Analytical techniques for volatiles: A case study using intermediate (andesitic) glasses

P.L. King, T.W. Vennemann, J.R. Holloway, R.L. Hervig, J.B. Lowenstern, and J.F. Forneris

1Geology Department, Arizona State University, Tempe, Arizona 85287, U.S.A.
2Institut Geochemie, Wilhelmstr. 56, D-72076, Tübingen, Germany
3Chemistry Department, Arizona State University, Tempe, Arizona 85287, U.S.A.
4Center for Solid State Science, Arizona State University, Tempe, Arizona 85287, U.S.A.
5U.S. Geological Survey, MS 910, 345 Middlefield Road, Menlo Park, California 94025, U.S.A.

ABSTRACT

Small-scale analyses of volatiles in minerals and glasses provide information on how volatiles influence high-temperature geologic processes and low-temperature alteration processes. Four techniques for determining the C-O-H volatile contents of andesitic glasses are compared: manometry, secondary ion mass spectrometry, micro-Fourier transform infrared spectroscopy, and a technique where the H2O content is calculated using the difference between electron microprobe analysis totals and 100% sum. We present a method to determine the H content of a wide range of glass and mineral compositions using secondary ion mass spectrometry and a model for calibration factors. The extinction coefficients for H-O volatile contents in intermediate composition synthetic glasses are determined, and it is demonstrated that C-O speciation changes as total H2O content increases, with molecular CO2 decreasing, CO3^2- increasing, and carbonate peak splitting increasing. For glasses with low H2O content and oxy-substituted minerals, the methods of choice for volatile analysis are secondary ion mass spectrometry or micro-Fourier transform infrared spectroscopy.

INTRODUCTION

Volatile components, such as water and carbon dioxide, influence the chemical and physical properties of minerals and igneous melts and, hence, have a controlling effect on many high-temperature geologic processes, as well as low-temperature alteration processes and weathering. For instance, the H content of a mineral may relate to its crystallization conditions, and volatile exsolution from a melt can trigger volcanic eruptions or contribute to an ore-bearing magmatic vapor phase (e.g., reviews in Carroll and Holloway 1994). To understand these processes better, it is useful to analyze volatiles in minerals and glasses using micro-analytical techniques such as secondary ion mass spectrometry (SIMS, or ion microprobe), micro-Fourier transform infrared spectroscopy (micro-FTIR), or by calculating the difference of an electron probe micro-analysis total from 100 wt%. These techniques allow the analyst to choose an appropriate analysis area and may provide information on the zonation of volatiles and diffusion processes for volatiles.

SIMS analysis has the advantage of ease of sample preparation and small areas of analysis (<200 μm²). However, calibrations are not straightforward because sample chemistry affects the yield of H ions (Delaney and Karsten 1981; Shimizu 1986; Steele 1986; Wilson et al. 1989; Ottolini et al. 1995; Hauri et al. 2002). Currently, H analysis of an unknown sample by SIMS relies on calibrations based on samples of similar and known composition. The curves are anchored by samples with a range of H content analyzed using bulk techniques, such as Karl-Fischer titration or manometry (Ihinger et al. 1994). Presently, the SIMS method suffers from the fact that appropriate calibrations are rare or non-existent. It would be useful if a model existed to determine the sensitivity of SIMS for measurements of H content in a wide range of mineral or glass compositions.

Micro-FTIR analysis has the advantage of detecting volatile speciation in samples; for example, OH–, H2O mol (molecular H2O), CO2 mol (molecular CO2), and CO3^2–, all of which are found in natural glasses. Analyses of geologic samples are generally performed in transmission mode on areas of about 1500 to 8000 μm². Transmission micro-FTIR analysis provides ample signal for the detector, but has several disadvantages: mineral specimens must be oriented crystallographically, samples must be prepared as doubly polished wafers (especially difficult for glass inclusion work), and FTIR calibration factors, known as extinction coefficients, must be known. Extinction coefficients for volatile species are known for some glass compositions and these data have been incorporated in empirical models, for H-O species extinction coefficients (Dixon et al. 1995; Jakobsson 1997; Ohlhorst et al. 2001; Mandeville et al. 2002) and CO3^2–...