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Infrared spectroscopy and hydrogen isotope geochemistry of hydrous silicate glasses

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The focus of this project is the combined application of infrared spectroscopy and stable isotope geochemistry to the study of hydrogen-bearing species dissolved in silicate melts and glasses. We are conducting laboratory experiments aimed at determining the fractionation of D and H between melt species (OH and H₂O) and hydrous vapor and the diffusivities of these species in glasses and melts. Knowledge of these parameters is critical to understanding the behavior of hydrogen isotopes during igneous processes and hydrothermal processes. These results also could be valuable in applications of glass technology to development of nuclear waste disposal strategies.

The important results from the current grant period are:

1. We have measured the partitioning of hydrogen isotopes between water vapor and silicate melts and glasses at temperatures of 550-850°C and pressures of 2-2000 bars. Our results make it possible to use hydrogen isotope data to model the degassing of high-level silicic magmatic centers of the sort being considered as geothermal resources. For example, the large vapor-melt fractionation factor we have determined suggests that rhyolitic domes (e.g., those found in the Mono craters and Inyo craters systems in California) evolved by open-system degassing of water-rich magmas.
2. Diffusive transport of water in silicate liquids and glasses plays an important role in many phenomena of interest in the geological and materials sciences. For example, the rate of water diffusion in silicate liquids controls the growth of bubbles in ascending magmas, and influences the degree to which magmas can dehydrate on ascent and the availability of compressed vapor in bubbles to power explosive volcanic eruptions. Hydration and dehydration of silicate glasses in geological and man-made environments are also limited by water diffusion, and relate to issues such as the chemical stability of glasses, the mechanical strength of glass fibers, the kinetics of SiO₂ film growth on Si substrates, water-rock reaction leading to ore deposition, and obsidian hydration dating of young volcanic rocks. We have shown that in volcanic glasses, the diffusivity of water molecules is much greater than that of hydroxyl groups. The uniqueness of our approach stems from our ability to measure the concentration profiles of these separate species, which allows us to treat the problem in terms of two diffusing, reacting species and to obtain diffusivities for both molecular water and hydroxyl groups.
3. We have used our results on volcanic glasses as a basis for understanding the "self diffusion" of oxygen in silicate minerals and glasses. In particular, it is well known that the diffusion of oxygen is significantly enhanced under hydrothermal conditions. We have developed the theory needed to understand the connection between the diffusivity of water and oxygen and have shown that diffusion of molecular water in nominally anhydrous minerals and melts is likely the control on measured self diffusion coefficients of oxygen.
4. We have extended our study of stable isotope fractionation factors between vapor and silicates to the fractionation of oxygen isotopes between CO₂ vapor and silicate minerals and glasses. We have shown the feasibility of measuring fractionation factors precisely by equilibrating small amounts of vapor with large amounts of silicate, followed by mass spectrometric analysis of the vapor. These data are critical to the interpretation of observed variations in stable isotope ratios in

nature and are complementary to our studies of the fractionation and mobility of hydrogen isotopes in silicates.

5. We have studied the kinetics of the reactions between water molecules and anhydrous silicate structural units to form hydroxyl groups in silicate glasses. This contributes fundamentally to our understanding of homogeneous equilibria in glassy and molten silicates. It is also of practical value in that it has allowed us to develop a practical cooling rate indicator and geothermometer for hydrous volcanic glasses.

6. We have applied our techniques for measurement of very small quantities of hydrogen in silicates and for determining the D/H ratio to pyroxenes and garnets from the earth's mantle. We have discovered that these nominally anhydrous minerals have detectable dissolved water and that the hydrogen isotopic composition of this water differs from those of hydrous mantle minerals, and thus may represent a significant, isotopically distinct reservoir of terrestrial hydrogen.

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Several publications have been supported by this DOE Grant:

Journal articles

Anderson, A.T., Jr., S. Newman, S.N. Williams, T. H. Druitt, C. Skirius, and E. Stolper (1989) H₂O, CO₂, Cl and gas in Plinian and ash-flow Bishop rhyolite. *Geology*, 17, p. 221-225.

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Zhang, Y., E.M. Stolper, and G.J. Wasserburg (1991) Diffusion of water in rhyolitic glasses. *Geochim. Cosmochim. Acta*, 55, p. 441-456.

Zhang, Y., E.M. Stolper, and G.J. Wasserburg (1991) Diffusion of a multi-species component and its role in oxygen and water transport in silicates. *Earth Planet. Sci. Lett.*, 103, p. 228-240.

Zhang, Y. and E.M. Stolper (1991) Water diffusion in a basaltic melt. *Nature*, 351, p. 306-309.

Stolper, E. and S. Epstein (1991) An experimental study of oxygen isotope partitioning between silica glass and CO₂ vapor. In: *Stable Isotope Geochemistry: A Tribute to Samuel Epstein*, Special Publication No. 3, The Geochemical Society (in press).

Jambon, A., Y. Zhang, and E.M. Stolper (1991) Experimental dehydration of natural obsidian and estimation of DH₂O at low water contents. *Geochim. Cosmochim. Acta* (submitted).

Thesis

Ihinger, P.D. (1991) An experimental study of the interaction of water with granitic melt. Ph.D. thesis. California Institute of Technology, Pasadena, California. 188 pp.

Abstracts

Zhang, Y., E.M. Stolper, and G.J. Wasserburg (1989) The mechanism of water diffusion in

silicate melts. EOS, 70, p. 501.

Blank, J.G., E.M. Stolper, J. Sheng, and S. Epstein (1989) The solubility of CO₂ in rhyolitic melt at pressures to 1500 bars. Abstracts with Programs 1989, 21, p. A157.

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Ihinger, P.D., E.M. Stolper, and S. Epstein (1990) Hydrogen isotope fractionation between rhyolitic melt and hydrous vapor at 850°C. V.M. Goldschmidt Conference 1990, p. 55.

Zhang, Y., E.M. Stolper, and P.D. Ihinger (1990) Reaction kinetics of H₂O + O = 2OH and its equilibrium, revisited. V.M. Goldschmidt Conference 1990, p. 94.

Bacon, C.R., S. Newman, and E.M. Stolper (1990) Water, CO₂, Cl, and F contents of glass inclusions in phenocrysts from three Holocene explosive eruptions, Crater Lake, Oregon. V.M. Goldschmidt Conference 1990, p. 69.

Zhang, Y., E.M. Stolper, and G.J. Wasserburg (1990) Role of water during hydrothermal oxygen diffusion in minerals. EOS, 71, p. 650.

Zhang, Y. (1990) An approximate treatment of uphill diffusion. EOS 71, p. 1664-1665.

Zhang, Y. and E.M. Stolper (1991) Water diffusion in basaltic melt. EOS 72, p. 312.

Blank, J.G., E.M. Stolper, and Y. Zhang (1991) Diffusion of CO₂ in rhyolitic melt. EOS 72, p. 312.

Ihinger, P.D. and D.R. Bell (1991) Isotopic composition of hydrogen in nominally anhydrous mantle minerals. EOS (in press)

Bell, D.R., G.R. Rossman, and P.D. Ihinger (1991) Hydroxyl in upper mantle minerals. EOS (in press)

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