Volatile diffusion in silicate melts and its effects on melt inclusions

Don R. Baker ([1])([2]), **Carmela Freda** ([2]), **Richard A. Brooker** ([3]) **and Piergiorgio Scarlato** ([2])

([1]) *Earth and Planetary Sciences, McGill University, Montreal, Quebec, Canada*
([2]) *Istituto Nazionale di Geofisica e Vulcanologia, Roma, Italy*
([3]) *Department of Earth Sciences, University of Bristol, U.K.*

Abstract
A compendium of diffusion measurements and their Arrhenius equations for water, carbon dioxide, sulfur, fluorine, and chlorine in silicate melts similar in composition to natural igneous rocks is presented. Water diffusion in silicic melts is well studied and understood, however little data exists for melts of intermediate to basic compositions. The data demonstrate that both the water concentration and the anhydrous melt composition affect the diffusion coefficient of water. Carbon dioxide diffusion appears only weakly dependent, at most, on the volatile-free melt composition and no effect of carbon dioxide concentration has been observed, although few experiments have been performed. Based upon one study, the addition of water to rhyolitic melts increases carbon dioxide diffusion by orders of magnitude to values similar to that of 6 wt% water. Sulfur diffusion in intermediate to silicic melts depends upon the anhydrous melt composition and the water concentration. In water-bearing silicic melts sulfur diffuses 2 to 3 orders of magnitude slower than water. Chlorine diffusion is affected by both water concentration and anhydrous melt composition; its values are typically between those of water and sulfur. Information on fluorine diffusion is rare, but the volatile-free melt composition exerts a strong control on its diffusion. At the present time the diffusion of water, carbon dioxide, sulfur and chlorine can be estimated in silicic melts at magmatic temperatures. The diffusion of water and carbon dioxide in basic to intermediate melts is only known at a limited set of temperatures and compositions. The diffusion data for rhyolitic melts at 800°C together with a standard model for the enrichment of incompatible elements in front of growing crystals demonstrate that rapid crystal growth, greater than 10^{-10} m s^{-1}, can significantly increase the volatile concentrations at the crystal-melt interface and that any of that melt trapped by the formation of melt inclusions may not be representative of the bulk melt. However, basaltic melt inclusions trapped at 1300°C are more likely to contain bulk melt concentrations of water and carbon dioxide.

Key words *diffusion – silicate melts – volatiles – water – carbon dioxide – sulfur – fluorine – chlorine – melt inclusion – igneous processes*

1. Introduction

Volatiles play an enormously important role in igneous processes. They are not only respon-

sible for dramatic volcanic eruptions, but also affect the transport (*e.g.*, diffusion and viscosity) and equilibrium (*e.g.*, phase equilibria) properties of magmas. Understanding the diffusion of volatiles in silicate magmas provides the framework necessary for the understanding of processes such as bubble formation and growth that can ultimately lead to violent volcanic eruptions.

The volatiles commonly found at the highest concentrations in magmatic systems are H_2O, CO_2, S-species, F, and Cl. The dominant volatile in magmas is H_2O; evidence of its abundance is manifested in measured volcanic emissions (Symonds *et al.*, 1994) and the presence of hydrous minerals (*e.g.*, amphibole, biotite, mus-

covite, apatite) in many igneous rocks. The second most abundant volatile in magmas is CO_2, whose presence can be found in volcanic gases (Symonds *et al*., 1994) and as fluid inclusions in minerals (Roedder, 1965, 1979). The existence of rare carbonate magmas also testifies to the importance of carbon in igneous petrogenesis, but these unique magmas are not discussed further in this review. The presence of S in magmatic gases is often obvious; quantitative measurements demonstrate that volcanoes can vent thousands of tonnes of S per day (Symonds *et al*., 1994; Wallace, 2001). Additional evidence of sulfur's role in magmatic processes is the presence of common magmatic sulfides and rare magmatic sulfates (Luhr *et al*., 1984). The halogens, F and Cl, have been measured in volcanic gases and plumes (Symonds *et al*., 1994), and they are important constituents of hydrous minerals and occasionally are found as halogen minerals in igneous rocks.

We begin with a selected review of diffusion measurements of H_2O, CO_2, S, F, and Cl that we believe are most germane to the study of volatile transport in magmatic silicate melts. We then apply simple models to explore the effects of volatile diffusion on the compositions of melt inclusions trapped in minerals.

2. Volatile diffusion measurements

The first study of volatile diffusion in magmatic melts of which we are aware is Shaw's (1974) measurements of water diffusion in a rhyolitic melt. Since that time more studies of water, carbon dioxide, sulfur and halogens have been completed; for an excellent summary of experimental techniques and results obtained before the mid-1990's the interested reader is referred to the review by Watson (1994).

All studies to date demonstrate Arrhenian behaviour of volatile diffusivity; thus the resulting diffusion coefficients can be succinctly expressed by equations of the general form

$$D = D_o \exp\left(\frac{-E_a}{RT}\right)$$

where D is the diffusion coefficient, in $m^2 s^{-1}$, D_o is the pre-exponential factor, also in $m^2 s^{-1}$, E_a is the activation energy, in $J mol^{-1}$, R is the gas constant, 8.3143 $J K^{-1} mol^{-1}$, and T is the temperature, in K.

Broadly speaking, volatile diffusion is measured in two diffusive regimes, which are distinguished by the absence or presence of a chemical potential gradient. The first regime is that of tracer diffusion where the volatile of interest is only present in trace amounts and its movement through the melt can be modelled as a random walk in the absence of a chemical potential gradient. Experiments that study tracer diffusion typically utilize radioactive isotopes of the element of interest applied as a thin layer to one end of the sample and then allowed to diffuse through a vanishingly small chemical potential gradient. The second regime is that of chemical diffusion, which occurs in the presence of a significant chemical potential gradient. One experiment of this type is the diffusion couple where a cylinder of glass with weight percent abundances of a selected element or elements is juxtaposed against a glass cylinder with low concentrations of the selected element or elements, and the elements diffuse from the high to the low concentration melts during the experiment. Another experimental technique for chemical diffusion allows a mineral with the element of interest to partially dissolve into the melt releasing the element and creating a diffusion profile away from the mineral; however, this technique often results in multicomponent diffusion, making data analysis difficult.

A third technique is to expose samples to a fluid phase with a low concentration of the volatile of interest resulting in devolatilization, or exposing the sample to a fluid phase with a high concentration of the volatile resulting in diffusion of the volatile into the sample. Researchers agree that tracer diffusion is a highly improbably process in magmatic systems, whereas chemical diffusion occurs whenever two melts, or a melt and a crystal, with differing chemical potentials of a chemical component come into contact.

2.1. *Water diffusion*

Water is present in silicate melts in both the molecular form and as hydroxyl (*e.g*., Stolper,

1982). Understanding this speciation is important for thermodynamic modelling and for the microscopic modelling of diffusion in the melt. However, for the purposes of this work we are interested in only the bulk water diffusion coefficients and refer the interested reader to the review by McMillan (1994) of water speciation in silicate melts.

For all of the volatiles considered in this review the diffusion data is provided for the transport of the bulk volatile, not for a particular species. A comparison of the water diffusion measurements discussed below are summarized in fig. 1.

Shaw (1974) found that water diffusion in a rhyolitic melt is a function of water concentration at 750 to 850°C and 200 MPa. Using a technique based upon weighing glass cylinders before and after hydration, and after subsequent dehydration, he determined the water diffusion coefficient. Shaw found that the diffusion coefficient for water was a function of the water concentration and estimated the activation energy for water diffusion at weight percent concentrations to be approximately 67000 $J\,mol^{-1}$. Watson (1994) used Shaw's data to estimate an Arrhenius equation water diffusion at

concentrations near 6 wt%

$$D_{water} = 1.8 \times 10^{-8} \exp\left(\frac{-65000}{RT}\right)$$

Watson (1994) also extracted an Arrhenius equation from Shaw (1974) for water diffusion at low, nominally anhydrous, concentrations

$$D_{water} = 1.6 \times 10^{-10} \exp\left(\frac{-74000}{RT}\right)$$

Shaw's (1974) diffusion measurements at 10 to 200 MPa, 850°C, demonstrated no measurable pressure effect on water diffusion.

Karsten *et al*. (1982) and Lapham *et al*. (1984) applied ion microprobe techniques to the study of water diffusion in rhyolitic melts and found similar values and clearly demonstrated the dependence of water diffusion upon its concentration. Karsten *et al*. (1982) measured water diffusion at 70 MPa and 650 to 950°C in rhyolitic melts. They found that the Arrhenius equations describing water diffusion changed with water content; for rhyolitic melts with 1, 2, and 3 wt% water the activation energies were 82000, 80000, and 78000 $J\,mol^{-1}$, re-
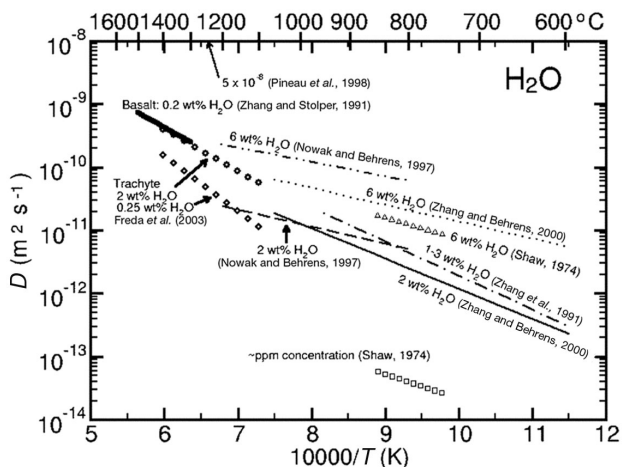

Fig. 1. Diffusion of water in magmatic silicate melts. Unless otherwise noted the measurements are made in melts of either rhyolitic or haplogranitic composition. Where calculations are pressure dependent a pressure of 200 MPa has been used.

spectively, and the pre-exponential factors were 1.44×10^{-8}, 2.65×10^{-8}, and 4.78×10^{-8} m^2s^{-1}, respectively. Although these results are slightly different from those of Shaw (1974) they are still consistent with his experimental measurements. Lapham *et al*. (1984) extended the work of Karsten *et al*. (1982) by investigating the effect of water concentration, from 0.42 to 3.48 wt%, and pressure, from 70 to 500 MPa, on the diffusion of water in rhyolite at 850°C. Lapham *et al*. (1984) further documented the effects of water concentration on water diffusion in rhyolitic melts and demonstrated that increasing the pressure from 70 to 500 MPa had no measurable effect on water diffusion at 850°C.

Zhang *et al*. (1991) utilized infra-red spectroscopy to characterize the diffusion of OH^- and H_2O species in rhyolitic melts and glasses. These measurements demonstrate that water diffuses predominantly as molecular H_2O and that the change from a rhyolitic glass to a melt had no effect on water diffusion. Combining their results with the previous measurements discussed above, Zhang *et al*. (1991) were able to construct a general Arrhenius equation for the diffusion of molecular, not bulk, water in rhyolitic glasses and melts from approximately 400 to 950°C and water concentrations between 1 and 3 wt%

$$D_{H_2O} = 4.6^{+18}_{-3.3}\times10^{-7}\exp\left(\frac{-103000\pm5000}{RT}\right).$$

Nowak and Behrens (1997) investigated water diffusion in a haplogranitic melt at temperatures between 800 and 1200°C, pressures of 50 to 500 MPa, and water concentrations between 0 and 9 wt%. They found that the activation energy for water diffusion drops from 64000 $Jmol^{-1}$ for 0.5 wt% water to 46000 $Jmol^{-1}$ for melts with 4 wt% water and remained at the latter value for high water concentrations. They observed a small effect of pressure on water diffusion and constructed a general equation for the diffusion of water, where H_2O is in weight percent and P is the pressure in MPa

$$\log D_{water} = \frac{(-8.81 - 0.045H_2O + 0.027(H_2O)^2) +}{}$$
$$\frac{-(3378 - 483H_2O + 46.9(H_2O)^2 + 0.475P)}{T}.$$

The most general expression for water diffusion in rhyolitic melts is that of Zhang and Behrens (2000) who present an equation for the diffusion of water at concentrations from 0 to 7.7 wt%, temperatures from 400 to 1200°C, and pressures from 0.1 to 810 MPa

$$D_{water} = 10^{-12}Xe^m\left(1 + \exp[(56 + m + Xa + -\sqrt{X}b)]\right)$$

where X is the mole fraction of total water in the melt based upon a one-oxygen mole (Stolper, 1982), and

$$m = -20.79 - \frac{5030}{T} - \frac{1.4P}{T}$$

$$a = -34.1 + \frac{44620}{T} + \frac{57.3P}{T}$$

and

$$b = 0.091 + \frac{4.77\times10^6}{T^2}.$$

For water contents between 0 and 2 wt% (inclusive) Zhang and Behrens (2000) provide a simpler equation

$$D_{water} = 10^{-12}(H_2O)\exp\left(10.49 - \frac{10661}{T} + -\frac{1.772P}{T}\right)$$

where in this case water is measured in weight percent. Although these expressions are only based upon the results of Zhang *et al*. (1991) and Zhang and Behrens (2000), they accurately describe the results of Karsten *et al*. (1982) and Nowak and Behrens (1997).

Only one study on the diffusion of water in basaltic melts has been published. Zhang and Stolper (1991) measured water diffusion in a basaltic melt at 1.0 GPa, 1300 to 1500°C, and found that for 0.2 wt% H_2O

$$D_{water} = 3.8^{+35}_{-3.4}\times10^{-6}\exp\left(\frac{-126000\pm32000}{RT}\right).$$

Freda *et al*. (2003) studied water diffusion in a

potassium-rich, trachytic melt at 1.0 Gpa, 1100 to 1400°C. They measured water diffusion at concentrations between 0.25 and 2 wt% H_2O; their results are described by

$$D_{water} = \exp(-11.924 - 1.003 \ln(H_2O)) \cdot$$
$$\exp\left(\frac{-\exp(11.836 - 0.139 \ln(H_2O))}{RT}\right).$$

During their study of water solubility and D/H fractionation between fluid and a basaltic andesite melt, Pineau *et al.* (1998) incidentally found an apparent diffusion coefficient for a few weight percent water at 1250°C: 5.1×10^{-8} $m^2 s^{-1}$. This value is 2 orders of magnitude higher than all other measurements of water diffusion at similar temperatures and indicates the need for more experiments designed to accurately measure water diffusion in basic melts.

The best constrained data for water diffusion in melts with 1 to 3 wt% H_2O at temperatures between approximately 1000 and 1300°C spans only about 1/2 an order of magnitude (fig. 1). At higher water concentrations and at

magmatic temperatures significantly below 1000°C important differences in water diffusion coefficients are observed. On the other hand, the effect of pressure on water diffusion is a second order effect and can often be neglected, but clearly needs more investigation.

2.2. *Carbon dioxide diffusion*

Carbon is found as both carbonate groups and molecular CO_2 in silicate melts and glasses (see review by Blank and Brooker, 1994), although a variety of different carbonate types may exist (Brooker *et al.*, 2001). In the same way as we treated water above we will only consider the bulk diffusion of carbon dioxide, which is the most important measurement for our applications. Figure 2 presents a summary of the diffusion results available for carbon dioxide.

The first experiments on carbon dioxide diffusion were tracer diffusion studies by Watson *et al.* (1982) on a sodium alumino-silicate melt with 60 wt% SiO_2 and a haplobasaltic melt with 53 wt% SiO_2. Watson *et al.* (1982) found car-
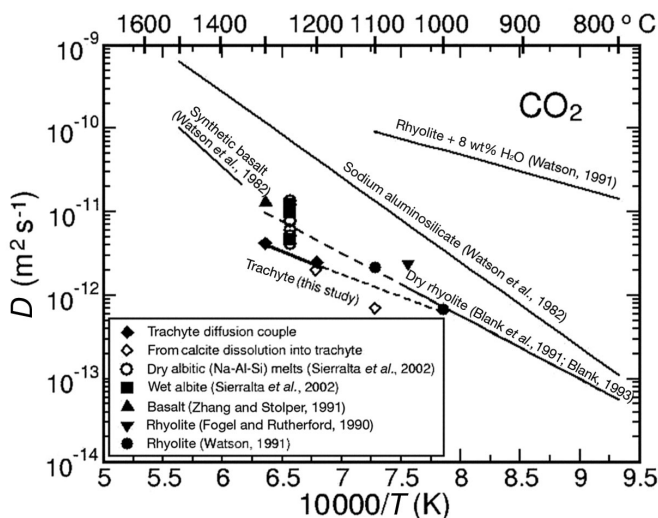

Fig. 2. Diffusion of carbon dioxide in magmatic silicate melts. Note that the variation of measurements in the work of Sierralta *et al.* (2002) is due to the variety of compositions used in their experiments, see text for further discussion.

bon dioxide diffusion in both melts to be similar and defined the Arrhenius relation for carbon dioxide diffusion in the sodium aluminosilicate melt between 800 and 1500°C at 500 MPa to be

$$D_{\text{carbon dioxide}} = 3.5 \times 10^{-4} \exp\left(\frac{-195\,000}{RT}\right).$$

Watson *et al*. (1982) demonstrated that at 1200°C the effect of increasing pressure by 2.5 GPa diminished the diffusion coefficient by approximately an order of magnitude. Carbon dioxide diffusion in the haplobasaltic melt at 1.5 GPa produced an activation energy 249000 $J\,mol^{-1}$ and a pre-exponential factor of 2.12×10^{-3} $m^2\,s^{-1}$. Fogel and Rutherford's (1990) study of carbon dioxide solubility in a rhyolitic melt produced chemical diffusion measurements at 1050°C and pressures between 100 and 295 MPa.

The pressure effect on diffusion at these conditions was not measurable and at this temperature the diffusion coefficient of CO_2 in rhyolite was 2.4×10^{-12} $m^2\,s^{-1}$, approximately a factor of two less than that found by Watson *et al*. (1982) in compositionally different melts. Watson (1991) investigated the effect of 8 wt% water on the tracer diffusion of carbon dioxide in rhyolitic melt at 1 GPa and found that carbon dioxide diffusion was significantly higher and the activation energy lower than in dry rhyolitic melts

$$D_{\text{carbon dioxide}} = 6.5 \times 10^{-8} \exp\left(\frac{-75\,000 \pm 21\,000}{RT}\right).$$

Furthermore, Watson (1991) measured similar diffusion coefficients for carbon dioxide in a dacitic melt and estimated that addition of 5 wt% water to a dry rhyolitic melt would result in a 10-fold increase in CO_2 diffusion.

Watson (1994) reports the results of CO_2 diffusion experiments in rhyolitic melts by Blank *et al*. (1991) and Blank (1993). These measurements were an extension of earlier infra-red investigations by E. Stolper's group at CalTech, who demonstrated the presence of both molecular CO_2 and carbonate groups in silicate glasses. These chemical diffusion experiments were performed at pressures from 50 to 105 MPa and

temperatures of 450 to 1050°C. Fourier-Transform Infrared (FTIR) measurements demonstrated that the only species present in the quenched glasses was CO_2 and that the measured diffusion coefficients can be described by

$$D_{\text{carbon dioxide}} = 6.2^{+4.3}_{-2.6} \times 10^{-7} \cdot$$
$$\cdot \exp\left(\frac{-114\,600 \pm 4100}{RT}\right).$$

Sierralta *et al*. (2002) investigated carbon dioxide diffusion at 500 MPa and 1250°C in hydrous albite and albitic melts modified through variation of the Na/Al ratio. These authors documented the presence of both molecular CO_2 and carbonate in their glasses and determined that both diffused at similar rates. Additionally, they determined that the effect of added alkalies and water on carbon dioxide diffusion were equivalent when expressed as the ratio of non-bridging oxygens to tetrahedral cations. These authors suggested that the small compositional effect on CO_2 diffusion was proportional to changes in the ratio of non-bridging oxygens to tetrahedral cations, NBO/T, as the alkalies were added to an albitic melt. However, new data by Nowak *et al*. (2004) failed to identify any compositional effect for a wide range of NBO/T in analogues of natural melts. One other explanation for the effect observed by Sierralta *et al*. (2002) is peralkalinity, as their diffusion coefficients also increase as a function of this parameter and extrapolate to agree with the highly peralkaline Na-aluminosilicate data of Watson *et al*. (1982). In contrast, the lack of an NBO/T effect observed by Nowak *et al*. (2004) is for non-peralkaline compositions. Brooker *et al*. (2001) have suggested that a very isolated carbonate group exists in peralkaline melts, and we suggest it is this complex that is diffusing at a high rate. Such effects are only likely to be important in rare, highly peralkaline magmas.

Zhang and Stolper's (1991) study of water diffusion in basalt at 1.0 GPa also produced a single measurement of carbon dioxide chemical diffusion in dry basaltic melt at 1300°C of 1.3×10^{-11} $m^2\,s^{-1}$.

We performed reconnaissance experiments at 1.0 GPa in which calcite partially dissolved into

the same potassium-rich, trachyte melts we used in our study of water diffusion (Freda *et al*., 2003). The melts were either anhydrous or contained 5 wt% H_2O and experiments were performed at 1.0 GPa, 1200 and 1100°C. We determined carbon dioxide concentrations in the melt using the electron microprobe and the «difference from 100%» technique. Because of the low quality of this analytical technique these measurements must be considered only as estimates of carbon dioxide diffusion. At 1200°C the diffusion of carbon dioxide in dry and hydrous melts appears similar within experimental uncertainty and equaled 2×10^{-12} $m^2 s^{-1}$; at 1100°C the diffusion profile in the anhydrous melt was too short to measure, but the hydrous melt produced a diffusion coefficient of 7×10^{-13} $m^2 s^{-1}$. Interestingly, these experiments plot along an extension of an Arrhenius relationship defined by combining the data of Watson *et al*. (1982) and Zhang and Stolper (1991) as shown in fig. 2. As there is a large increase in the Ca content of the melt (and therefore in NBO/T) near the interface of the dissolving calcite, but the CO_2 profile is consistent with a single diffusion value, our data appear to confirm the conclusions of Nowak and Screen (2003): there is little melt compositional effect on bulk CO_2 diffusion.

Initially surprised by these results we performed diffusion couple experiments for CO_2 at 1.2 GPa in the same trachytic melt using the diffusion couple technique and analyzing the quenched glass using FTIR spectroscopy. Carbon dioxide-bearing trachytic glass was prepared by creating a mixture of oxides and carbonates equivalent in composition to the trachyte. A portion of this mixture was devolatilized and melted at 1400ºC, 1 atm and then mixed with a small fraction of the oxide+ +carbonate mix; this mix was melted at 0.9 GPa, 1350 ºC for 2 h in a piston-cylinder apparatus to produce a carbon-bearing trachyitic glass for use in the diffusion couple experiments. During this synthesis a small amount of water, approximately 1 wt%, was absorbed by the melt. This carbon-bearing glass was powdered and juxtaposed against a glass cylinder of the same natural trachyte composition. We performed experiments at 1.2 GPa in a piston-cylinder for 720 s at 1200ºC and for 600 s at 1300ºC; after each

experiment the diffusion couple was ground and polished to approximately 50 μm thickness for analysis by FTIR spectroscopy. The extinction coefficients necessary to quantify the FTIR spectra were determined using trachyte glasses synthesized at high pressure with differing amounts of dissolved carbon dioxide. These glasses were prepared by mixing different ratios of the trachytic oxide+carbonate mix and the glass made from this mix followed by melting at 0.9 GPa, 1350ºC; the bulk CO_2 concentration in aliquots of these glasses was determined with a LECO carbon analyzer (Brooker *et al*., 1999), and the absorption spectra of polished samples was measured. Based upon this calibration, the extinction coefficient for the molecular CO_2 band at 2348 cm^{-1} is 975 L $mol^{-1} cm^{-1}$, and for the carbonate bands at 1550 and 1412 cm^{-1} are 191 ± 4 L $mol^{-1} cm^{-1}$ and 193 ± 6 L $mol^{-1} cm^{-1}$, respectively.

The diffusion of bulk carbon dioxide in trachytic melt at 1.2 GPa is 2.5×10^{-12} $m^2 s^{-1}$ at 1200ºC and 4.2×10^{-12} $m^2 s^{-1}$ at 1300ºC. Over the range of concentrations along the diffusion profiles a small variation in D_{CO_2} was observed, but it is less than a factor of 2 and probably due to the small amounts of water present in the carbon-bearing trachytic glass that diffused together with the carbon into the volatile-free melt during the experiment (fig. 3). Although the data are limited in temperature, they define an E_a of 100000 $J mol^{-1}$ and a D_o of 8.8×10^{-9} $m^2 s^{-1}$. Remarkably, the CO_2 diffusion coefficients extracted from the calcite dissolution experiments are consistent with the diffusion couple results and support the former's validity.

With the exception of Watson's measurements of carbon dioxide diffusion in wet rhyolite, all CO_2 diffusion measurements in natural melt compositions are similar at magmatic temperatures. These results demonstrate the very small dependence of carbon dioxide diffusion upon melt composition. At magmatic temperatures the carbon dioxide diffusion measurements in all the dry melts can be combined to yield a single Arrhenius relation. However, water has a significant effect on carbon dioxide diffusion in rhyolite melts. Watson's results indicate the ability of 8 wt% water addition to increase carbon dioxide diffusion in rhyolitic
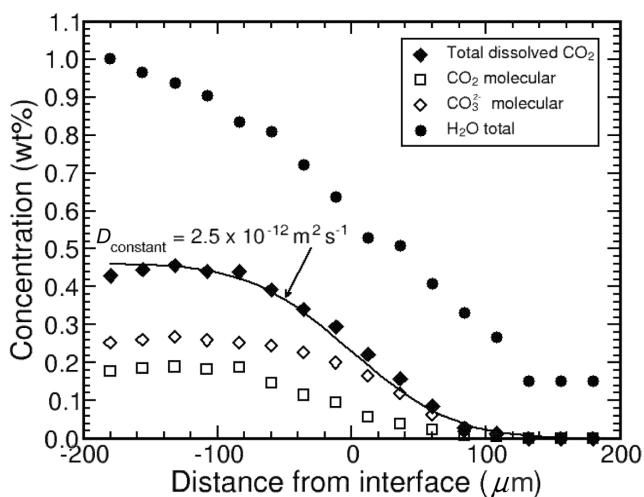
Fig. 3. Carbon dioxide diffusion in trachyte melt from a diffusion couple experiment at 1.2 GPa, 1200ºC, and 720 s. Diffusion profiles are displayed for total water, molecular CO_2, carbonate, and total CO_2, calculated as the sum of molecular CO_2 and carbonate. Concentrations of all species were determined by FTIR as discussed in the text. Also plotted is the theoretical diffusion profile for a diffusion coefficient of 2.5×10^{-12} $m^2 s^{-1}$. Further details of this experiment can be found in the text.

melt by 2 orders of magnitude. On the other hand, our preliminary results demonstrate no significant effects of water on carbon dioxide diffusion in a trachytic melt.

2.3. *Sulfur diffusion*

We know less about sulfur behaviour in silicate melts than water and carbon dioxide.

Many studies have found that sulfur is present in silicate melts as either SO_4^{2-} or S^{2-} species (see review by Carroll and Webster, 1994). But, Winther *et al*. (1998) demonstrate that this speciation picture is clouded by the presence of S_2^- and S_3^- radicals detected in quenched albite glasses. All agree that sulfur solubility and the relative abundances of the dissolved species are a function of oxygen fugacity and melt composition, but the exact relationships remain to be discovered. Research on sulfur diffusion is only beginning, however there is sufficient experimental data for petrologic investigations (fig. 4).

Watson (1994) discusses Watson *et al*.'s (1993) study of sulfur diffusion in dacite and andesite at 1 GPa and 1300 to 1500°C. These experiments were performed under reducing conditions, near the iron-wustite buffer, where S^{2-} is expected to be the dominant sulfur species in the melt. Diffusion in the dacite melt is described by

$$D_{sulfur} = 1.4 \times 10^{-4} \exp\left(\frac{-263\,000}{RT}\right)$$

and in the andesite melt by

$$D_{sulfur} = 1.0 \times 10^{-6} \exp\left(\frac{-191\,000}{RT}\right).$$

Addition of 5.5 wt% water to the andesite melt resulted in almost halving the activation energy

$$D_{sulfur} = 3.2 \times 10^{-8} \exp\left(\frac{-115\,000}{RT}\right).$$

Baker and Rutherford (1996) investigated the diffusion of sulfur in a rhyolitic melt at 1 atm to 200 MPa and 800 to 1100°C. They found that S diffusion in dry rhyolite is described by

$$D_{\text{sulfur}} = 5.0 \times 10^{-6} \exp\left(\frac{-221\,000 \pm 80\,000}{RT}\right)$$

and that addition of 7 wt% water increased sulfur diffusion by 1.5 to 2 orders of magnitude. Unfortunately, the hydrous experiments covered too small a temperature range to define an Arrhenius relationship, but the sulfur diffusion data of Baker and Rutherford (1996) in hydrous rhyolite all plot close to the low temperature extrapolation of Watson et al.'s (1993) Arrhenius line for sulfur diffusion in a hydrous andesite (fig. 4).

Baker and Rutherford performed experiments at geological oxygen fugacities ranging from the fayalite-quartz-magnetite buffer (~1 order of magnitude below the nickel-nickel oxide buffer) to the MnO-Mn₃O₄ buffer (~2 orders of magnitude above the nickel-nickel oxide buffer) and found no oxygen fugacity effects on S diffusion. Baker and Rutherford argued that this insensitivity to oxygen fugacity reflected the presence of a single diffusing S species, which they identified as S^{2-}. Their argument rests upon a comparison of their results to other diffusion experiments, theoretical calculations of how the size of the diffusing

species affects the diffusion coefficient, and their experiments in air, where virtually no S^{2-} should be dissolved in the melt, which demonstrated significantly lower diffusion coefficients than the other experiments at lower oxygen fugacities.

Winther et al.'s (1998) measurements of S diffusion in dry albitic melt at 1.0 GPa, 1300 to 1500°C, yielded

$$D_{\text{sulfur}} = 14.7 \exp\left(\frac{-458\,100}{RT}\right).$$

This activation energy is surprisingly large when compared to those for sulfur diffusion in other anhydrous melts. Using a variety of spectroscopic methods Winther et al. (1998) found that sulfur is present in the quenched glasses as SO_4^{2-}, SO_2^- and SO_3^-. They provided evidence that at least some of the species previously thought to be S^{2-}, based upon the sulfur peak location during electron microprobe analysis, were instead a combination of the radicals S_2^- and S_3^-. These authors found that the reduced species S_2^- and S_3^- diffuse more rapidly than SO_4^{2-}, consistent with the findings of Baker and Rutherford (1996).
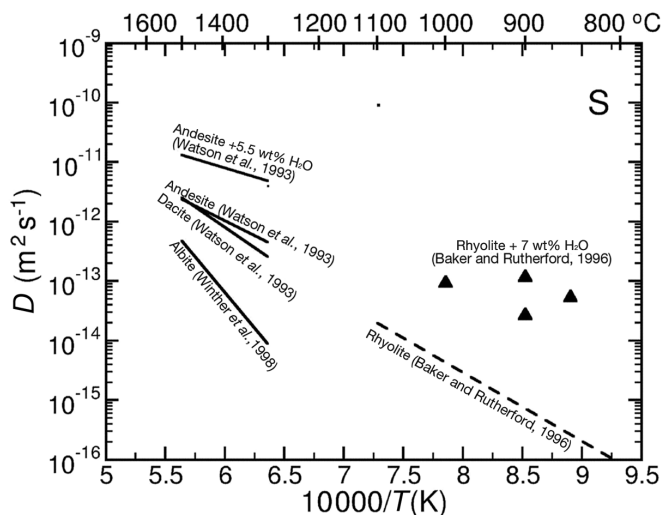

Fig. 4. Diffusion of sulfur in magmatic silicate melts.

Measurements of sulfur diffusion in silicate melts of geological interest are rare and much more work is needed. However, most of the results to date are consistent and suggest that within the range of anhydrous andesite to rhyolite there is little effect of melt composition on sulfur diffusion. The effect of water is significant, increasing S diffusion by up to 2 orders of magnitude in rhyolitic melts, but Arrhenius relations for most hydrous melts remain to be accurately determined.

2.4. *Fluorine and Chlorine*

Fluorine and chlorine are not uncommon magmatic components (Carroll and Webster, 1994). Both elements are found at concentrations of 1000's of ppm and in some granitic rocks F can reach weight percent concentrations. Studies of the diffusion of these volatiles in magmatic melts are quite rare, but still sufficient to provide an idea of the diffusion coefficients of these elements (fig. 5).

Dingwell and Scarfe (1984, 1985) were the first to measure fluorine diffusion in a geologically relevant melt composition. They measured F and oxygen interdiffusion in anhydrous jadeite melt at high pressure using a diffusion couple in which one half of the couple was composed of jadeite melt and the other half was composed of a jadeite melt in which some of the oxygen was replaced by fluorine. Over the temperature range of 1200 to 1400°C and pressure range of 1.0 to 1.5 GPa, Dingwell and Scarfe found that F diffusion in jadeite melt is pressure insensitive and follows the Arrhenius equation:

$$D_{\text{fluorine}} = 5.9 \times 10^{-6} \exp\left(\frac{-159\,000}{RT}\right).$$

These authors also measured fluorine-oxygen diffusion in albite at 1 atm at the same temperatures (Dingwell and Scarfe, 1985) by exposing a fluoridated albitic melt to air at high temperature, which resulted in the diffusion of fluorine out of and oxygen in to the sample. Interestingly, this study produced a lower activation energy

$$D_{\text{fluorine}} = 1.8 \times 10^{-9} \exp\left(\frac{-121\,000}{RT}\right).$$

Chlorine tracer diffusion in a geological melt was first measured by Watson and Bender (1980) in a simple Na-Ca-Al-Si-O melt with 56 wt% silica at temperatures from 1100 to 1300°C, and
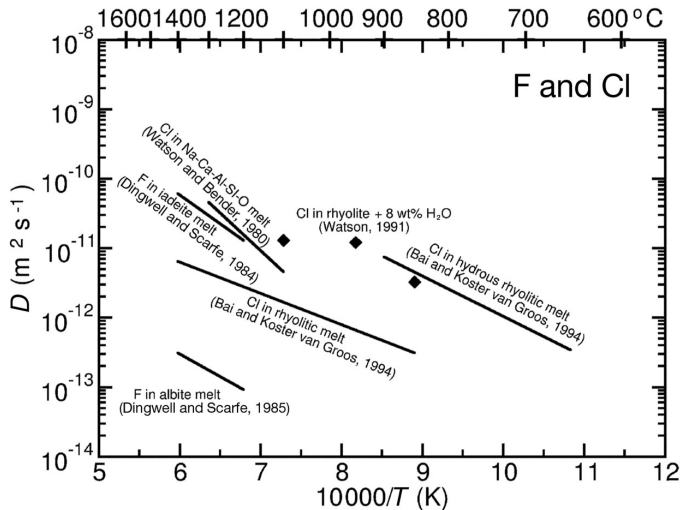

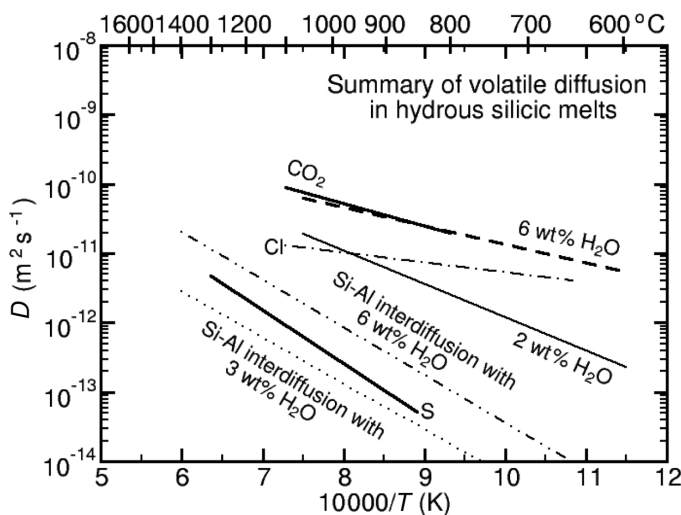**Fig. 5.** Diffusion of halogens in magmatic silicate melts.

Fig. 6. Comparison of volatile diffusion in hydrous silicic (almost exclusively rhyolitic) melts. Water diffusion, for 2 and 6 wt% total, is calculated from Zhang and Behrens (2000). CO_2 diffusion is calculated from Watson (1991) in a melt with 8 wt% dissolved water. S diffusion is a combination of the high-temperature results of Watson *et al.* (1993), see also Watson (1994), and the low-temperature results of Baker and Rutherford (1996). Cl diffusion is a combination of the high temperature results of Watson (1991) and the low temperature results of Bai and Koster van Groos (1994). Note that the apparent activation energies for S and Cl diffusion may be an artifact of combining data from two different studies. Lines for Si-Al interdiffusion in silicic melts containing either 3 or 6 wt% H_2O are extrapolated using the Arrhenius relationships determined by Baker (1991).

pressures from 0.6 to 1.8 GPa. At 0.6 GPa they found

$$D_{\text{chlorine}} = 3.4 \times 10^{-4} \exp\left(\frac{-207\,000}{RT}\right).$$

Comparison of diffusion coefficients measured at different pressures indicated no pressure dependence of Cl diffusion.

Watson (1991) investigated Cl tracer diffusion in a rhyolitic and a dacitic melt with 8 wt% water at 1.0 GPa. The temperature of these experiments spanned 850 to 1100°C, which was not sufficient to define an Arrhenius relation, but the diffusion coefficients ranged from 3×10^{-12} to 4×10^{-11} m²s⁻¹.

Bai and Koster van Groos (1994) measured chlorine chemical diffusion in a haplogranitic melt with 75 wt% SiO_2 and a natural obsidian melt with 78 wt% SiO_2 at pressures from 1 atm to 460 MPa. Their anhydrous experiments at low pressure produced an Arrhenius relation of

$$D_{\text{chlorine}} = 3.16 \times 10^{-9} \exp\left(\frac{-86\,190}{RT}\right)$$

for temperatures between 850 and 1400°C. Chemical diffusion of chlorine in a hydrous, granitic melt saturated with a NaCl brine at 200 MPa, 650 to 900°C is described by

$$D_{\text{chlorine}} = 6.46 \times 10^{-7} \exp\left(\frac{-110\,900}{RT}\right).$$

These authors demonstrate that over the pressure range of 200 to 460 MPa the Cl diffusion coefficient decreases by approximately a factor of 2.

The results for chlorine diffusion are exciting in that the few data available from different labs using differing techniques on rhyolitic compositions are very consistent, with the interesting exception of the pressure dependence for Cl diffusion. Regrettably there are not sufficient data to better evaluate fluorine diffusion. Clearly, more research in this area is urgently needed.

2.5. *Comparison of the different volatiles*

Figure 6 presents a comparison of the measured diffusion coefficients of water, carbon dioxide, sulfur and chlorine in a hydrous rhyolitic melt. At this time there are insufficient data to depict the diffusion of fluorine. The lines shown for sulfur and for chlorine are constructed by combining the high-temperature results of one study with the low-temperature results of another; thus, they only represent the diffusion of these volatiles in a general way. Nevertheless, the data demonstrate that over a broad range of magmatic temperatures, from ~1200 to 600°C , the diffusion coefficients of water, carbon dioxide, and chlorine are expected to be within an order of magnitude of each other. Sulfur, diffuses much more slowly, and its diffusion coefficient is approximately 2, or more at lower temperatures, orders of magnitude less than those of the other dominant magmatic volatiles. As we shall see this difference in diffusion coefficients can result in some interesting effects.

3. Effects of crystal growth rate and diffusion on the composition of melt inclusions

It is well known that the dynamics of bubble growth controls the physics of volcanic eruptions (*cf*., Sparks *et al*., 1994). In turn, bubble growth is mainly controlled by two processes: diffusion of volatiles from the melt into the bubbles and the expansion of the bubbles due to decompression (Sparks *et al*., 1994). Since the formulation of Scriven's (1959) growth law for bubbles in a superheated one-phase system

$$R = 2\beta \sqrt{Dt}$$

where R is the radius of the bubble, t the time, D the diffusion coefficient and β is a growth rate constant, many researchers created more complex models taking into account additional parameters such as advection, viscosity, pressure and variable volatile concentration (*e.g*., Proussevitch *et al*., 1993; Proussevitch and Sahagian, 1998; Blower *et al*., 2001). It is apparent that knowledge of volatile diffusion coeffi-

cients in silicate melts is a fundamental necessity for the modelling of magma vesiculation.

It is probably less well known that knowledge of volatile diffusivity aids the interpretation of data obtained studying melt inclusions in crystals. Melt inclusions are small (tens of microns) samples of melt trapped by magmatic crystals during their growth and are considered witnesses of petrologic processes, thus they are used as petrogenetic indicators (*cf*., Hauri *et al*., 2002). Because some melt inclusions are trapped at relatively high pressure, they are a useful tool to estimate volatile contents in magmas (*e.g*., Roedder, 1979; Hauri, 2002). Importantly, melt inclusions might form at different stages of crystal growth and they record only the composition of the melt at the crystal-melt interface. If the diffusion coefficient in the melt of an incompatible element in the crystal is slow compared to the crystal growth rate, the melt-crystal interface will become enriched in the incompatible element (*e.g*., Smith *et al*., 1955; Watson *et al*., 1982; Harrison and Watson, 1984); this phenomenon is often referred to as pile-up or the snowplow effect. Because of the common use of melt inclusions as volatile records (*e.g*., Massare *et al*., 2002), we performed calculations to estimate the volatile (H_2O, CO_2, Cl, and S) concentration curve in front of a growing crystal. Our conceptual model is that of a crystal whose growth rate suddenly increases for a short duration and then decreases, trapping melt at the crystal-melt interface forming melt inclusions.

We modelled the pile-up of volatiles at the crystal-melt interface for both rhyolitic and basaltic melts. All volatiles are incompatible elements with a crystal-liquid partition coefficient of 0.001. Decreasing this partition coefficient by one order of magnitude insignificantly affects the results. Two crystal growth rates were used in the calculations, 10^{-8} and 10^{-10} m s^{-1}. These values are based upon the results of Swanson (1977) who investigated plagioclase, alkali feldspar and quartz growth in a granitic melt containing 3.5 wt% H_2O at temperatures between 690 and 810°C and measured maximum growth rates of 10^{-8}, 10^{-9}, and 10^{-10} m s^{-1}, respectively. At temperatures between 600 and 1000°C, plagioclase growth rates varied from 10^{-9} to 10^{-8} m s^{-1}, alkali feldspar growth rates

were from 10^{-11} to 10^{-9} m s^{-1}, and quartz growth rates spanned 10^{-11} to 10^{-10} m s^{-1} (Swanson 1977). We previously studied crystal growth in the system orthoclase-quartz-H_2O and measured similar growth rates, between 1×10^{-10} and 5×10^{-9} m s^{-1} (Baker and Freda, 2001). Growth rates of ferromagnesian minerals in compositionally simple, basic melts range from 1×10^{-4} to 1×10^{-6} m s^{-1} (see summary in Lasaga, 1998). Recently, Simakin *et al*. (2003) have measured clinopyroxene and olivine growth rates near 1100ºC in a hawaiite melt at undercoolings of 25 and 45ºC, respectively, and found them to be both approximately 1×10^{-8} m s^{-1}. The high growth rate used in our modelling, 10^{-8} m s^{-1}, appears to be close to the maximum expected growth rate in magmatic systems, whereas the low growth rate used in the models, 10^{-10} m s^{-1}, is probably more common in nature, but still potentially rapid compared to normal growth rates in igneous systems (*cf*., Lu *et al*., 1995).

We modelled linear crystal growth of 10, 50 and 100 μm and calculated the volatile profile in the melt following eq. 26 of Smith *et al*. (1955). The diffusion coefficients for volatiles in granitic melts were extracted from fig. 5 for calculations at 800°C ($D_S = 2.5 \times 10^{-14}$, $D_{2\,wt\%H_2O} = 2.6 \times 10^{-12}$, $D_{Cl} = 6.6 \times 10^{-12}$, $D_{CO_2} = 2.0 \times 10^{-11}$, $D_{6\,wt\%H_2O} = 2.0 \times 10^{-11}$ m^2 s^{-1}). Crystal growth rates are affected by diffusion of their components in the melt, in this case primarily silicon and aluminum (Lasaga, 1998); at these conditions the chemical interdiffusion of Si and Al in silicic melts (fig. 6) is approximately 1×10^{-14} m^{2}s^{-1} at 2 wt% H_2O in the melt, and 1×10^{-13} m^{2}s^{-1} at 6 wt% H_2O (Baker, 1991). The diffusion coefficients of water and CO_2 measured by Zhang and Stolper (1991) in a basaltic melt were used in modelling the effects of crystal growth at 1300°C ($D_{H_2O} = 2.5 \times 10^{-10}$ and $D_{CO_2} = 1.3 \times 10^{-11}$ m^{2}s^{-1}). Although no measurements of Si and Al diffusion in hydrous basaltic melts are available, water is unlikely to significantly affect diffusion in this composition and we expect that Si-Al interdiffusion in hydrous basaltic melts is probably at most an order of magnitude above that measured in dry melts at 1300ºC, $\sim 1 \times 10^{-12}$ m^{2}s^{-1} (Watson, 1982).

We do not consider changes in the volatile diffusion coefficients due to changing water concentrations because once melts attain approximately 3 to 4 wt% water the diffusion coefficients of all elements are relatively insensitive to the exact water concentration (Watson, 1994). The only diffusion profile this simplification might significantly affect is that of 2 wt% H_2O. However, because of the effect of water concentration on water diffusion, our results at 2 and 6 wt% H_2O bracket the possible enrichment profiles for water concentrations in this range, and probably at water concentrations up to 8 wt%. In all cases we ignore the possibility of reaching fluid saturation and subsequent vesiculation. In order to compare calculations for different volatiles, we plot the results of the calculations as the enrichment factor of the melt near the crystal-melt interface relative to the bulk concentration of the volatile in the melt (figs. 7a-d and 8).

The volatile enrichment in front of a crystal growing from a hydrous rhyolitic melt at 800ºC is displayed in fig. 7a-d. If 10 μm of crystal grow at 10^{-8} ms^{-1} (fig. 7a) the maximum volatile enrichment factor is $6x$; this is the enrichment factor for sulfur and is due to its low diffusion coefficient. However, only 10 μm away from the crystalmelt interface the S reaches the bulk concentration in the melt. The maximum enrichment of the other volatiles is $1.25x$. In contrast to sulfur, these volatiles only reach the bulk melt concentrations at 100 to 275 μm from the crystal-melt interface. At 800°C the diffusion coefficients of 6 wt% H_2O and CO_2 are the same, which results in overlapping enrichment profiles in fig. 7a-d. If the crystal grew 50 μm (fig. 7b), the S enrichment reaches $22x$ in this case, and for a bulk melt with 2 wt% water the concentration at the interface is enriched $1.6x$ (3.2 wt% H_2O). Chlorine is enriched by $1.35x$ and both CO_2 and water for a melt with a bulk water concentration of 6 wt% are enriched $1.2x$. The region of enriched melt extends to 20 μm in front of the crystalmelt interface for sulfur and 300 to 600 μm away for the other volatiles. Allowing the crystal to grow 100 μm (fig. 7c) results in a sulfur enrichment of $42x$, but the 20 μm-wide enriched region in front of the crystal is approximately the same length as in the case of 50 μm of growth. The enrichment factor for a melt with a bulk compo-
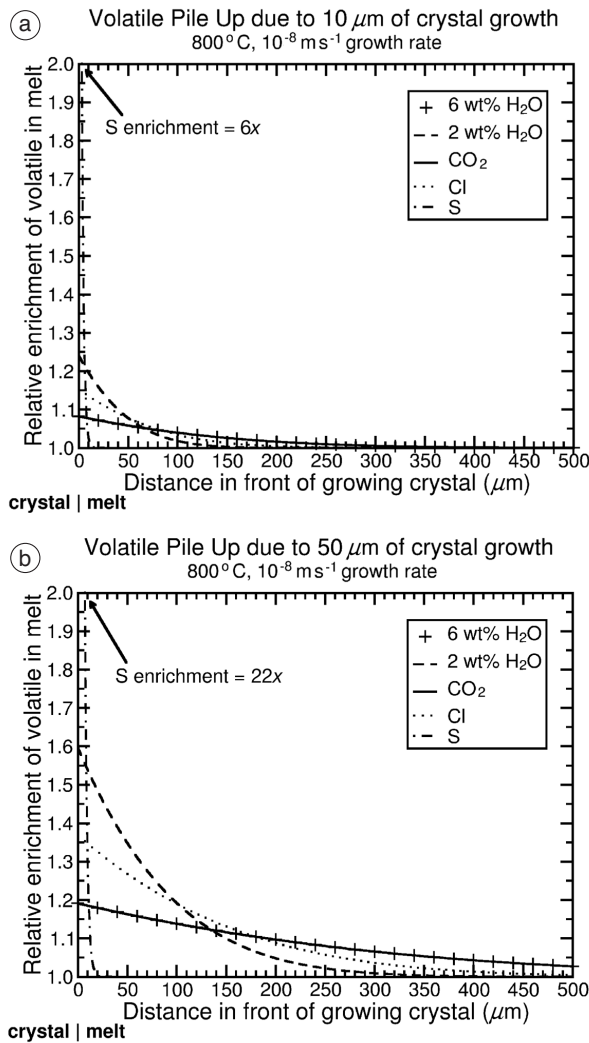
Fig. 7a,b. Volatile concentration enrichment profiles in front of a crystal growing in a rhyolitic melt at 800°C. The diffusion coefficients for volatiles are from fig. 5 and the sources of the crystal growth rates are discussed in the text. Note that composition enrichment profiles for 6 wt% H_2O and CO_2 plot on top of one another because their diffusion coefficients are identical at the conditions studied (see fig. 5). The effects of crystal growth on volatile concentration enrichment profiles relative to the concentration at infinite distance near the crystal-melt interface are modelled at a growth rate of 10^{-8} m s^{-1} for a total growth of 10 μm (a), 50 μm (b). Further discussion is found in the text.

sition of 2 wt% water is 1.9x at the interface; for chlorine the enrichment is 1.55x and for 6 wt% water and CO_2 is 1.28x. The profiles for the 2 and 6 wt% H_2O, Cl and CO_2 extend from approximately 400 to 1100 μm into the melt.

If the growth rate is decreased two orders of magnitude to 10^{-10} m s^{-1}, the volatile enrichment at the crystal-melt interface is significantly less (fig. 7d). For 50 μm of growth the enrichment of sulfur is only a factor of 1.6x (compared to

$22x$ at a growth rate of 10^{-8} m s^{-1}) and all of the other volatiles are enriched by less than a factor of $1.06x$, which is below analytical uncertainty in many cases.

These calculations for crystal growth from a rhyolitic melt at 800°C demonstrate that at high growth rates any melts trapped from the crystal-melt interface into melt inclusions may not con-
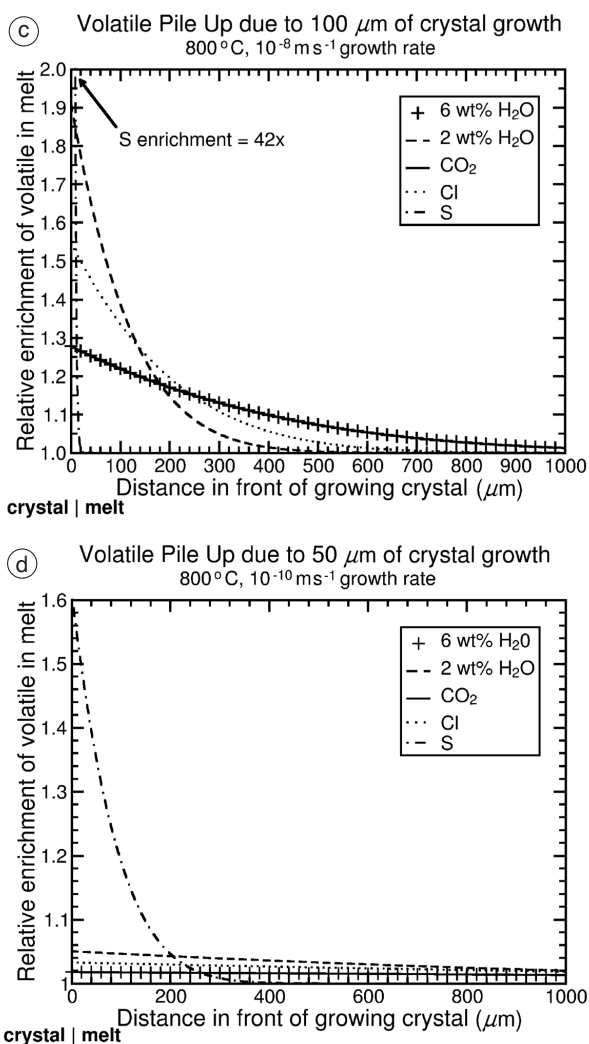

(c) Volatile Pile Up due to 100 μm of crystal growth
800°C, 10^{-8} m s^{-1} growth rate

S enrichment = 42x

+	6 wt% H_2O
--	2 wt% H_2O
—	CO_2
⋯	Cl
·-	S

Relative enrichment of volatile in melt

Distance in front of growing crystal (μm)

crystal | melt

(d) Volatile Pile Up due to 50 μm of crystal growth
800°C, 10^{-10} m s^{-1} growth rate

+	6 wt% H_2O
--	2 wt% H_2O
—	CO_2
⋯	Cl
·-	S

Relative enrichment of volatile in melt

Distance in front of growing crystal (μm)

crystal | melt

Fig. 7c,d. Volatile concentration enrichment profiles in front of a crystal growing in a rhyolitic melt at 800°C. The diffusion coefficients for volatiles are from fig. 5 and the sources of the crystal growth rates are discussed in the text. Note that composition enrichment profiles for 6 wt% H_2O and CO_2 plot on top of one another because their diffusion coefficients are identical at the conditions studied (see fig. 5). The effects of crystal growth on volatile concentration enrichment profiles relative to the concentration at infinite distance near the crystal-melt interface are modelled at a growth rate of 10^{-8} m s^{-1} for a total growth of 100 μm (c). The volatile concentration enrichment profiles after 50 μm of crystal growth at 10^{-10} m s^{-1} are also modelled to demonstrate the effect of crystal growth rate on volatile enrichment (d). Further discussion is found in the text.

713

tain volatile concentrations representative of the bulk melt. In fact, our one-dimensional model provides a conservative estimate of enrichment that would occur during growth and entrapment of a spherical melt inclusion. A more positive way of considering the results of these calculations is that concentrations of H_2O, CO_2 and Cl measured in melt inclusions are unlikely to be more than twice the bulk melt concentration of these volatiles. The existing data on crystal growth in silicic melts (discussed above) indicate that quartz is the slowest growing silicate crystal, with a maximum of approximately 10^{-10} m s^{-1}, and should contain melt inclusions representative of the bulk melt. Our study reinforces the conclusions of Lu *et al.* (1995) who through their study of melt inclusions in crystals from the Bishop Tuff, California, found that melt inclusions larger than 50 μm in diameter should be compositionally equivalent to the bulk melt. If melt inclusions can be trapped near 800°C at what appear to be crystal growth rates below 10^{-10} m s^{-1} (*cf.*, Lu *et al.*, 1995) their volatile concentrations of

H_2O, CO_2 and Cl almost certainly will be representative of the bulk melt, but the minimum growth rate necessary for a crystal-melt interface to become unstable and potentially lead to the entrapment of melt inclusions remains unknown. For example, our experiments on crystal growth in the orthoclase-quartz-water system (Baker and Freda, 2001) did not trap melt inclusions even at a growth rate 5×10^{-9} m s^{-1}.

Modelling the effects of a 10^{-8} ms^{-1} growth rate on H_2O and CO_2 concentration profiles in a basaltic melt at 1300°C (fig. 8) demonstrates that the maximum enrichment, in this case for CO_2, is only a factor of $1.35x$ for 100 μm of growth. The water concentration is insignificantly enriched by a factor of less than 1.08 for the conditions investigated. Despite the small volatile enrichment factors at the crystal-melt interface the concentration profiles do not reach the bulk melt composition until at least 300 μm away from the crystal. This modelling suggests that melt basaltic inclusions trapped at 1300°C contain concentrations of CO_2 and H_2O similar to those of the bulk melt.
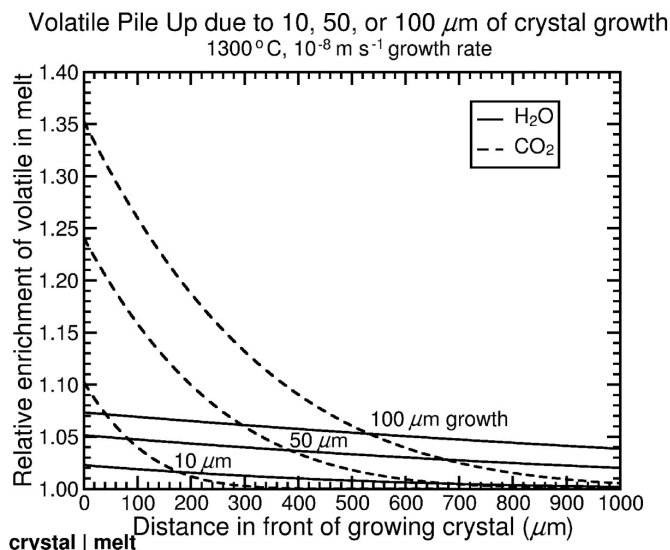

Fig. 8. Volatile concentration enrichment profiles in front of a crystal growing in a basaltic melt at 1300°C. Diffusion coefficients of H_2O and CO_2 are from Zhang and Stolper (1991) and crystal growth rates are based on data in Lasaga (1998) and Simakin *et al.* (2003). For further discussion please see the text.

The calculations highlight the need to know both the diffusion coefficients for volatiles (and other elements for that matter) and crystal growth rates in order to assess whether or not melt inclusions are representative of the bulk melt. Differences of approximately 4 orders of magnitude between diffusion coefficients and crystal growth rates are sufficient to enrich the crystal-melt interface significantly, greater than 10 relative percent, above the bulk melt. The conclusion that melt inclusions formed in basaltic systems trap samples that may be compositionally representative is based only upon calculations for water and carbon dioxide at an unrealistically high temperature of crystallization.

Although the calculations above purposely ignore the possibility of volatile saturation and exsolution due to rapid crystal growth, it is worthwhile to qualitatively consider this possibility. Even though the bulk melt may not be volatile saturated, rapid crystal growth could cause the concentration of a volatile at the crystal-melt interface to reach saturation and exsolve a fluid phase. The concentration necessary to reach saturation in magma chambers at a few kilometres depth varies from the weight percent level for H_2O to only hundreds to thousands of ppm for CO_2, S, and Cl (Carroll and Holloway, 1994). Thermodynamics demands that once one volatile reaches saturation and exsolves the other components in the system must partition between the melt and the fluid phase in order to reach, or attempt to reach, equilibrium. Obviously this process affects volatile concentrations in the melt at the crystal-melt interface and causes them to deviate from those in the bulk melt. If these bubbles were able to separate from the interface before the melt was trapped, there might be no record of exsolution (presuming these bubbles ascend into the bulk, fluid undersaturated, melt they would be resorbed). Only recently are we beginning to measure the equilibrium partitioning of volatile components, primarily H_2O and CO_2 (*e.g.*, Tamic *et al*., 2001), between silicate melts and fluids, so that we are at the beginning stage of quantitatively modelling this process.

Anomalous volatile enrichment of melt inclusions might be detected by measuring volatile concentrations in contemporaneous melt inclusions of differing sizes. Modelling suggests that slowly diffusing sulfur is only enriched within approximately 20 μm of the crystal-melt interface in rhyolitic melts at 800°C (fig. 6), which is consistent with the results of Lu *et al*. (1995); thus if anomalous enrichment due to pile-up during crystal growth occurred, smaller inclusions are expected to be significantly enriched in sulfur compared to larger ones. Once the size of the melt inclusion significantly exceeds the enriched region at the crystal-melt interface, the sulfur concentration should reach a constant, bulk, value. However, our models demonstrate that even when sulfur reaches the bulk melt concentration in large melt inclusions, the concentrations of other volatiles in the inclusion may still be significantly higher than the bulk melt concentrations.

The measurement of volatile diffusion in silicate melts has advanced significantly since Shaw published his work in 1974. Our knowledge of water diffusion in silicic melts is particularly extensive. However, we still need additional measurements of CO_2, S, F and Cl in silicic melts and of the diffusion of all volatiles in intermediate and basic compositions. Additionally, we need to know how water concentration and pressure affect diffusion of other volatiles in all magmatic silicate melts. Our simple models indicate that under conditions of rapid crystal growth diffusion pile-up can occur at crystal-melt interfaces and the melts trapped as melt inclusions may not contain volatile concentrations representative of the bulk melt; this problem appears particularly severe for rhyolitic systems at high crystal growth rates and probably minor for high-temperature basaltic systems.

REFERENCES

BAI, T.B. and A. KOSTER VAN GROOS (1994): Diffusion of chlorine in granitic melts, *Geochim. Cosmochim. Acta*, **58**, 113-123.

BAKER, D.R. (1991): Interdiffusion of hydrous dacitic and rhyolitic melts and the efficacy of rhyolite contamination of dacitic enclaves, *Contrib. Mineral. Petrol.*, **106**, 462-473.

BAKER, D.R. and C. FREDA (2001): Eutectic crystallization in the undercooled orthoclase-quartz-H_2O system: experiments and simulations, *Eur. J. Mineral.*, **13**, 453-466.

BAKER, L.L. and M.J. RUTHERFORD (1996): Sulfur diffusion in rhyolite melts, *Contrib. Mineral. Petrol.*, **123**, 335-344.

BLANK, J.G. (1993): An experimental investigation of the behavior of carbon dioxide in rhyolitic melt, *Ph.D. Thesis* (California Institute of Technology, Pasadena, CA).

BLANK, J.G. and R.A. BROOKER (1994): Experimental studies of carbon dioxide in silicate melts: solubility, speciation, and stable carbon isotope behavior, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 157-186.

BLANK, J.G., E.M. STOLPER and Y. ZHANG (1991): Diffusion of CO_2 in rhyolitic melt, *Eos Trans. Am. Geophys. Un.*, **72**, 312 (abstract).

BLOWER, J.D., H.M. MADER and S.D.R. WILSON (2001): Coupling of viscous and diffusive controls on bubble growth during explosive volcanic eruptions, *Earth Planet. Sci. Lett.*, **193**, 47-56.

BROOKER, R.A., S.C. KOHN, J.R. HOLLOWAY, P.F. MCMILLAN and M.R. CARROLL (1999): Solubility, speciation, and dissolution mechansims for CO_2 in melts on the $NaAlO_2$-SiO_2 join, *Geochim. Cosmochim. Acta*, **63**, 3549-3565.

BROOKER, R.A., S.C. KOHN, J.R. HOLLOWAY and P.F. MCMILLAN (2001): Structural controls on the solubility of CO_2 in silicate melts, Part II. IR characteristics of carbonate groups in silicate glasses, *Chem. Geol.*, **174**, 241-254.

CARROLL, M.R. and J.R. HOLLOWAY (Editors) (1994): Volatiles in magmas, *Rev. Mineral.*, **30**, pp. 517.

CARROLL, M.R. and J.D. WEBSTER (1994): Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 231-279.

DINGWELL, D.B. and C.M. SCARFE (1984): Chemical diffusion of fluorine in jadeite melt at high pressure, *Geochim. Cosmochim. Acta*, **48**, 2517-2525.

DINGWELL, D.B. and C.M. SCARFE (1985): Chemical diffusion of fluorine in melts in the system Na_2O-Al_2O_3-SiO_2, *Earth Planet. Sci. Lett.*, **73**, 377-384.

FOGEL, R.A. and M.J. RUTHERFORD (1990): The solubility of carbon dioxide in rhyolitic melts: a quantitative FTIR study, *Am. Mineral.*, **75**, 1311-1326.

FREDA, C., D.R. BAKER, C. ROMANO and P. SCARLATO (2003): Water diffusion in natural potassic melts, in *Volcanic Degassing*, edited by C. OPPENHEIMER, D.M. PYLE and J. BARCLAY, *Geol. Soc., London, Spec. Publ.* **213**, 53-62.

HARRISON, T.M. and E.B. WATSON (1984): The behavior of apatite during crustal anatexis: equilibrium and kinetic considerations, *Geochim. Cosmochim. Acta*, **48**, 1467-1477.

HAURI, E. (2002): SIMS analysis of volatiles in silicate glasses, 2. Isotopes and abundances in Hawaiian melt inclusions, *Chem. Geol.*, **183**, 115-141.

HAURI, E., A.J.R. KENT and N. ARNDT (2002): Melt inclusions at the millennium; toward a deeper understanding of magmatic processes, *Chem. Geol.*, **183**, 1-3.

KARSTEN, J.L., J.R. HOLLOWAY and J.R. DELANEY (1982): Ion microprobe studies of water in silicate melts: temperature-dependent water diffusion in obsidian, *Earth Planet. Sci. Lett.*, **59**, 420-428.

LAPHAM, K.E., J.R. HOLLOWAY and J.R. DELANEY (1984): Diffusion of H_2O and D_2O in obsidian at elevated temperatures and pressures, *J. Non-Cryst. Solids*, **67**, 179-191.

LASAGA, A. (1998): *Kinetic Theory in the Earth Sciences* (Princeton University Press, Princeton, New Jersey), pp. 810.

LU, F., A.T. ANDERSON and A.M. DAVIS (1995): Diffusional gradients at the crystal-melt interface and their effect on the composition of melt inclusions, *J. Geol.*, **103**, 591-597.

LUHR, J.F., I.S.E. CARMICHAEL and J.C. VAREKAMP (1984): The 1982 eruption of El Chichon volcano, Chiapas, Mexico: mineralogy and petrology of the anhydrite-bearing pumices, *J. Volcanol. Geotherm. Res.*, **23**, 69-108.

MASSARE, D., N. MÉTRICH and R. CLOCCHIATTI (2002): High-temperature experiments on silicate melt inclusions in olivine at 1 atm: inference on temperatures of homogenization and H_2O concentrations, *Chem. Geol.*, **182**, 87-98.

MCMILLAN, P.F. (1994): Water solubility and speciation models, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 131-156.

NOWAK, M. and H. BEHRENS (1997): An experimental investigation of diffusion of water in haplogranitic melts, *Contrib. Mineral. Petrol.*, **126**, 365-376.

NOWAK, M., D. SCHREEN and K. SPICKENBOM (2004): Argon and CO_2 on the race track in silicate melts: a tool for the development of a CO_2 speciation and diffusion model, *Geochim. Cosmochim. Acta*, **68** (24), 5127-5138.

PINEAU, F., S. SHILOBREEVA, A. KADIK and M. JAVOY (1998) Water solubility and D/H fractionation in the system basaltic andesite-H_2O at 1250°C and between 0.5 and 3 kbar, *Chem. Geol.*, **147**, 173-184.

PROUSSEVITCH, A.A. and D.L. SAHAGIAN (1998): Dynamics and energetics of bubble growth in magmas: Analytical formulation and numerical modeling, *J. Geophys. Res.*, **103B**, 18,223-18,251.

PROUSSEVITCH, A.A., D.L. SAHAGIAN and A.T. ANDERSON (1993): Dynamics of diffusive bubble growth in magmas: isothermal case, *J. Geophys. Res.*, **98B**, 22,283-22,307.

ROEDDER, E. (1965): Liquid CO_2 inclusions in olivine-bear-

ing nodules and phenocrysts from basalts, *Am. Mineral.*, **50**, 1746-1782.

ROEDDER, E. (1979): Origin and significance of magmatic inclusions, *Bull. Mineralogie*, **102**, 487-510.

SCRIVEN, L.E. (1959): On the dynamics of phase growth, *Chem. Eng. Sci.*, **10**, 1-13.

SHAW, H.R. (1974): Diffusion of H_2O in granitic liquids: Part I. Experimental data, Part II. Mass transfer in magma chambers, in *Geochemical Transport and Kinetics*, edited by W. HOFMANN, B.J. GILETTI, H.S. YODER JR. and R.A. YUND (Carnegie Institution of Washington, Washington), 139-170.

SIERRALTA, M., M. NOWAK and H. KEPPLER (2002): The influence of bulk composition on the diffusivity of carbon dioxide in Na aluminosilicate melts, *Am. Mineral.*, **87**, 1710-1716.

SIMAKIN, A.G., T.P. SALOVA and P. ARMIENTI (2003): Kinetics of clinopyroxene growth from a hydrous hawaiite melt, *Geochem. Int.*, **41**, 1165-1175.

SMITH, V.G., W.A. TILLER and J.W. RUTTER (1955): A mathematical analysis of solute redistribution during solidification, *Can. J. Phys.*, **33**, 723-744.

SPARKS, R.S.J., J. BARCLAY, C. JAUPART, H.M. MADER and J.C. PHILLIPS (1994): Physical aspects of magma degassing, I. Experimental and theoretical constrains on vesiculation, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 413-445.

STOLPER, E. (1982): The speciation of water in silicate melts, *Geochim. Cosmochim. Acta*, **46**, 2609-2620.

SWANSON, S.E. (1977): Relation of nucleation and crystal-growth rate to the development of granitic textures, *Am. Mineral.*, **62**, 966-978.

SYMONDS, R.B., W.I. ROSE, G.J.S. BLUTH and T.M. GERLACH (1994): Volcanic-gas studies: methods, results, and applications, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 1-66.

TAMIC, N., H. BEHRENS and F. HOLTZ (2001): The solubility of H_2O and CO_2 in rhyolitic melts in equilibrium with a mixed H_2O-CO_2 fluid phase, *Chem. Geol.*, **174**, 333-347.

WALLACE, P.J. (2001): Volcanic SO_2 emissions and the abundance and distribution of exsolved gas in magma bodies, *J. Volcanol. Geotherm. Res.*, **108**, 85-106.

WATSON, E.B. (1982) Basalt contamination by continental crust: some experiments and models, *Contrib. Mineral. Petrol.*, **80**, 73-87.

WATSON, E.B. (1991): Diffusion of dissolved CO_2 and Cl in hydrous silicic to intermediate magmas, *Geochim. Cosmochim. Acta*, **55**, 1897-1902.

WATSON, E.B. (1994): Diffusion in volatile-bearing magmas, in *Volatiles in Magmas*, edited by M.R. CARROLL and J.R. HOLLOWAY, *Rev. Mineral.*, **30**, 371-411.

WATSON, E.B. and J.F. BENDER (1980): Diffusion of cesium, samarium, strontium, and chlorine in molten silicate at high temperatures and pressures, *Geol. Soc. Am. Abstr. Program*, **12**, 545.

WATSON, E.B., M.A. SNEERINGER and A. ROSS (1982): Diffusion of dissolved carbonate in magmas: experimental results and applications, *Earth Planet. Sci. Lett.*, **61**, 346-358.

WATSON, E.B., D.A. WARK and J.W. DELANO (1993): Initial report on sulfur diffusion in magmas, *Eos, Trans. Am. Geophys. Un.*, **74**, 620.

WINTHER, K.T., E.B WATSON and G.M. KORENOWSKI (1998): Magmatic sulfur compounds and sulfur diffusion in albite melt at 1 GPa and 1300-1500°C, *Am. Mineral.*, **83**, 1141-1151.

ZHANG, Y. and H. BEHRENS (2000): H_2O diffusion in rhyolitic melts and glasses, *Chem. Geol.*, **169**, 243-262.

ZHANG, Y. and E.M. STOLPER (1991): Water diffusion in basaltic melts, *Nature*, **351**, 306-309.

ZHANG, Y., E.M. STOLPER and G.J. WASSERBURG (1991): Diffusion of water in rhyolitic glasses, *Geochim. Cosmochim. Acta*, **55**, 441-456.