illite. Without the analysis of O and N, the conventional analytical total is 91.5%. The elemental analysis totals 99.4% and thus provides a measure of confidence in the quality of the analysis, particularly the determination of N content. The analytical conditions for the measurement of N are given in Wilson et al. (1992). The estimated H₂O content of the tobelitic illite is 4.8%. The determination of O contents in hydrous B-bearing minerals would also be advantageous because it would permit an assessment of the analytical accuracy, a problem experienced by McGee et al. (1991).

TABLE 2. Analyses of hornblende and N-bearing illite

	Hornblende AS-10 <i>n</i> = 10	Illite FM-9 <i>n</i> = 8
Si	22.5	23.0
Ti	0.81	0.06
Al	3.34	19.1
Fe	10.4	0.37
Mn	0.45	—
Mg	8.64	0.71
Ca	8.34	0.04
Na	0.73	0.12
K	0.47	3.29
Cl	0.08	—
F	0.00	0.60
N	—	1.55
O	43.9	50.6
Total	99.8	99.4

Note: AS-10 = hornblende from Alta Stock, Utah; FM-9 = tobelitic illite from Oquirrh Mountains, Utah (Wilson et al., 1992).

ACKNOWLEDGMENTS

Financial support was provided by NSF grants EAR-8618101 and EAR-8720627. James Webster provided the SIMS analyses of H, and Thomas Gavigan assisted in EPMA analyses of melt inclusions and performed the manometric water determinations. Paul Lyons provided the ancient (!) melt inclusions. F.H. Brown reviewed an early draft of the manuscript. Subsequent reviews by James McGee and an anonymous reviewer further improved the paper.

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MANUSCRIPT RECEIVED DECEMBER 30, 1991

MANUSCRIPT ACCEPTED FEBRUARY 12, 1992