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observations can provide near-global monitoring of aerosol distribution, but cannot separate natural aerosols from those associated with human activity. Observations made from Earth's surface are thus important for validating and improving observations from space. In situ measurements can be made from the ground or from aircraft and balloons. In conjunction with laboratory studies, they can provide important information on the precise chemical composition and physical properties of aerosols, which are necessary for determining how efficiently aerosols scatter and absorb sunlight. However, such observations can never be global in extent and are restricted to small areas that cannot be resolved by global climate models. Data regarding the vertical distribution of aerosols are also important for understanding radiative forcing, but few such observations are currently available from aircraft campaigns and groundor balloon-based remote sensing techniques. All of these data can then be used to test the validity of three-dimensional chemical transport models (CTMs), which are numerical tools that employ observed or analyzed meteorological conditions (such as winds, moisture, and temperature) to model the transport and reactions of atmospheric species as a function of time. These

models include processes that transform chemical species into aerosols, that remove chemical species and aerosols through rain out processes, and that transport them through the atmosphere. They produce three-dimensional distributions of aerosols as they vary with time.

Reduced uncertainties in aerosol forcing will only be achieved through coordinated integration of these observational and modeling techniques. Haywood *et al.*'s approach is a step toward this coordination. They combine results from various CTMs along with satellite measurements of reflected sunlight to directly determine the forcing effect due to various aerosol types. Additional observations on chemical composition would further improve their estimates of aerosol direct forcing.

Is there reason for optimism in solving the aerosol problem? Haywood *et al.*'s study, in conjunction with some new observational programs, gives reason to believe there is. In February and March of this year, a major field campaign will take place in the Indian Ocean near the Maldives. The Indian Ocean Experiment (INDOEX) is an international field program designed to observe the direct and indirect effects of aerosols. The experiment includes surface, aircraft, and satellite observing systems and aerosol simulations with CTMs. Also, NASA will soon launch the Earth Observing System (EOS), a satellite that carries several instruments for measuring aerosol properties. Finally, a joint U.S.-French satellite called PICASSO-CENA will measure aerosols with a two-wavelength laser that will provide high-vertical resolution profiles of aerosol properties. A prototype of this instrument flew on the space shuttle in 1994 and gave a glimpse of the three-dimensional distribution of aerosols in Earth's atmosphere.

These studies will be invaluable for solving the aerosol puzzle. Nevertheless, as Haywood *et al.* have demonstrated, the ultimate success of putting the pieces together rests on close integration of observations and modeling programs (5).

References

- J. M. Haywood, V. Ramaswamy, B. J. Soden, *Science* 283, 1299 (1999).
- C. D. O'Dowd et al., Atmos. Environ. 31, 73 (1997).
 X. Li-Jones and J. M. Prospero, J. Geophys. Res. 103,
- 16073 (1998).
- A. Jones and A. Slingo, Q. J. R. Meteorol. Soc. 122, 1573 (1996).
- National Research Council, Aerosol Radiative Forcing and Climate Change (National Academy Press, Washington, DC, 1996).
- J. T. Houghton et al., Eds., Climate Change 1995: The Science of Climate Change (Cambridge University Press, Cambridge, UK, 1996).

PERSPECTIVES: GEOCHEMISTRY

A Slippery Problem with Explosive Consequences

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Ithough its ultimate planetary origin is debated, there is no doubt regarding the important role played by water in many geological processes. The properties of water, either as a condensed low-temperature fluid or dissolved in crystalline, glassy, or molten silicates, influence myriad geochemical phenomena extending from Earth's surface to its deep interior. On page 1314 of this issue, Ochs and Lange (1) report important new results on the behavior of water-bearing silicate liquids.

In surficial processes, the role of water-rich fluids is self-evident. Geothermal waters, brines, and fluids within both continental and oceanic crust act to transport chemicals and heat in many lithospheric environments, including sedimentary basins, orogenic belts, crustal fault zones, and hydrothermal systems. In deep-seated environments, even small amounts of water—a fraction of a weight percent—can drastically influence the properties of geomaterials. For instance, the heat capacity of glassy silica increases by 30% as the concentration of water (as hydroxyl) increases from several parts per million by mass (ppm) to 1000 ppm (2).

The effects of water on the rheological properties of materials are remarkable. Small concentrations of water in the range of 100 to 1000 ppm dramatically weaken strong crystalline silicates, making them prone to ductile flow at temperatures typical of the crust and mantle (3). Recent experiments (4) show that 200 to 500 ppm of water can be dissolved in garnet and carried to transition zone or lower mantle depths (depths exceeding 400 km) within Earth. Integrated over the past 2.5 billion years, a substantial fraction of the hydrosphere could have been recycled by subduction of water-bearing lithosphere (and perhaps even some continental lithosphere). Water's lubricating action facilitates the plate tectonic cycle responsible for earthquakes, mountain building, subduction, and the growth of continents. The tectonic role of water may even extend to Earth's closest planetary neighbor, Venus. Differences in the tectonics of Venus and Earth have been ascribed to the relative dryness of Earth's twin and its attendant lack of a ductile asthenosphere (5).

Because the effects of dissolved water on the properties of magma are critical for analysis of many magma transport phenomena as well as an understanding of the atomic structure of hydrous silicate liquids, these conclusions are of broad interest. In particular, magma density is relevant to the segregation and ascent of magma, compositionally driven mixing of magma, and the dynamics of explosive eruptions driven by volatile exsolution. Ochs and Lange (1) address the volumetric properties of water dissolved in silicate melts at magmatic conditions, a relatively poorly known quantity. They have measured the density of hydrous glasses from which they infer the partial molar volume of water component (\bar{V}_{H_2O}) dissolved in silicate melts at elevated temperatures and pres-

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sures. They argue that \bar{V}_{H_2O} is independent of silicate framework composition, the total water content, and speciation of dissolved water (6).

The effects of dissolved water on the properties of magma have been studied for nearly a century (7). Despite this, there are still many mysteries regarding

the solution mechanism and thermodynamics of water in magma. Early



Big bang. Explosive volcanism (**left**) and mildly effusive volcanism (**right**) at Mount St. Helens; the difference results from differing water content of magma. Graph shows density of rhyolite melt (900°C, 0.2 GPa, dark brown circles) and andesite melt (1000°C, 0.2 GPa, red circles) as a function of weight percent of dissolved water (*1*). Compositional buoyancy commonly exceeds thermal buoyancy, and this leads to large reservoirs of density-stratified magma within the continental crust. Eruptions from such magma are often explosive and of large volume.

surements demonstrated that typical crustally derived magmas had the capacity to dissolve large amounts of water (~10 weight %) at pressures corresponding to only a few kilometers depth. However, quantification of the thermodynamic properties of dissolved water in melts and an understanding of the underlying molecular dynamics have proven difficult. Development of new spectroscopic and experimental techniques and more focused thermodynamic models has afforded geochemists an improved view of water-bearing silicate liquids within the last decade: The contribution of Ochs and Lange (1) is an important piece of the puzzle.

Two different methods have been used to estimate the partial molar volume of water dissolved in melts. In the solubility method, the heterogeneous $[H_2O (vapor) =$ $H_2O_{mol} (melt)]$ and homogeneous $[H_2O_{mol}$

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(melt) + O^{2-} (melt) = 2OH⁻ (melt)] equilibria that govern water solubility and speciation, respectively, are used with (i) the total water concentration as a function of water fugacity along an isotherm, (ii) the assumption of ideal mixing (or some other activity-composition relation), and (iii) spectroscopic measurements that independently fix the speciation of water (ratio of dissolved molecular water to dissolved hydroxyl) to extract the partial molar volume of molecular water ($V_{\rm H_2Omol}$). However, extraction of $V_{\rm H_2Omol}$ from solubility data de-

mands accurate knowledge of water speciation at high temperature and pressure. Laboratory quench rates are often too slow to ensure quenching of high-temperature speciation. Because in situ infrared (IR) and nuclear magnetic resonance spectroscopic studies are difficult, petrologists have been

forced to collect speciation data on quenched melts (glasses) and to take account of the kinetics of the homogeneous reaction. To further complicate matters, the molar absorptivities of the IR bands that correspond to molecular water and hydroxyl depend on water concentration as well as temperature and perhaps even the anhydrous composition of the silicate framework. Although progress has been made, calibration of spectroscopic models is slow and painstaking because many factors need to be carefully accounted for (8, 9).

A second method was used by Ochs and Lange (1). The hydrous melt is quenched, and the resulting glass density is measured at room temperature. Water speciation in the room temperature glass is assumed to

be identical to that in the melt at the glass transition temperature (T_g) and is determined by room temperature IR spectroscopy. The thermal expansion of each glass is then measured from room temperature up to the glass transition temperature; melt density equals glass density at $T_{\rm g}$. Because samples with different bulk water contents were used and because water speciation depends on total water content, glasses with variable hydroxyl to molecular water ratio were included in their study. When combined with partial molar volume data of other oxide components from independent experiments on anhydrous melt (10), the partial molar volume of water component and its temperature and pressure dependence may be determined. Ochs and Lange conclude that $V_{\text{H}_2\text{Ototal}} = 22.9 \pm 0.6 \text{ cm}^3/\text{mol}$ at 1000°C and 1 bar and that $V_{\text{H}_2\text{Ototal}}$ is independent of silicate melt composition, the total water content, and the speciation (OH or H_2O_{mol}). The latter point is consistent with recent independent observations (11).

The results of Ochs and Lange have both macroscopic and atomic implications. At large scale, the gravitational stability of water-bearing crustal magma is strongly governed by the ratio of compositional to thermal buoyancy (12). Explosive eruptions exceeding several thousand cubic kilometers in volume occur frequently along plate boundaries with global implications. At the smallest scale, the independence of the partial molar volume of water component on melt matrix composition must be explained. The observation that \bar{V}_{H_2O} is independent of melt matrix composition is consistent with the homogeneous speciation reaction involving rupture of bridging oxygen bonds. However, the lack of compositional dependence of $\bar{V}_{\rm H_2O}$ is at odds with some recent melt structure studies (13). Water, it seems, remains a slippery component in silicate melts worthy of further study.

References and Notes

- F. A. Ochs and R. A. Lange, *Science* 283, 1314 (1999).
 J. C. Lasjaunias *et al., Solid State Commun.* 17, 1045 (1975).
- The enhanced creep or hydrolytic weakening of silicates is well known. A recent example is given by T. Kubo, E. Ohtani, T. Kato, T. Shinmei, and K. Fujino [*Sci*ence 281, 85 (1998)].
- K. Lu and H. Keppler, Contrib. Mineral. Petrol. 129, 35 (1997).
- P. J. McGovern and G. Schubert, *Earth Planet. Sci. Lett.* 96, 27 (1989).
- Water dissolves in silicate melt in at least two forms: hydroxyl groups (OH⁻) and molecular water (H₂O_{mol}). At high total water content (4 weight %) and low temperature, molecular water (H₂O_{mol}) is the dominant dissolved species, whereas hydroxyl predominates at low water content and high temperatures [(9); L. Silver et al., Contrib. Mineral. Petrol. 104, 142 (1990); Y. Zhang et al., Am. Mineral. 80, 593 (1995); E. Stolper, Contrib. Mineral. Petrol. 94, 178 (1982); Geochim. Cosmochim. Acta 46, 2609 (1982); Am. Mineral. 74, 1247 (1989)].
- Early studies include both experimental work [such as R. W. Goranson, Am. J. Sci. 22, 227 (1931); *ibid.* 23, 227 (1932); C. W. Burnham and R. H. Jahns, *ibid.* 260, 721 (1962); G. C. Kennedy *et al., ibid.*, p. 501; G. P. Orlova, Int. Geol. Rev. 6, 254 (1962); C. W. Burnham and N. F. Davis, Am. J. Sci, 274, 902 (1974)] and thermodynamic modeling based on these data [such as G. J. Wasserburg, J. Geol. 65, 15 (1957); H. R. Shaw, *ibid.* 72, 601 (1964); C. W. Burnham, Geochim. Cosmochim Acta 39, 1077 (1975)].
- High-temperature in situ near-IR spectroscopy [for example, M. Nowak and H. Behrens, *Geochim. Cosmochim. Acta*. 59, 3445 (1995)] is a promising technique that remains to be fully explored.
- Y. Zhang et al., Geochim. Cosmochim. Acta 61, 2167 (1997); Y. Zhang et al., ibid., p. 3089.
- R. A. Lange and I. S. E. Carmichael, *Rev. Mineral.* 24, 25 (1990).
- 11. P. Richet and A. Polian, Science 281, 396 (1998).
- F. J. Spera et al., Geophys. Res. Lett., 13, 153 (1986);
 S. Clark et al., in Magmatic Processes: Physicochemical Principles (Geochem. Soc. Spec. Publ. no.1 (1987), p. 289.
- p. 289. 13. S. C. Kohn *et al., Geochimica Cosmochima Acta*, **62**, 79 (1998); J. A. Tossell *et al., ibid.* **61**, 1171 (1997).