Final Report

Infrared Spectroscopy and Stable Isotope Geochemistry of Hydrous Silicate Glasses

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Executive Summary

The focus of this DOE-funded project has been the study of volatile components in magmas and the atmosphere. Over the twenty-one year period of this project, we have used experimental petrology and stable isotope geochemistry to study the behavior and properties of volatile components dissolved in silicate minerals and melts and glasses. More recently, we have also studied the concentration and isotopic composition of CO$_2$ in the atmosphere, especially in relation to air quality issues in the Los Angeles basin.

We began with a study of the degassing history of the 1400 A.D. eruption of Mono Craters, in central California. Using hydrogen isotopic studies coupled with infrared analyses of the H$_2$O and CO$_2$ dissolved in the tephra glasses, we determined that degassing occurred in a closed system with a CO$_2$-rich vapor. The ratio of hydroxyl groups to molecules of water in the melts was important to the understanding of the evolution of the isotopic composition during degassing. This initial study led to experimental investigation of the speciation of dissolved water in glass compositions in addition to the rhyolites at Mono Craters. The kinetics of exchange between dissolved hydroxyl groups and H$_2$O molecules gave insight into cooling rates. We determined fractionation factors for hydrogen isotopes (D-H) between vapor and melt and between the dissolved water species, as well as the kinetics of D-H exchange. Study of CO$_2$ in rhyolitic glasses led to experiments to determine the fractionation of oxygen and carbon isotopes between CO$_2$ vapor and silicate melts/glasses and minerals of varying compositions.

Recently, we have returned to our studies from ~1990 of the diffusion of water in silicate glasses and melts. The diffusion of water in silicate melts has important applications in petrology, volcanology, and materials science. We studied the diffusion of water in several melt compositions, with particular emphasis on understanding the very strong dependence of the diffusivity of water on its concentration in the melt. We showed that this can be modeled successfully by using the current understanding of melt structure and the speciation of dissolved water. In addition, we found a correlation between the diffusivity of water and melt viscosity that can be useful for estimating the diffusion coefficient of water in melts for which experiments are not available.

Since 1998, we have added the study of the concentration and stable isotopic composition of CO$_2$ in air in the Los Angeles, CA, area which has produced several significant results. We have been collecting and analyzing CO$_2$ during the mid-afternoon every one to two days on the Caltech campus in Pasadena since 1998, to compare with a set of data collected in 1972-1973 in a similar location, as well as clean oceanic/coastal air from similar latitudes and clean air from California mountain and desert locations. Good correlations between the carbon isotopic ratios and CO$_2$ concentrations indicate that the CO$_2$ during both time periods is consistent with mixing between clean and polluted air end members. The polluted air end member for each time period can be described by the CO$_2$ released during cement production and, especially, combustion of fossil fuels (coal, natural gas, and petroleum products) during each time period. No local contribution from photosynthesis and respiration of plants is required. The Los Angeles basin has a
different pattern of seasonal variations in the local contribution of CO$_2$ to the atmosphere than do clean air sites, which are characterized by a pattern produced by the seasonal cycle of terrestrial plant processes. These seasonal patterns are disrupted in the Los Angeles area because of the local contribution of anthropogenic sources, dominated by burning of fossil fuels. Looking at the seasonal pattern of the CO$_2$ composition in excess of the clean air background, we have found a pronounced signature of increased CO$_2$ concentrations with the isotopic composition of the pollutant end member during warm seasons, when the local power plant burns more natural gas to provide the increased electrical power needed to drive air conditioners. Our results provide further evidence that the increase in CO$_2$ in the atmosphere is due to anthropogenic sources, dominated in the urban environment of Los Angeles by burning of fossil fuels.

Comparison of actual accomplishments with goals and objectives of the project

We have had many goals and objectives over the course of this award. Below we briefly summarize these for two on-going projects.

1) We proposed to measure the chemical diffusion coefficient of water in basaltic melts. We completed a pilot study of diffusion of water not only in high-Al basaltic, but also Fe-free basaltic and Fe-free andesitic, melts. Based on this pilot study, we proposed a definitive study of the dependence of water diffusivity on water content in melts of these three compositions.

2) We proposed to continue our measurements of CO$_2$ and its isotopic ratios in air in the Los Angeles basin. With a time series extending over several years, determination of diurnal and seasonal variations, and measurements of clean air sites in southern California, we proposed to develop this as a useful probe of sources of pollution in urban areas. We have followed this plan, showing that the excess CO$_2$ concentration, relative to that from clean oceanic and coastal sites from the same latitude, has stable carbon and oxygen isotopic compositions that can be explained solely by introduction of anthropogenic sources, dominantly sub-equal amounts of combustion of natural gas and petroleum products with minor amounts from cement production and coal combustion. Observed seasonal variations demonstrate increased anthropogenic contribution during warmer seasons, when power plants burn more natural gas for running air conditioners.
Summary of project activities

Our research activities can be seen in our many publications resulting from this award, listed at the end of this report. Below we summarize two of our ongoing projects.

1) Experimental determination of the chemical diffusion of water in silicate melts

This project is an expansion on a single measurement of water diffusivity in basaltic melt supported during a prior funding period by DOE and reported in 1991 by Zhang and Stolper. During this grant period, we worked with our colleagues Youxue Zhang (University of Michigan) and Eduard Persikov (Russian Academy of Sciences) to investigate the relationship between water diffusivity and water concentration in the compositions high-Al basalt, Fe-free basalt, and Fe-free andesite, in order to these different compositions. We also wanted to understand how water diffusivity relates to melt structure. Samples were synthesized in a specially designed internally heated pressure vessel that uses water as the pressurizing medium and can accommodate up to six samples simultaneously.

Two types of experiments have been done: (1) Diffusion couple experiments, in which two glasses identical in composition except for their water contents are placed in contact; brought to elevated temperature and pressure for a specified time, during which water diffuses from the high-water side of the couple to the low-water side of the couple; and then quenched. (2) Hydration experiments in which a water-poor melt is exposed to H$_2$O at elevated temperature and pressure for a specified time, during which water diffuses into the melt; followed by quenching. Analyses of concentration profiles on doubly polished sections were done by Fourier Transform infrared (FTIR) spectroscopy. A key element of these measurements is a computer-automated stage that was implemented to make these profiles highly reproducible. Since FTIR calibrations were not available for all of these compositions, we developed a calibration scheme relating the structural chemical parameter NBO/T to the molar absorptivities. This scheme results in smaller errors than previously proposed calculated calibrations based on chemical composition (e.g., Dixon et al., 1995).
Examples of two such experiments and measured profiles for basaltic glasses are shown in Figure 1.

Diffusion couple and hydration experiments have different initial and boundary conditions and somewhat different experimental challenges; consequently, when these two types of experiments give similar results (as they do for our study; see Figure 3), it gives considerable confidence that we are on the right track.

Figure 2 shows the water concentration profile of one basalt hydration experiment and several fits to the data based on simple models of diffusion. The first thing to notice is that the fit for a constant (i.e., concentration independent) $D$(H$_2$O) matches the data poorly. That a simple error function fits hydration profiles in silicate melts and glasses poorly is well known and is the basis for our understanding that $D$(H$_2$O) must increase significantly with increasing water content. The other three model profiles are based on various parameterizations of the dependence of $D$(H$_2$O) on water content, c(H$_2$O); the best-fit $D$(H$_2$O) vs. c(H$_2$O) parameterizations are compared in Figure 3. The three models shown are (1) $D$(H$_2$O) is a linear function of c(H$_2$O) (Shaw, 1974); (2) $D$(H$_2$O) as an exponential function of c(H$_2$O) (Delaney and Karsten, 1981; Karsten et al., 1982); and (3) a model in
which water is assumed to be dissolved as both mobile water molecules (which are assumed to have a constant diffusion coefficient) and hydroxyl groups (which are assumed to be immobile) where the concentrations of the two species are related via the reaction \( \text{H}_2\text{O}_{\text{mol}} + \text{O}^2- = 2\text{OH} \), which has a constant equilibrium constant, \( K \) (Behrens and Nowak, 1997; Zhang, 1999; Zhang and Behrens, 2000; Zhang et al., 1991; Zhang and Stolper, 1991).

There are several interesting features of the results shown in Figures 2 and 3. (1) The three models for which \( D(\text{H}_2\text{O}) \) varies with \( c(\text{H}_2\text{O}) \) all produce excellent fits to the observed concentration profiles. (2) These successful models all have significant variation in \( D(\text{H}_2\text{O}) \) with \( c(\text{H}_2\text{O}) \), and the contrast with the unsuccessful constant \( D \) model (i.e., the error function in Figure 2) confirms that this is a robust feature of diffusion of water in silicate melts, extending from highly polymerized compositions such as rhyolite (in which this feature was first demonstrated by Shaw (1974)) to the relatively depolymerized basaltic composition shown here. (3) Although the shapes of the \( D(\text{H}_2\text{O}) \) vs. \( c(\text{H}_2\text{O}) \) functions of the three successful models shown in Figure 3 are generally similar, they diverge both at low and high water contents, suggesting that it might be possible to distinguish them with appropriate experiments but that caution should be used in extrapolating these and other models beyond the range of the experiments on which they are based. (4) Also shown in Figure 3 is the \( D(\text{H}_2\text{O}) \) vs. \( c(\text{H}_2\text{O}) \) function for the multi-species model for a diffusion couple experiment (the other fits are for a hydration experiment) run at the same conditions as the hydration experiment. The best fits of the two experiments are clearly nearly identical, demonstrating, as emphasized above, the robustness of our results and their independence of the experimental technique used. (5) Although it is not superior to the other functional forms for \( D(\text{H}_2\text{O}) \) vs. \( c(\text{H}_2\text{O}) \) shown in Figure 3, the success of the multi-species model at fitting the observed concentration profiles is suggestive that the goal of linking diffusion phenomena (and particularly the strong concentration dependence of \( D(\text{H}_2\text{O}) \)) to molecular level structures and melt species may be achievable. We note, however, that despite the success of this relatively simple species-based approach, there are some complications. For example, some studies (Behrens and Zhang, 2001; Lyakhovsky et al., 1996; Zhang and Behrens, 2000; Zhang et al., 1991) have suggested that the diffusion coefficient for molecular water increases with total water content, and the mobility of OH groups may be significant under some circumstances, especially at very low water contents (Zhang et al., 1991).
Although we have emphasized here the results on basaltic melts, our results on other compositions show similar overall behavior. However, at a given temperature and water content, $D(H_2O)$ can vary strongly from composition to composition. Behrens et al. (2004) showed that although much of the variability correlates with silica content, this is not entirely successful, and in particular, it could not account for the available result on basaltic melt from Zhang and Stolper (1991). We have been exploring an alternative approach to systematizing the dependence of $D(H_2O)$ on melt composition. Our approach has been to compare values of $D(H_2O)$ with viscosity. There has been considerable work on parameterizing the viscosity of silicate melts as a function of major element composition, and thus, if a connection between these two transport properties could be demonstrated, it would provide an approach to estimating $D(H_2O)$ in melt compositions that had not been studied experimentally.

Figure 4 shows that calculated viscosities for a wide range of hydrous silicate melts (all at 1% $H_2O$ to take out the variation with water content illustrated in Figure 3, but spanning 54-77% SiO$_2$; 1150-1540°C; 1 bar to 15 kbar) correlate well with $D(H_2O)$. Note in particular that this relationship successfully accounts for the diffusion of water in basaltic melts (from this study and Zhang and Stolper, 1991), whereas the simple correlation with silica content suggested by Behrens et al. (2004) failed in this composition range. For this particular comparison, viscosity was calculated with the structural chemical model developed by Persikov and his coworkers (Persikov, 1998; Persikov et al., 1990). Although this relationship is unlikely to be a substitute for experiments, it could be a useful approach to estimating $D(H_2O)$ at 1% $H_2O$ for compositions or conditions (pressure and temperature) for which experiments are not available.

References:


3) Concentrations and isotopic ratios of atmospheric CO$_2$ and H$_2$O as measures of pollution in the Los Angeles basin

We have continued our sampling of CO$_2$ in air on the Caltech campus, originally begun in 1998. Analyses include manometric determination of CO$_2$ concentration and measurements of carbon and oxygen isotopic ratios by mass spectrometer. Air samples collected on the campus of the California Institute of Technology in Pasadena, CA, contained ~30 ppm more CO$_2$ in 1998-2003 than they did in 1972-1973 (averaging 369 ppm in 1972-1973 and 397 ppm in 1998-2003). Yet the ranges of the carbon and oxygen isotopic ratios remain essentially constant ($\delta^{13}$C$_{VPDB}$ was -13.4 to -7.7‰ in 1972-1973 and -14.1 to -8.0‰ in 1998-2003; $\delta^{18}$O$_{VPDB-CO_2}$ was -4.0 to -0.3‰ in 1972-1973 and -4.0 to +0.5‰ in 1998-2003). A tighter distribution for the more recent measurements, as shown in Figure 5, is consistent with fewer days with highly polluted air relative to 30 years ago. Both data sets display a significant correlation between $\delta^{13}$C and 1/CO$_2$ concentration, indicating mixing between clean air and a high-CO$_2$ content end member (Keeling, 1958, 1961). The two data sets project to similar intercepts at infinite CO$_2$ (-31.8 ± 0.4‰ for 1972-1973 and -30.6 ± 0.2‰ for 2002-2003; Figure 6). Based on mass balance considerations, this reflects a changing mix of natural gas and petroleum products burned in the region.

The $\delta^{13}$C of the CO$_2$ inventory in Pasadena can be explained by a local addition to “clean” air (defined by the average of the GMD-ESRL oceanic and coastal sites located 25-40°N listed in the caption to Figure 6) of 16 to 36 ppm CO$_2$ from exhaust from burning of fossil fuels (petroleum products and natural gas) and emissions from cement production, as shown in the seasonal variations plotted in Figure 7. Figure 7d shows the local, anthropogenic, contribution to the CO$_2$ inventory. Because of southern California’s warm climate, larger amounts of isotopically light fossil fuel are consumed during the summer for energy generation for air conditioning; much smaller amounts are required.

Figure 5. Histograms comparing (a,b) CO$_2$ concentration, (c,d) $\delta^{13}$C, and (e,f) $\delta^{18}$O during the 1972-1973 and 1978 time periods. Also noted are the average compositions for Pasadena (solid vertical lines) and for clean air from oceanic and coastal sites from similar latitudes (vertical dashed lines), except that the clean $\delta^{18}$O value shown for 1972-1973 is that estimated for average southern California clean air.
during the winter for heating (Figure 7e). This offsets the effects of vegetation due to photosynthesis/respiration and masks the periodic seasonal variation observed in clean air from oceanic/coastal sites at similar latitudes, and thus there is little regular seasonality to the Pasadena carbon isotopic ratios (Figure 7b). However, the error limits do allow up to 32% of the local contribution to be derived from biological activity. In contrast, cities in cold climates, such as Salt Lake City, UT, and Krakow, Poland, have seasonal cycles with increased anthropogenic input during cold seasons, reflecting burning of fossil fuels for heating (Pataki et al., 2003; Kuc, 1991, respectively).

Unlike carbon, the isotopic composition of oxygen in the CO$_2$ of Pasadena air does exhibit seasonal variations, similar to clean air sites at similar latitudes, reflecting the global signal of the biosphere’s annual cycle (Figure 7c). The effect of photosynthesis/respiration processes is three times greater on the oxygen isotopic composition than on the carbon isotopic composition because oxygen exchanges with the very large biosphere water reservoir, whereas carbon is affected only by the net flux from the plant processes (e.g., sources quoted in Yakir, 2003). Added to this is the high-CO$_2$ end member added locally, which is a product of combustion of fossil fuels, whose oxygen is from atmospheric O$_2$, as determined by analysis of plots of 1/CO$_2$ vs. $\delta^{18}$O (Figure 7f). The $\delta^{18}$O of clean air in Pasadena is $\sim -0.9\%$ heavier than clean air from oceanic and coastal sites from similar latitude.
Figure 7. Average seasonal time series comparing the 1998-2003 Pasadena data to averaged seasonal data for 25-40°N oceanic and coastal GMD-ESRL sites (see Figure 6) for (a) CO$_2$ concentration, (b) $\delta^{13}C$, and (c) $\delta^{18}O$. The data for the GMD-ESRL sites were derived by averaging the seasonal means for all eight sites from 1998-2003 for samples collected mid-day. (d) Seasonal excess CO$_2$ in ppm calculated by subtracting the average for the GMD-ESRL sites from the average for Pasadena for the same season. Seasonally averaged $\delta^{13}C$ intercepts. (f) Seasonally averaged $\delta^{18}O$ intercepts. Seasonally averages are plotted at the midpoints of the seasons. To help guide the eye, vertical lines indicate January 1 of each year.

References:

Publications resulting from this project

Journal Articles


**Theses**


**Abstracts**


