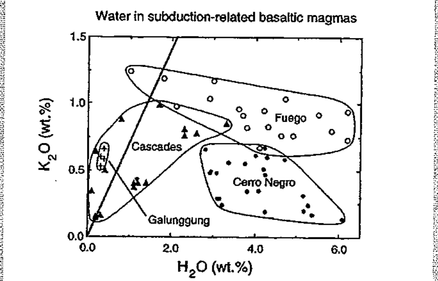

VOLATILES IN MAGMAS

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GLOSSARY

exsolved gas Gas that has been released from solution in a magma. Gas exsolution occurs when pressure is decreased, such as when magma moves toward Earth's surface.

fugacity A gas is considered to be perfect if its behavior can be described by the ideal gas law: $PV = nRT$, where P is pressure, V is volume, n is number of moles, R is the ideal gas constant, and T is temperature. Most gases are not perfect, especially at high pressures or low temperatures. The fugacity is a kind of equivalent pressure that accounts for the deviation of a real gas from ideal gas behavior.

glass If a liquid is cooled very rapidly, it may harden to a glass and not crystallize. Magma contains silicate liquid that, if cooled rapidly enough, forms glass.

immiscible Some types of liquids such as molten iron sulfide will not fully mix with or dissolve into a silicate melt to form a homogeneous solution. Such coexisting liquids are described as immiscible.

magma Natural silicate melt with or without suspended crystals and bubbles.

melt (glass) inclusion During crystallization of magma, many crystals grow imperfectly, trapping small blebs of silicate melt inside the crystals. If the magma is erupted and cooled rapidly, then these trapped inclusions of silicate melt become glass.

saturation A melt can be saturated with respect to certain chemical elements in three ways: It may contain bubbles of a pure gas like H_2O, it may contain crystals rich in the element, such as anhydrite ($CaSO_4$, rich in S), or it may contain droplets of immiscible liquid rich in the element, such as drops of sulfide melt (rich in S). In this review we use the word saturation to refer to saturation with respect to a gas (bubbles of an impure gas are present) and to refer to saturation with respect to a crystal or immiscible melt.

solubility The maximum amount of a volatile species or component that can be dissolved in a silicate melt under a given set of conditions such as pressure, temperature, and melt composition.

viscosity All fluids will flow in response to an applied shear stress, but some fluids flow more slowly than others.

Viscosity can be thought of as the resistance of a fluid to flow. A high-viscosity fluid flows very slowly.

volatile An element or compound such as H_2O or CO_2 that forms a gas at relatively low pressure and magmatic temperature. Volatiles can be dissolved in silicate melts, can occur as bubbles of exsolved gas, and can crystallize in minerals such as biotite and amphibole.

I. DEFINITION AND SIGNIFICANCE OF MAGMATIC VOLATILES

> The observatory worker who has lived a quarter of a century with Hawaiian lavas frothing in action, cannot fail to realize that gas chemistry is the heart of the volcano magma problem.
> —*T. A. Jaggar, 1940*

The quote from T. A. Jaggar, founder of the Hawaiian Volcano Observatory and an influential volcanologist in the first half of the 20th century, attests to the importance of gases in governing volcanic eruptive phenomena. As early as the middle of the 19th century, it was recognized that gas plays a fundamental role in forcing magma to the Earth's surface and generating explosive eruptions. Many different species of gas can dissolve in a molten silicate liquid in the same way that carbon dioxide can dissolve in water. Such gas species are referred to as *volatile components* or *magmatic volatiles* because of their tendency to form gas bubbles at relatively low pressure. The amount of a volatile component that can dissolve in silicate melt increases with pressure. As magma ascends toward the Earth's surface, pressure decreases, thereby decreasing the solubility of volatiles and causing them to come out of solution to form bubbles. In addition, the bubbles expand with further decrease in pressure. At 1 atm pressure and typical magma temperatures, an amount of exsolved H_2O equivalent to one one-thousandth of total magma mass is sufficient to produce a magmatic foam that has more than 90% bubbles by volume! Truly tremendous expansion occurs near the surface as a result of such volatile exsolution, and this provides the driving force for volcanic eruptions, similar to the fountaining of champagne from an uncorked bottle.

Water and carbon dioxide are the most important volatile components in natural magmas. At higher pressures, deeper within the Earth, most of the water and carbon dioxide are dissolved in the silicate melt portion of the magma, and they have important effects on magma crystallization, temperature, density, and viscosity. In the upper mantle, where basaltic magmas are generated by partial melting, volatiles affect the composition of melts and their physical segregation from the residual mantle minerals. After H_2O and CO_2, the most abundant volatiles are sulfur, chlorine, and flourine; sulfur is particularly important for understanding the composition and fluxes of volcanic gas, and all can be significant in the formation of ore deposits. Many other volatiles, such as He, Ar, and B, can dissolve in natural silicate melts (magmas), but they are generally much less abundant. The noble gases, for example, are usually present at concentration levels of <1 part per million (ppm, 0.0001% by weight) in natural magmas. Despite such low concentrations, the isotopic compositions of noble gases have been studied extensively because of their value in understanding large-scale degassing of the Earth and the formation of the atmosphere.

In this chapter, we focus on the abundant volatiles: H_2O, CO_2, and S. We review (1) experimental data on the solubility of volatiles in natural silicate melts, (2) analytical and sampling techniques used for measuring the abundances of volatiles in magmas, (3) volatile abundances in basaltic and silicic magmas typical of various tectonic environments, and (4) Earth degassing and volatile recycling by subduction. We also discuss the evidence for volatile gradients in magmas and pre-eruptive vapor saturation, because both of these are important for understanding explosive eruptive behavior of volcanoes, fluxes of volcanic gases, and the formation of ore deposits. Solubilities and abundances of Cl and F are also mentioned, and we present several references at the end of the chapter that treat Cl and F in more detail.

II. SOLUBILITY OF VOLATILES IN SILICATE MELTS

A. Water and Carbon Dioxide

Solubility refers to the maximum amount of a volatile species or component that can be dissolved under a given set of conditions, such as pressure, temperature, and melt composition. Laboratory measurements of the solubilities of H_2O, CO_2, S, and many other volatile components have been made for a number of different melt compositions. In such laboratory experiments, it is possible to control the parameters that affect solubility. As an example, a silicate melt can be equilibrated with water vapor at high temperature and a variety of

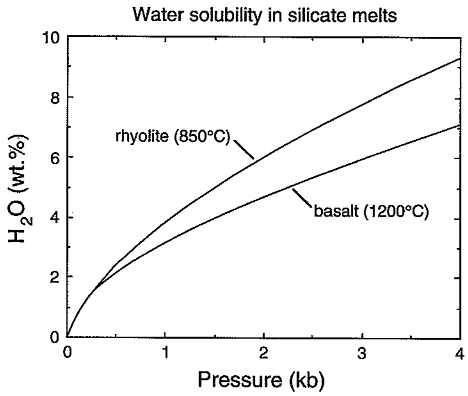

FIGURE 1 Experimental determinations of water solubility in basaltic and rhyolitic melts at typical magmatic temperatures. The solubility of water is greater in rhyolitic melt than in basaltic melt at pressures greater than 0.5 kb. (See Carroll and Holloway, 1994, for reviews of experimental solubility data.)

pressures in order to determine the solubility of water (Fig. 1). Such melt is described as *water saturated* because in the experiment, the melt coexists with water vapor. As seen in the experimental data, the solubility of H_2O in silicate melts is strongly dependent on pressure. This pattern, in which the solubility increases with increasing pressure, is observed for many volatile components, and occurs because the gaseous form of a volatile component has a larger molar volume than does the same component when it is dissolved in a silicate melt. The solubility of H_2O in silicate melts is also dependent on temperature and melt composition, such that H_2O solubility is greater in silica-rich melts (rhyolite) than in silica-poor ones (basalt) at comparable pressures (Fig. 1).

Early studies on the solubility of water in silicate melts recognized that there is a linear relationship between the partial pressure (or fugacity) of H_2O and the square of the mole fraction of dissolved water in the melt. Such a relationship is consistent with a solution mechanism in which water dissolves by forming OH^- groups that are structurally bound to the aluminosilicate network of the melt. More recent studies using infrared spectroscopy have shown that dissolved water in silicate melts occurs as two different species: OH^- groups and H_2O molecules. The relative proportions of the two species vary systematically with total water concentration. At low total dissolved water concentrations, virtually all of the water is present as OH^- groups. As total dissolved water concentration increases, the relative proportion of molecular H_2O increases as well. In rhyolitic melts, the proportions of OH^- groups and H_2O molecules are equal at about 3 wt% total dissolved water, whereas in basaltic melt, the proportions of the two species are equal at about 3.5 wt% total water.

As with H_2O, the solubility of CO_2 in silicate melts is strongly dependent on pressure (Fig. 2). However, CO_2 solubilities are much lower than for H_2O. The amount of CO_2 that dissolves into both basaltic and rhyolitic melts is 50–100 times less, by weight, than the solubility of H_2O at comparable pressure and temperature. Carbon dioxide dissolves in silicate melts in two different species, but in contrast to water, the speciation is controlled by the bulk silicate melt composition. Thus in silica-poor glasses (basalts, basanites, nephelinites), CO_2 is present as structurally bound carbonate (CO_3^{2-}), whereas in high-silica (rhyolitic) melts it occurs as CO_2 molecules. Glasses with intermediate silica contents (andesitic) contain both species. Experimental studies have demonstrated that the solubility of CO_2 is strongly dependent on melt composition, and this compositional dependence reflects, in part, the differences in speciation. For example, carbon dioxide is more soluble in rhyolitic melt (as molecular CO_2) than in basaltic melt (as CO_3^{2-}) (Fig. 2). However, in silica-poor melts, the solubility of CO_2 as carbonate increases with decreasing silica content. Thus the solubility of CO_2 in basanitic

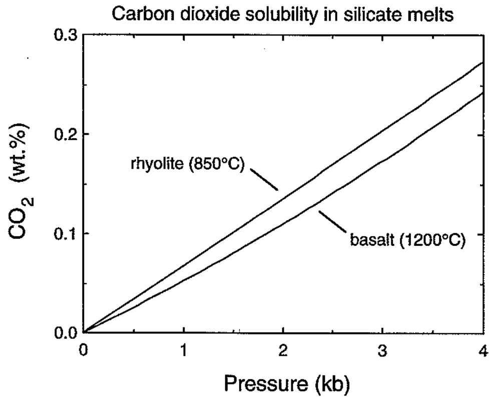

FIGURE 2 Carbon dioxide solubility in basaltic and rhyolitic melts at typical magmatic temperatures as determined by experimental studies and thermodynamic models. As with water, the solubility of carbon dioxide is greater in rhyolitic melt than in basaltic melt. Carbon dioxide dissolves in rhyolitic melts as molecular (CO_2), whereas in basaltic melt it is present as a dissolved carbonate ion (CO_3^{2-}). The slight curvature of the solubility curve for basaltic melt relative to rhyolitic melt results from two factors: (1) small differences in the pressure dependence of solubility for the different melt compositions and (2) greater nonideal behavior for CO_2 gas at the lower temperature of the rhyolitic melt. (See Carroll and Holloway, 1994, for reviews of experimental solubility data.)

melt is similar to that in rhyolitic melt and greater than that in the basaltic melt shown in Fig. 2.

In discussing solubility, it is important to distinguish between saturation and undersaturation with a particular volatile component. *Solubility* refers to the maximum amount of a volatile species or component that can be dissolved in silicate melt at a given set of conditions. In both natural and experimental silicate melts, however, the melt can have a concentration of a dissolved volatile component that is less than the maximum possible. Such a melt is described as *undersaturated* with respect to the volatile component of interest. As an example, laboratory experiments show that a rhyolitic melt can contain about 6% dissolved H_2O at 2 kbar, but this does not mean that all natural rhyolitic melts that are at 2-kbar pressure in the Earth's crust contain this much water. Instead, they could have any amount from 0 to 6 wt%. A rhyolitic melt containing less than the dissolved H_2O needed to saturate the melt at a given temperature and pressure is thus *water undersaturated.*

It is possible in laboratory solubility experiments, as described earlier, to equilibrate a melt with a single gas component such as H_2O. However, in magmas, many volatile components are present together. It is therefore important to distinguish between the dissolved concentrations of individual volatile components and their concentrations in the separate exsolved gas phase. If the sum of the partial pressures of all dissolved volatile components in a magma is equal to the local confining pressure, then the magma is saturated with bubbles of a multicomponent gas containing H_2O, CO_2, S, and other minor gases like Cl, F, and noble gases. Because the volatile species have different solubilities, their relative abundances dissolved in the melt will differ from their relative abundances in the gas phase.

For vapor-saturated silicate melts, the solubilities of individual volatile components are dependent in part on the abundances of other volatiles that are present in the system. This is because the amount of a given component that is dissolved in the melt is proportional to the partial pressure of the volatile component in the coexisting equilibrium vapor. As a example, consider a silicate melt that is saturated with vapor consisting only of H_2O and CO_2. The sum of the partial pressures (P_{H_2O} and P_{CO_2}) of these components in the vapor phase must equal the total pressure in a vapor-saturated melt. Thus at constant total pressure an increase in P_{H_2O}, and hence dissolved H_2O in the melt, must result in a decrease in P_{CO_2} and dissolved CO_2. On a diagram of dissolved H_2O versus dissolved CO_2 in silicate melts, vapor saturation isobars, which show the maximum dissolved H_2O and CO_2 at a given total pressure, have negative slopes (Fig. 3). In many common igneous systems, the partial pressures of other volatile components (e.g., Cl, F, S) are probably relatively small compared with those of H_2O and CO_2. Knowledge of the pre-eruptive concentrations of H_2O and CO_2 in a magma can thus potentially constrain the pressure at which the magma was stored before eruption.

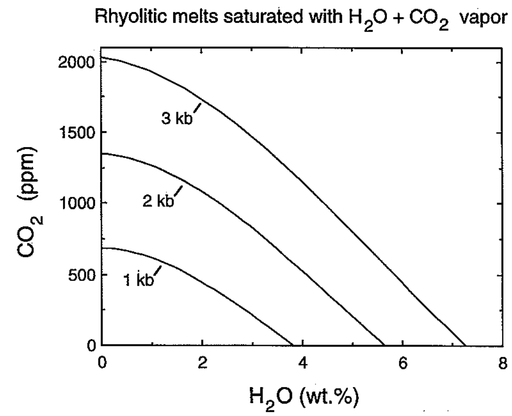

FIGURE 3 H_2O and CO_2 solubility in vapor-saturated rhyolitic melts at 850°C and 1- to 3-kb pressure based on experimental data and thermodynamic models. The curvature of the saturation curve for a given pressure results from the nonlinear dependence of H_2O solubility on pressure (see Fig. 1). (See Carroll and Holloway, 1994, for reviews of experimental solubility data and thermodynamic models.)

B. Sulfur

The behavior of S in silicate melts is complex because the solubility of S is controlled by the stabilities of sulfide and sulfate-bearing phases and because dissolved S can occur in multiple valence (oxidation) states. The speciation of dissolved S in silicate melts is related to the relative magmatic oxygen fugacity (Fig. 4). At relatively low oxygen fugacities, S is present in solution mainly in the reduced form sulfide (S^{2-}), whereas under more oxidizing conditions, sulfate (S^{6+}) appears to be the dominant species. For the range of oxygen fugacities from slightly lower than the nickel-nickel oxide (NNO) buffer to almost 2 $\log_{10}$ units above NNO, both dissolved sulfide and sulfate are present in significant quantities (Fig. 4). The maximum S that can be dissolved in silicate melt is controlled by saturation of the melt with an S-bearing phase. At relatively low oxygen fugacities, this phase is either an immiscible iron-rich sulfide liquid (with as much as 10% oxygen), which occurs in high-temperature basaltic melts, or crystalline pyrrhotite ($Fe_{1-x}S$) in intermediate (andesitic) and silicic (rhyolitic) melts. A Cu-Fe sulfide mineral known as *intermediate solid solution*

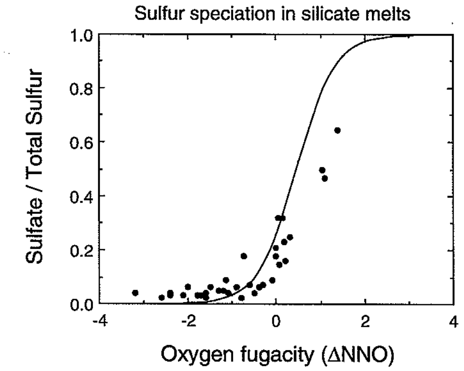

FIGURE 4 Percent of total sulfur that is present as sulfate (sulfate/total sulfur) as a function of oxygen fugacity, relative to the nickel-nickel oxide buffer (ΔNNO). The curve shows the experimental relationship for hydrous andesitic to dacitic melts. Filled circles are data for natural submarine glasses ranging from basalt to andesite in composition. (See Carroll and Holloway, 1994, for reviews of sulfur speciation data.)

may also crystallize from andesitic to rhyolitic melts. At higher oxygen fugacities, the sulfate mineral anhydrite ($CaSO_4$) crystallizes from a wide range of melt compositions. Silicate melts at intermediate oxygen fugacities can crystallize both pyrrhotite and anhydrite, an assemblage that was found, for example, in trachyandesite tephra from the 1982 eruption of El Chichón in Mexico. Experimental solubility studies show that S is more soluble at high oxygen fugacities, under which conditions the dissolved S is present as sulfate, and anhydrite is the stable S-bearing mineral (Fig. 5). The solubility of reduced S (S^{2-}) increases with the Fe concentration in the silicate melt (Fig. 6), which indicates that S^{2-} dissolves largely by complexing with Fe^{2+}. Sulfur solubility under both oxidizing and reducing conditions increases with temperature (Fig. 5).

C. Halogens (Cl and F)

As with S, the solubility of Cl is complex because silicate melt can be saturated with an immiscible alkali chloride melt (molten salt). If water is present, as it invariably is in natural melts, then the immiscible alkali chloride melt will also contain dissolved water and is referred to as a hydrosaline melt. Chlorine solubility in silicate melts is strongly dependent on silicate melt composition, and the solubility generally increases as the ratio (Na + K)/Al in the silicate melt increases. A silicate melt saturated with molten salt has the maximum dissolved Cl. The saturation concentration of Cl varies with pressure, temperature, dissolved water concentration, and silicate melt composition. For silicate melts that are saturated with an H_2O and CO_2-rich vapor phase, maximum Cl solubilities range from several thousand parts per million to ~2 wt%. Thus, Cl solubility in silicate melts is somewhat intermediate between that of H_2O and that

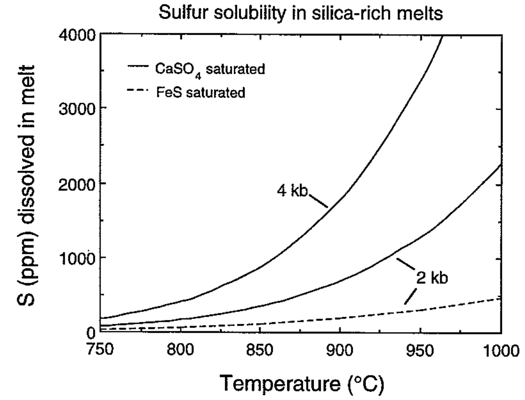

FIGURE 5 Experimental determinations of sulfur solubility versus temperature for hydrous silica-rich melts at different pressures and oxygen fugacities. Curves are shown for both sulfide-saturated melts (oxygen fugacity at the NNO buffer) and sulfate-saturated melts (oxygen fugacity at the MnO-Mn_3O_4 [MNO] buffer). At 2-kbar pressure, S is more soluble under oxidizing conditions (MNO) than under reducing conditions (NNO). The solubility curve for sulfate-saturated melts (MNO buffer) at 4 kbar shows that sulfate solubility increases with increasing pressure. (See Carroll and Holloway, 1994, for reviews of experimental solubility data.)

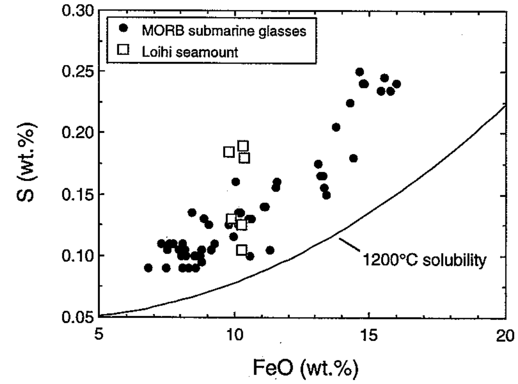

FIGURE 6 Covariation of sulfur and FeO in submarine mid-ocean ridge basalt (MORB) glasses and submarine basaltic glasses from an oceanic island volcano (Loihi seamount). Experimental solubility curve for S in basaltic melts at 1200°C is shown for comparison. Both natural and experimental data are for total S. The natural glasses form an array parallel to the experimental solubility data but offset to higher S contents. This is due to the lower oxygen fugacities of the experimental data compared with natural basaltic magmas. (Data from Wallace and Carmichael, 1992.)

of CO_2. In addition, it is possible for a silicate melt to be saturated with both hydrosaline melt and an H_2O and CO_2-rich vapor phase.

A natural silicate melt may contain less dissolved Cl than the amount needed to saturate the melt with either molten salt or hydrosaline melt. Many common magma types do not contain Cl-rich mineral phases or evidence of hydrosaline melt. By comparison with experimental Cl solubility studies, most magmas probably have insufficient dissolved Cl to be saturated with hydrosaline melt. In some Cl-rich magmas, however, formation and separation of a hydrosaline melt phase or alkali-chloride-rich vapor may play an important role in the formation of magmatic-hydrothermal ore deposits. For magmas that are saturated with an H_2O and CO_2-rich vapor phase, Cl partitions strongly into the vapor. Experimental studies suggest that the concentration, by mass, of Cl in the vapor phase can be 5–20 times or more greater than the mass concentration dissolved in the melt.

The solubility and speciation of dissolved F in silicate melts is complex and still not well understood, but available data clearly show that solubility is strongly dependent on silicate melt composition. In general, F is highly soluble in silicate melts, similar to H_2O. In granitic composition melts, as much as 10 wt% F can be dissolved. Natural melts generally have much lower dissolved F. Rare melts, such as those in tin and topaz-bearing rhyolitic magmas, may contain as much as 5 wt% F, and ultrapotassic mantle-derived magmas can contain as much as 2 wt% F.

III. MEASURING MAGMATIC VOLATILE CONTENTS

All terrestrial magmas contain dissolved volatiles, the most abundant being H_2O, CO_2, S, Cl, and F. If the dissolved concentrations of volatiles are sufficiently high, a magma may be vapor saturated such that the magma also contains an exsolved vapor (gas) phase. Assessing the total volatile content of magma requires that both dissolved and exsolved volatile abundances be known. Because the solubility of most volatile components is strongly pressure dependent, magmas exsolve gas during ascent to the surface. To understand the crystallization and physical properties of magma, as well as to understand eruptive behavior, it is important to know the total volatile content of magma during its pre-eruptive storage within the Earth's crust. Dissolved volatiles may be estimated in many ways, but exsolved volatiles are difficult to assess. The following discussion focuses primarily on dissolved volatiles; we discuss exsolved volatiles in a subsequent section.

A. Experimental Phase Equilibria

One of the most valuable methods for estimating dissolved volatile concentrations in magmas, particularly H_2O and CO_2, is through the use of phase equilibrium experiments. The assemblage of minerals that crystallizes from a melt of a given bulk composition and the sequence and temperature of appearance of those minerals during cooling, varies depending on pressure and dissolved H_2O concentration (Fig. 7). By equilibrating a given rock composition at various temperatures, pressures, and H_2O concentrations, it is frequently possible to find a relatively narrow range of conditions under which the observed phenocryst assemblage in the rock is in stable equilibrium. This technique is particularly suited to constraining the dissolved concentrations of H_2O during pre-eruptive crystallization and storage of magma within the Earth's crust. Experimental studies

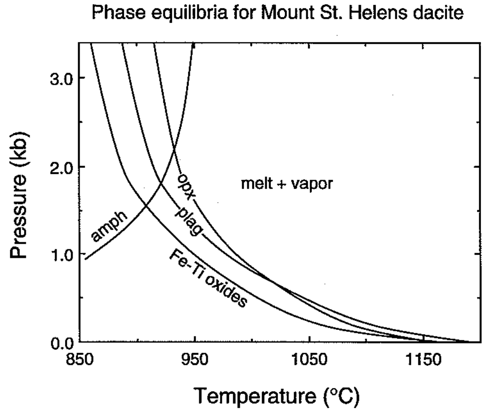

FIGURE 7 Experimental phase equilibria for 1980 Mount St. Helens dacite as a function of temperature and pressure for water-saturated melts. Because dissolved H_2O increases with pressure (Fig. 1), the water contents of the experimental melts increase along the vertical axis of the diagram. With increasing pressure (and dissolved H_2O), the temperatures at which anhydrous minerals (pyroxene, plagioclase, Fe-Ti oxides) begin to crystallize are significantly diminished. In contrast, increasing pressure and dissolved H_2O increase the stability of amphibole, which therefore crystallizes at higher temperatures as pressure increases. Comparison with the actual observed mineral assemblage in the 1980 Mount St. Helens dacite indicates pre-eruptive temperature and pressure of 920°C and ~2.2 kbar. (Modified from Rutherford *et al.*, 1985.)

have been applied with great success to a number of recent volcanic eruptions, most notably, the eruptions of Parícutin (1943–1951), Mount St. Helens (1980), El Chichón (1982), Mt. Pinatubo (1991), and Montserrat (1996–1998).

In addition to its effect on phase stability, dissolved H_2O also affects the composition of minerals that crystallize from silicate melts. The most useful effect related to magmatic H_2O concentrations is the change in plagioclase composition that occurs with variations in dissolved H_2O. As the dissolved H_2O concentration in a melt is increased, the equilibrium plagioclase composition becomes more calcic (anorthite-rich). As discussed later, anorthite-rich plagioclase phenocrysts are common in subduction-related basaltic magmas, providing evidence of relatively high concentrations of H_2O compared to basaltic magmas from other tectonic environments.

B. Analysis of Quenched Glass (Submarine Glasses, Melt Inclusions, Matrix Glass)

Subaerially cooled volcanic rocks and tephra have lost nearly all of their original magmatic volatiles because of the low pressures of Earth's atmosphere. In contrast, during deep submarine eruptions, the confining pressure exerted by the overlying water may prevent exsolution and loss of many volatile species. Such pressures can be as great as 500–600 bar. Submarine-erupted magmas typically form glassy skins where hot magma is rapidly quenched against cold seawater. Volatiles may be retained dissolved within such glassy basalt, which can be analyzed for volatiles directly. H_2O is relatively soluble in basaltic melt and as much as 2 wt% may be retained in deep sea basalt glass without eruptive loss. In contrast, for relatively insoluble CO_2, the pressures on the seafloor are commonly insufficient to prevent exsolution. This results in small vesicles in quenched submarine glasses, usually less than 1% by volume. The small size of these vesicles and their relatively low volumetric abundance result in isolated (noninterconnected) bubbles trapped in the quenched glass. Bulk analyses of these glassy rocks can therefore be used to assess total volatile concentration in the erupted magma, but the magma may have gained or lost bubbles before eruption. Bulk analyses of low-solubility volatiles like CO_2 in samples of glass with trapped bubbles commonly give greater concentrations than do direct microanalyses of the glass.

Another important source of information on the dissolved volatile concentrations of magmas is through the analysis of glass inclusions trapped inside of crystals. When melts crystallize, the crystals grow imperfectly, causing small amounts of melt to be trapped inside of the crystals. If the magma erupts and cools rapidly, then these trapped melt inclusions quench to glass (Fig. 8). Because the crystalline host for the inclusions is relatively rigid, they act as tiny pressure vessels and keep the trapped melt at high pressure, even though the bulk magma decompresses to surface pressure during eruption. For this reason, trapped melt (glass) inclusions commonly retain their original dissolved volatiles. However, melt inclusions may in many instances leak volatiles during explosive eruption due to cracks in the host mineral. This is especially problematic for inclusions in minerals with relatively good cleavages, such as hornblende and plagioclase. Melt inclusions in phenocrysts are trapped during crystal growth and thus sample the liquid from which the crystals grew at the time of entrapment. Inclusions that are trapped at different times during crystallization may preserve a record of changing magma compositions due to processes such as crystal fractionation and magma mixing. Glassy reentrants and hourglass inclusions (Fig. 8C) reveal the composition of melt just before eruption. Pressure-dependent concentrations of volatiles in melt inclusions, hourglass inclusions, and reentrants can reveal crystal settling and decompressive ascent of magma.

Quenched glassy scoria or pumice that formed during subaerial eruptions can also be analyzed for volatiles. Generally such material has extensively degassed during eruption and quenching, so measured volatile contents do not reflect those before eruptive decompression. Analyses of scoria glass or pumice can, nevertheless, be useful for interpreting degassing and eruptive processes.

C. Thermodynamic Calculation Based on Mineral Compositions

One method that has commonly been used to estimate volatile concentrations in magmas is the application of thermodynamic calculations. For example, reactions involving hydrous minerals and their anhydrous breakdown products can be used along with thermodynamic properties of the phases to estimate water concentrations. One exemplary reaction is:

$$\begin{array}{ll} \mathrm{KFe_3AlSi_3O_{10}(OH)_2} & + \ 1/2\mathrm{O_2} \\ \text{biotite} & + \ \text{gas} \end{array}$$

$$\begin{array}{l} = \mathrm{KAlSi_3O_8} + \mathrm{H_2O} + \mathrm{Fe_3O_4} \\ = \text{feldspar} + \text{gas} + \text{magnetite} \end{array}$$

This equation can be used to calculate the water fugacity at the time of crystallization for any volcanic rock containing biotite, feldspar, and magnetite, provided the oxygen fugacity can also be estimated. Then a thermodynamic solubility model calibrated on experimental data can be used to convert the H_2O fugacity to dissolved H_2O concentration. Comparison of this technique with estimates of dissolved H_2O from phase equilibrium and melt inclusion studies shows variable agreement. In general, this approach does not offer the precision or accuracy of modern techniques used to analyze directly volatile concentrations in glasses, but it can be very useful if other types of data are unavailable.

Another way in which thermodyamic equations are commonly used to infer volatile concentrations is through the use of pyrrhotite composition to estimate fugacities of S species. Pyrrhotite ($Fe_{1-x}S$) has variable Fe (and other minor element) concentrations. Experimental data on pyrrhotite combined with thermodynamic calculations make it possible to use pyrrhotite composition to estimate S_2 fugacity. Provided the oxygen and water fugacities are independently known, one can calculate the fugacities of both H_2S and SO_2. It is not possible, however, to convert the fugacities of the various S species into concentrations of dissolved S, as is done with H_2O, because experimentally calibrated solution models for pyrrhotite-saturated melts are not available.

D. Fluid Inclusions

The presence of primary fluid inclusions in minerals from volcanic or plutonic rocks provides evidence that crystallizing melts were vapor and/or brine saturated. However, it can be difficult to distinguish between primary fluid inclusions, trapped during igneous crystallization, and secondary inclusions formed by lower temperature hydrothermal processes. Many volcanic phenocrysts from basaltic rocks contain dense CO_2-rich, primary fluid inclusions, indicating that the basaltic magma was CO_2 saturated during crystallization. Such inclusions can be used to estimate the pressure of inclusion entrapment. Knowledge of this, coupled with experimentally determined CO_2 solubilities in basaltic melt, can be used to

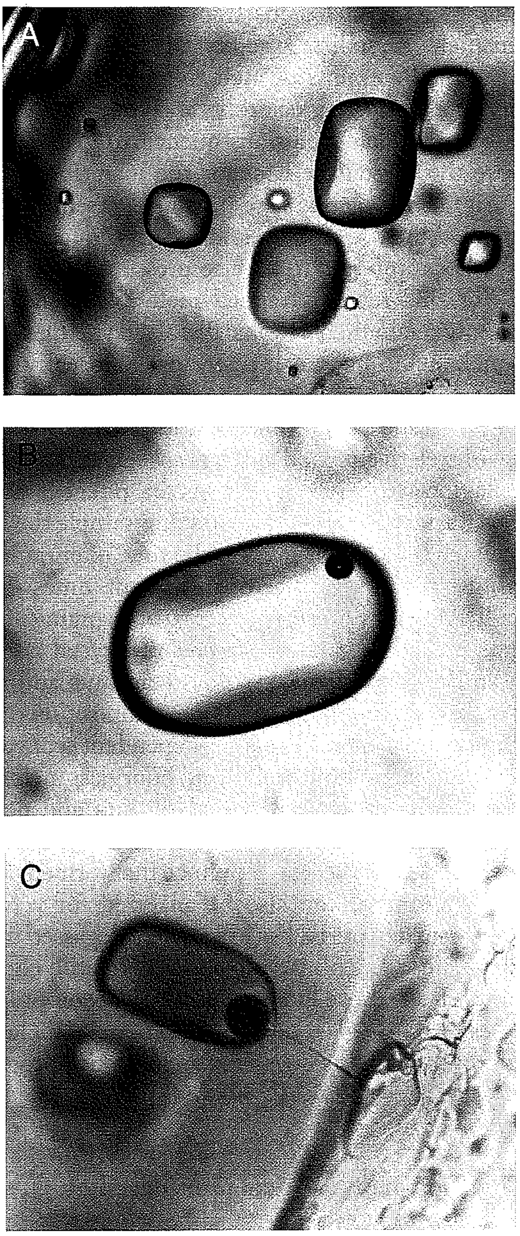

FIGURE 8 Glass (melt) inclusions in crystals from volcanic rocks. (A) A fragment of an ~3-mm quartz phenocryst from the rhyolitic Bishop Tuff containing inclusions of glass up to about 100 μm in diameter. (B) Close-up of a melt inclusion containing a small vapor bubble. The inclusion is about 80 μm long and is partly faceted. Bubbles that are small relative to the inclusion size form during cooling after the inclusion is trapped because the melt in the inclusion contracts more on cooling than does the surrounding quartz host crystal. (C) An hourglass inclusion in a late Bishop quartz. The neck of the hourglass is about 3 μm in diameter and it connects the inclusion to a small depression or dimple on the exterior surface of the quartz phenocryst. The main body of the hourglass is partly faceted, partially finely devitrified, and it contains a ~5 vol% bubble near the neck. The bubble grew as melt moved outward from the inclusion through the neck to the ascending (decompressing) melt outside of the crystal. Study of hourglass inclusions provides a way to estimate the rate of magma rise and the duration of eruption.

estimate the dissolved CO_2 concentration of the basaltic magma at depth. Phenocrysts in more evolved volcanic rocks (dacites, rhyolites) may contain inclusions containing one or more of the following: fluid, vapor, hydrosaline melt, daughter crystals. The presence of these inclusions also can be taken as evidence for vapor saturation during crystallization, but the multicomponent nature of such inclusions (H_2O–CO_2–NaCl) makes it difficult to infer the original dissolved volatile concentrations in the coexisting silicate melt.

E. Saturation with Volatile-Rich Minerals and Immiscible Liquids

The most common volatile-rich minerals and immiscible liquids that occur in magmas are sulfide and sulfate minerals and immiscible sulfide (Fe-S-O) liquid. The presence of one or more of these phases in a quenched volcanic rock indicates pre-eruptive saturation with a S-rich phase. By comparison with experimental solubility data, this makes it possible to infer a pre-eruptive dissolved S concentration. For basaltic melts at low oxygen fugacities, thermodynamic solution models similar to those for H_2O and CO_2 are available, allowing precise estimates of dissolved S for sulfide-saturated melts. Under oxidizing conditions and for more silica-rich magmas, no such solution models are available, but there is an excellent experimental database covering a wide range of melt compositions and oxygen fugacities that can be used to make estimates of dissolved S concentration.

For volatile species whose solubility in a melt is controlled by the presence of a volatile-rich mineral or melt, such as a sulfide phase, complex changes in solubility can occur during magma cooling and differentiation. As an example, it has been observed in quenched glassy submarine pillow rinds from midocean ridge basalts (MORB) that only a small amount ($<1.5\%$ by mass) of the total S in the magma is present as quenched sulfide globules. This observation may seem somewhat surprising when one considers that the strong temperature dependence of S solubility should cause considerable precipitation of immiscible sulfide liquid during cooling. However, the observed low quenched sulfide globule abundance is consistent with thermodynamic and experimental assessment of the effects of differentiation on S solubility. During the cooling and crystallization of MORB magmas, residual liquids become increasingly Fe enriched due to fractional crystallization of silicate phases. The increase in Fe content increases the S solubility in the melt by an amount that is greater than the decrease in S solubility brought about by cooling. This results in differentiated Fe-Ti basalts that have higher dissolved S than the parental (unfractionated) magmas. This effect, combined with the increase in residual melt S brought about by crystallization, keeps MORB magmas finely balanced just at the S saturation point, causing the total mass of S in immiscible sulfide liquid to be small throughout the course of differentiation. In contrast, Kilauean tholeiitic magmas do not show an Fe-enrichment trend because crystallizing and fractionating olivine contains approximately the same weight percent FeO as the liquid from which it precipitates. In the absence of Fe enrichment, if the melt is saturated with immiscible sulfide liquid, then the solubility of S will decrease significantly as temperature decreases.

IV. ANALYTICAL TECHNIQUES FOR MEASURING VOLATILE ABUNDANCES IN SILICATE GLASSES

A large number of analytical techniques have been used to measure volatile concentrations in silicate glasses. These techniques fall into two main categories—bulk extraction techniques, in which a bulk rock or glass sample is crushed and analyzed, and microanalytical techniques, in which a tiny portion of glass is analyzed. Bulk extraction techniques can make it difficult to distinguish between the volatiles that are actually dissolved in quenched magmatic liquid (e.g., glassy submarine pillow rinds) and the volatiles that may be present in unopened vesicles. Furthermore, it is critical to select material for analysis that is free of alteration. Microanalytical techniques offer high spatial resolution, making it possible to analyze a tiny portion of alteration-free glass. The variety of analytical techniques available for volatile analysis makes a thorough review beyond the scope of this chapter. References to detailed reviews of analytical techniques are given at the end of the chapter.

V. VOLATILE ABUNDANCES IN BASALTIC MAGMAS

As an introduction to discussing volatiles in basaltic magmas, we first briefly review the abundance and storage of volatiles in Earth's mantle, from which basaltic magmas are generated by partial melting. Volatiles in the Earth's mantle can reside in a number of potential minerals. Recent infrared spectroscopic studies have demonstrated that significant quantities of water can be present as structurally bound OH^- in the nominally anhydrous minerals olivine, pyroxene, and garnet. Water and other volatiles, such as Cl and F, could also be stored in hydrous minerals such as amphibole, phlogopite, and apatite. Carbon may be stored in magnesian carbonate minerals or as diamond, graphite, or amorphous carbon along grain boundaries of other minerals. Sulfur is bound in sulfide minerals. Estimates of the water content of the depleted upper mantle that is the source region for normal midocean ridge basalts (N-MORB) are on the order of 100–200 ppm H_2O, based on studies of water in MORB glasses. If the depleted mantle extends to the 670-km discontinuity, then an amount of water equivalent to ~10% of the mass of water in the present-day ocean could be contained in the upper mantle. The mantle source regions for enriched midocean ridge basalts (E-MORB) probably contain 300–500 ppm H_2O.

During partial melting, water and other volatiles generally behave as incompatible elements—elements that are enriched in the melt phase—because they are not stoichiometric constituents of the major mantle silicates. Even S, which is contained in sulfides, behaves as an incompatible element because of the low modal abundance of sulfide. Thus basaltic magmas act as agents for outgassing the Earth's mantle by carrying volatiles to the surface.

In the following sections, we discuss the volatile concentrations of basaltic magmas from various tectonic settings. We focus particularly on H_2O because it is the most abundant volatile and exerts the strongest influence on magma physical properties, crystallization and differentiation, and eruptive style. Because of its relatively high solubility, little or no water is degassed from basaltic magmas that are quenched on the seafloor or basaltic melt inclusions trapped inside of growing phenocrysts at crustal pressures. In contrast, less soluble volatiles like CO_2 and the noble gases are strongly concentrated into a coexisting CO_2-rich vapor phase because of their low solubility. Thus quenched basaltic glasses and melt (glass) inclusions do not generally have dissolved CO_2 concentrations that reflect their deep mantle (original) values. Instead, their CO_2 contents are an indication of the pressure at which the glass was quenched on the seafloor or was trapped inside a phenocryst. Other volatiles such as S, Cl, and F remain largely dissolved in melt like H_2O. They are useful in basaltic magmas as indicators of crystallization, degassing, and, in the case of Cl, pre-eruptive contamination of basaltic magma by seawater.

A. Midocean Ridge Basalts

N-MORB magmas have relatively low H_2O contents, typically less than 0.4 wt%, but frequently as low as 0.1–0.2 wt% (Fig. 9). E-MORB magmas, which form a volumetrically minor component of the oceanic crust, have systematically higher concentrations, as great as 1.5 wt%. Water concentrations from comagmatic suites of MORB glasses typically show positive covariation with K_2O. Because K_2O is a non-volatile, incompatible trace element, these correlations indicate that H_2O behaves as an incompatible element during partial melting of the mantle and that significant H_2O is neither lost by degassing nor gained by assimilation in magma reservoirs.

Dissolved CO_2 concentrations in quenched MORB glasses vary from 50 ppm to nearly 400 ppm. Most MORB glasses contain small vapor-filled bubbles as well, indicating vapor saturation of the melt at the time of eruption and quenching. Equilibrium thermodynamic calculations, using measured H_2O and CO_2 contents and experimental solubility data, suggest that the coexisting vapor phase would be 93–100 mol% CO_2. Actual measurements of the vapor composition in MORB vesicles are limited, but most have more than 90 mol% CO_2. Because MORB magmas are saturated with a nearly pure CO_2 vapor, the dissolved CO_2 mea-

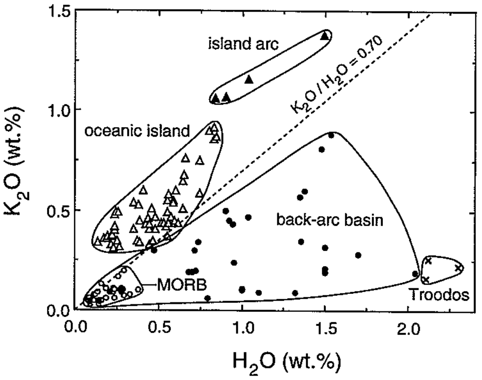

FIGURE 9 Variations in H_2O and K_2O in submarine basaltic glasses from different tectonic environments. Data are shown for midocean ridge basalt (MORB), backarc basin basalt (BAB), ocean island basalt (OIB), island arcs, and for unaltered vesicular glasses from the Troodos ophiolite. (Modified from Muenow *et al.*, 1990.)

surements can be used to estimate a pressure of quenching. Such calculations indicate that many MORB melts were supersaturated with CO_2; that is, they contain more CO_2 than should be dissolved given the pressure equivalent to their depth of eruption on the seafloor. This supersaturation is probably caused by slow diffusion of CO_2 in the basaltic melt during ascent, eruption, and quenching.

Sulfur concentrations in MORB glasses are typically between about 800 and 1400 ppm, but may reach as high as 2500 ppm in Fe-Ti rich basalts. Sulfur contents show strong positive correlation with the FeO content of the melt, consistent with isothermal experimental solubility relations (Fig. 6). Most MORB glasses contain small amounts of quenched immiscible Fe-S-O liquid, indicating that the melts were S saturated at the time of eruption. The most primitive MORB magmas contain 20–50 ppm Cl. In contrast, highly differentiated Fe-Ti-rich basalts contain as much as 1100 ppm Cl, an amount that greatly exceeds what would be expected during closed-system crystallization of basaltic magma. These high concentrations likely reflect assimilation of wallrocks that have been hydrothermally altered by seawater. Fluorine contents of MORB glasses are very low, generally about 0.01–0.06 wt%. Fluorine contents in suites of comagmatic glasses show F increasing with increasing fractionation, in accordance with enrichment in residual liquids during closed-system fractionation.

B. Ocean Island Basalts

Dissolved H_2O in submarine basaltic glasses from ocean island volcanoes ranges from about 0.2 to nearly 1 wt%, significantly higher than N-MORB glass (see Fig. 9). Sulfur concentrations are commonly similar to those in MORB, suggesting that ocean island basaltic magmas, like their midocean ridge counterparts, are saturated with immiscible Fe-S-O liquid before eruption (Fig. 9). Some ocean island basaltic magmas contain as much as 3000 ppm dissolved S but are not highly enriched in FeO, in contrast to S-rich MORB magmas, which are FeO rich. This contrast is consistent with higher oxygen fugacities for these S-rich ocean island basaltic magmas. The higher oxygen fugacities decrease the stability of immiscible Fe-S-O liquid, and a higher dissolved S concentration is required before the basaltic melt is saturated with immiscible Fe-S-O liquid. Thus some ocean island basaltic melts contain more dissolved S than MORB at comparable melt FeO (Fig. 9). Chlorine and F concentrations in ocean island basaltic magmas are relatively low and are comparable to those found in MORB glasses.

An unusual and voluminous series of deep submarine sheet flows composed of highly silica-undersaturated lavas (alkali basalts, basanites, nephelinites) was recently discovered in the North Arch volcanic field, located north of the Hawaiian island of Oahu. Dissolved H_2O in glass samples dredged from these sheet flows are variable and in part high, 0.7–1.4 wt%. Dissolved CO_2 varies from 260 to 800 ppm. These magmas have compositional similarities to the posterosional alkalic volcanics that are erupted on many of the Hawaiian islands after the shield-building stage has ended. Thus the North Arch volcanics provide important information on the volatile contents of alkalic magmatism on oceanic islands.

The best understood oceanic island volcano, and probably the most thoroughly studied volcano on Earth, is Kilauea on the island of Hawaii. The dissolved H_2O concentrations in a variety of basaltic melt inclusions and submarine glasses from Kilauea are shown in Fig. 10. MgO-rich (picritic) glasses from the submarine east rift zone contain mostly 0.37–0.56 wt% dissolved H_2O. In contrast to this rather narrow range, the H_2O contents of basaltic glasses (6.2 ± 0.4 wt% MgO) from the submarine east rift zone vary from 0.10 to 0.85 wt%,

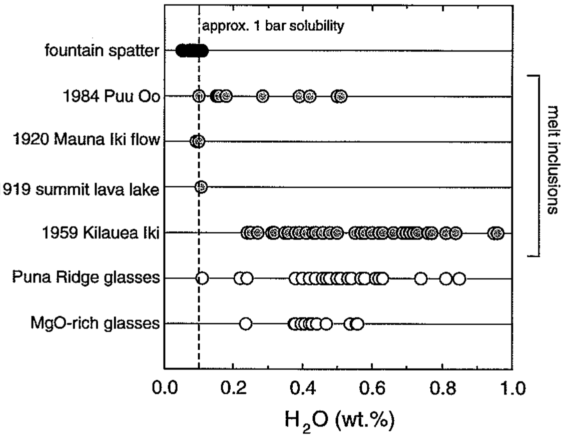

FIGURE 10 Dissolved H_2O concentrations of submarine basaltic glasses (open circles), melt inclusions in olivine phenocrysts (shaded circles), and glassy tephra from lava fountains (solid circles) from Kilauea volcano. Data are shown for MgO-rich glasses, which occur as sand grains in turbidites (Clague *et al.*, 1995) and basaltic glasses (Dixon *et al.*, 1991) from the Puna Ridge, the submarine extension of Kilauea's east rift zone. Data for melt inclusions from the Kilauea Iki eruption of 1959 are from Anderson and Brown (1993). The approximate solubility of H_2O in basaltic melt at 1-bar pressure is shown by the vertical dashed line. (Modified from Wallace and Anderson, 1998.)

and basaltic melt inclusions from olivines in the 1959 Kilauea Iki picrite contain 0.24–0.96 wt%. Melt inclusions from episode 16 of the Puu Oo eruption (1984) contain 0.10–0.51 wt% H_2O. Other melt inclusions from glassy fountain spatter erupted in the summit region and on the southwest rift zone (Mauna Iki) contain about 0.10 wt% dissolved H_2O, which is approximately the 1-bar solubility of water in basaltic melt. Glass from fountain spatter from Kilauea Iki, the 1919 summit lava lake, and Puu Oo all have $\leq$0.10 wt% H_2O.

Degassing at Kilauea is inferred from gas monitoring studies to occur mainly in two stages that are related to subsurface storage and transport of magma. New batches of mantle-derived magma that enter Kilauea from below are probably saturated with a gas rich in CO_2. The solubility of CO_2 at the pressures within the summit magma reservoir is low, and the first stage of degassing occurs as most of the CO_2 is lost through noneruptive degassing. The amount of H_2O that is lost with the CO_2 in the first stage depends on the amount of CO_2 and the pressure, but is generally small, because H_2O is highly soluble in melt. The second stage of degassing occurs when CO_2-depleted magma from the summit reservoir moves along one of the two rift systems through dikes several kilometers below the surface, and then erupts, releasing H_2O-rich gas.

Recognizing primary magmatic volatile contents and undersanding eruptive degassing can be complicated by drainback of magma. Drainback was well documented for the 1959 Kilauea Iki eruption: Magma that degassed during eruption collected into a surface lava lake and then drained back into the vent. Drainback magma can mix with unerupted magma stored at depth to yield partially degassed hybrid magmas. Degassed hybrid magmas, with variable and in part low concentrations of H_2O (0.1–0.85 wt%) and S (0.02–0.15 wt%), have been erupted on the deep submarine flanks of Kilauea. Although the submarine basalts erupted and were collected from depths at which hydrostatic pressure would have prevented significant coeruptive loss of H_2O, the low concentrations of H_2O have been interpreted as reflecting low-pressure degassing prior to repressurized submarine eruption. Such degassing could have occurred by (1) eruption and drainback in the summit region prior to magma being transported down the rift, (2) existence of open fractures connecting magma storage zones to the surface such that pressures were much less than lithostatic, or (3) noneruptive degassing by magma convection in a conduit. The wide range in both submarine glass and melt inclusion H_2O contents and, in particular, some very low values that occur (Fig. 10), presumably reflect degassing at pressures substantially less than those in Kilauea's summit magma storage reservoir.

C. Island Arc and Continental Margin (Subduction-Related) Basalts

It was first suggested in the early 1960s, before the advent of the modern concept of plate tectonics, that subduction of altered oceanic rocks beneath the Aleutian arc was responsible for recycling water into the mantle source region of arc magmas. Early measurements of the H_2O content of submarine basaltic glasses from the Marianas arc (0.8–1.5 wt% H_2O) and in melt inclusions from the 1974 eruption of Fuego, Guatemala, led to a view that water played a relatively minor role in the generation of arc basalts. More recent experimental studies on plagioclase-melt equilibria in low-MgO, high-alumina basalts, which are common in arcs worldwide, suggested H_2O concentrations of 4–6 wt%. Recent measurements of melt inclusions from arc basalts by ion microprobe and IR spectroscopy have yielded H_2O concentrations as high as 6 wt% (Fig. 11).

High H_2O concentrations in arc basaltic melts support the view that water is recycled into the mantle by subduction, where it fluxes significant partial melting and formation of hydrous basaltic magma. However, there are other possible sources for some of the water in arc basaltic magmas apart from a recycled oceanic crustal component, especially in arcs built on continental crust, in which significant assimilation of lower crustal material

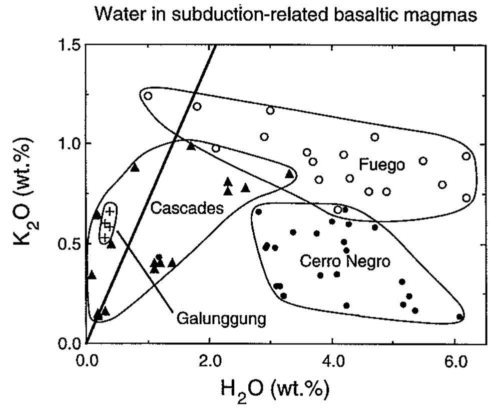

FIGURE 11 Variations in H_2O and K_2O in subduction-related basalt and basaltic andesite melt inclusions from Cerro Negro (Nicaragua), Galunggung (Indonesia), Fuego (Guatemala), and the southern Cascades, western United States. Data are from studies by Roggensack *et al* (1997), Sisson and Layne (1993), and Sisson and Bronto (1998). Heavy line shows a K_2O/H_2O ratio of 0.7 (c.f. Fig. 9).

may occur. On a global scale, it is now recognized that arc basaltic magmas may vary considerably in H_2O content, both within and between arcs. Some arc basaltic magmas also contain significant dissolved carbonate, with reported concentrations as high as 1000 ppm in melt inclusions in olivine phenocrysts from Central America and Indonesia. The carbonate may, in part, have ultimately been derived from subduction of carbonate-rich marine sediments. Indeed, the isotopic composition of carbon in CO_2 from gases at some arc volcanoes provides evidence for such recycling of carbon by subduction processes. The complex relationship between recycling of volatiles by subduction to the mantle beneath arcs and the generation of basaltic magmas is still poorly understood.

D. Backarc Basin Basalts

Basaltic magmas from backarc basins show wide variations in H_2O concentration, ranging from values as low as those in the most H_2O-poor N-MORBs (0.1–0.2 wt%) to values as high as 2 wt% (Fig. 9). Such variations reflect the range of bulk chemical composition of backarc basin basalts, which can vary from MORB-like to showing many similarities to island arc volcanics. Dissolved CO_2 in submarine basaltic glass samples from the Marianas Trough are between 100 and 200 ppm. Negative covariation between H_2O and CO_2 in these glasses and pressure estimates based on experimental solubility data suggest that the samples were vapor saturated at their depth of eruption and quenching, consistent with the presence of vesicles in the glassy pillow rims. Therefore, the bulk magmatic concentrations of H_2O and CO_2 may be significantly greather than the dissolved concentrations. Chlorine concentrations vary from 100 to 800 ppm and show positive correlation with H_2O in some comagmatic suites of glasses.

Some H_2O-rich basaltic magmas erupted in backarc basins or the submarine portions of island arcs have high enough water concentration that they vesiculate and degas dissolved H_2O even during eruption in very deep water. These glasses are distinguished by their relatively high vesicularities (as much as 50% vesicles by volume). As expected, they also have anomalously low concentrations of volatile components, such as S, that exsolve from magma together with H_2O.

Vesicular fresh glasses from pillow margins in the Troodos ophiolite (Cyprus) have volatile contents that are similar to backarc basin basaltic glasses (Fig. 9). These similarities support the interpretation that this ophiolite originated in a backarc basin tectonic setting.

E. Flood Basalts and Large Igneous Provinces

Huge outpourings of basaltic lava to form continental flood basalts and oceanic plateaus (or large igneous provinces; e.g., Kerguelen plateau, Ontong Java plateau) have various ages and tectonic settings. Large igneous provinces were common during the Cretaceous and may reflect a mode of heat loss (and consequent outgassing) from the interior of the planet that is fundamentally different than in currently active plate tectonics. Few data are available on pre-eruptive magmatic volatile abundances in these types of magmas. Such data would be of considerable importance because these very large volume units could have released sufficient volatiles to Earth's atmosphere in a short time to significantly perturb global climate. For example, flood basalts of the Deccan traps erupted near the Cretaceous–Tertiary boundary, leading to the idea that their associated ashes and sulfuric acid aerosols cooled the planet enough to cause the mass extinction. This idea does not have wide acceptance now that a large impact structure has been identified as dating from the Cretaceous–Tertiary boundary. However, the rates of formation of provinces of flood basalts and large igneous provinces, and thus their effects on climates and oceans, are poorly constrained.

VI. VOLATILE ABUNDANCES IN SILICIC MAGMAS

A. Andesites

Andesitic magmas typify convergent plate margins and their volatiles play major roles in planetary degassing and differentiation. However, volatile abundances have been less well studied in andesitic magmas than in either basaltic or silicic magmas. Several reasons for this are that (1) deep submarine-erupted andesitic glasses are rare, and typical subaerial andesites have 30 wt% or more of phenocrysts set in a more siliceous matrix or glass; (2) andesitic magmas do not normally contain either olivine or quartz, the minerals that commonly have large melt inclusions and are the best containers for melt inclusions to prevent posteruptive volatile leakage; and (3) experimental studies of H_2O-rich andesitic compositions have been hampered both by technical problems as well as by problematic application to natural disequilibrium mineral assemblages. Probably the most important result of phase equilibrium studies on andesitic magmas is that a minimum of ~3 wt% dissolved H_2O is necessary to stabilize hornblende, a common phenocryst mineral in andesites. However, hornblende stability is also strongly affected by other factors, such as the Na_2O content of the coexisting silicate melt. Thermodynamic analysis of plagioclase-liquid equilibria in andesitic magmas from the western Mexican volcanic belt suggests about 2.5–4 wt% H_2O in hornblende-bearing andesites and about 1 wt% in andesites that lack hornblende. Analyzed melt inclusions from andesitic magmas in other subduction-related volcanic arcs vary from about 1–4 wt% H_2O. We should reemphasize, however, that these analyses are from phenocryst-rich andesitic magmas in which the interstitial melt portion of the magma, as well as trapped melt inclusions, are relatively silica rich (69–74 wt% SiO_2).

Sulfur concentrations measured in andesitic melt inclusions from subduction zone magmas are normally ≤1000 ppm, with typical values of 200–400 ppm. Sulfur generally shows a positive correlation with the FeO content of the melt. There is a significant difference in the origin of this correlation and the one observed for MORB magmas, though both are related to the effect of melt FeO content on S solubility. During cooling, crystallization, and differentiation of MORB magmas, there is an increase in melt FeO in residual liquids that increases S solubility. In contrast, during crystal fractionation of andesitic magmas, residual liquids have decreasing FeO contents, such that the S solubility in andesitic melts decreases during cooling and crystallization. A further complexity of interpreting S variations in andesitic magmas is related to oxygen fugacity. The range of oxygen fugacity for typical andesitic magmas varies from slightly below the NNO buffer reaction to about 2 log units more oxidized than NNO. Over this range, sulfur speciation changes from dominantly sulfide to dominantly sulfate (see Fig. 4). Thus solubility limits for S in andesitic magmas and their variations during crystallization differentiation are potentially complex. In a few cases, S in andesitic melt inclusions is as great as 3000 ppm; this probably reflects a relatively high magmatic oxygen fugacity because sulfate is much more soluble than sulfide.

Limited data on halogen abundances in andesitic melt inclusions indicate ~1500 ppm Cl and ~500 ppm F.

B. Dacites and Rhyolites

Water and many other volatiles are relatively abundant in silicic magmas both as dissolved species and in exsolved gas. High concentrations of H_2O, in particular, provide the energy for the powerful explosive eruptions that typify silicic magmas. Glassy dacitic and rhyolitic melt inclusions are common in rapidly quenched phenocrysts from explosive eruptions, and analyses of the inclusions commonly reveal 3–7 wt% H_2O. Experimental phase equilibrium studies reveal temperatures and depths of equilibration, and dissolved H_2O concentrations. Analytical (melt inclusion) and experimental results are broadly consistent for dissolved volatiles. Experimental phase equilibria studies cannot be used, however, to determine whether a magma was vapor saturated before eruptive decompression. For cases where independent data suggest pre-eruptive vapor saturation, phase equilibria can constrain the composition of the vapor.

Water-rich rhyolitic melt inclusions are typical of low-temperature (700–800°C) melts containing hydrous phenocrysts of biotite and amphibole. Less H_2O is found in rhyolitic glasses that cooled from higher temperatures (900–1000°C) and contain pyroxene but no hydrous phenocrysts. Wide variations in dissolved CO_2 are found in rhyolitic melt inclusions, varying from 10 to about 1200 ppm. Based on the pressure-dependent solubilities of H_2O and CO_2 in rhyolitic melts, the melt inclusion data can be used to compute the pressure at which the melt would be saturated with a vapor phase (the vapor-saturation pressure) and thereby constrain pressures of crystallization (inclusion formation). For vapor-saturated magmas the indicated vapor-saturation pressure equals the pressure of crystallization. For magmas lacking vapor (vapor undersaturated), the actual pressure of crystallization is greater than the vapor-saturation pressure. Vapor-saturation pressures based on melt inclusion H_2O and CO_2 concentrations vary from about 1 to 4 kbar, implying a range of upper crustal depths through which silicic volcanic magmas differentiate and reside before eruption.

Detailed experimental phase equilibrium studies have been performed on the 1980 Mount St. Helens dacite (Fig. 7) and the 1991 Mt. Pinatubo dacite. The results for both indicate crystallization pressures of ~2.2 kbar and temperatures of 920 and 780°C, respectively, as well as significant dissolved H_2O. For the Mount St. Helens dacite, the experimentally synthesized mineral assemblage and mineral compositions match the natural assemblage when there is about 4.6 wt% H_2O dissolved in the melt. If the magma was vapor saturated before eruption, then the experimental data can be used to infer a vapor phase composition of 50–70 mol% H_2O and 30–50 mol% CO_2. In contrast, the experimental data for Mt. Pinatubo dacite indicate a higher H_2O concentration of ~6 wt%, consistent with analyses of melt inclusions trapped in quartz phenocrysts. These pre-eruptive dacitic magmas appear to have contained a vapor phase during crystallization, because the vapor-saturation pressures and pressures based on phase equilibria are equal.

One of the best studied rhyolitic eruptions in terms of magmatic volatile abundances is the 0.76-Ma explosive, caldera-forming eruption that formed the 500-km^3 Bishop Tuff. Melt inclusions in Bishop quartz phenocrysts reveal systematic, pre-eruptive gradients in dissolved H_2O and CO_2 during crystallization (Fig. 12). Melt inclusions from early erupted pumice fall deposits contain 5.3 ± 0.4 wt% H_2O and 60 ± 40 ppm CO_2, whereas those from the middle of the eruption contain higher H_2O (5.7 ± 0.2 wt%) and CO_2 (120 ± 60 ppm). Thus early erupted magma contained less dissolved H_2O and CO_2 than magma from the middle of the eruption. Compared with melt inclusions from early and middle Bishop Tuff samples, inclusions from late erupted magma have much lower H_2O (4.1 ± 0.3 wt%), and higher and variable CO_2 (150–1100 ppm). The estimated pressures of crystallization (vapor-saturation pressures) are lower for inclusions from the earliest erupted samples than in samples from the middle of the eruption. This pattern is consistent with sequential tapping of a large zoned body of gas-saturated magma, because the first material erupted would likely come from the shallowest (lowest pressure) portion of the magma body.

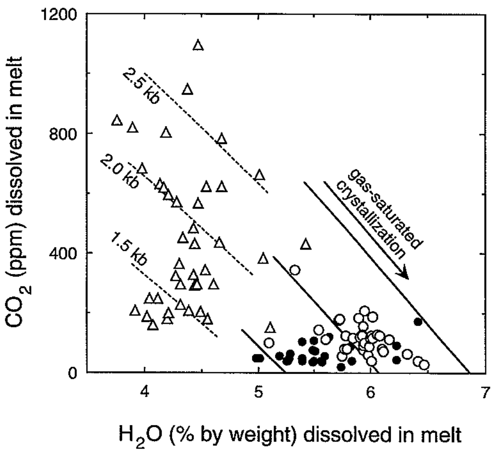

FIGURE 12 Dissolved H_2O and CO_2 in rhyolitic melt inclusions in quartz phenocrysts from the 0.76-Ma Bishop Tuff. Data are shown for samples from the early (solid circles), middle (open circles), and late (open triangles) parts of the eruption. Diagonal lines show the H_2O and CO_2 contents of rhyolitic melt saturated with H_2O-CO_2 gas at pressures from 1.5 to 2.5 kbar and temperatures of 725°C (solid lines) and 790°C (dashed lines), which correspond to the pre-eruptive temperatures for the early and late erupted magmas, respectively. The arrow indicates the trend of H_2O and CO_2 contents in successive residual liquids formed by isobaric, gas-saturated crystallization. (Modified from Wallace *et al.,* 1995, *Nature.*)

Dissolved S concentrations in silicic magmas tend to be relatively low (≤200 ppm), and are frequently below the minimum detection limit of common analytical techniques. These low concentrations occur despite the fact that most silicic magmas are saturated with a sulfide (pyrrhotite) and/or sulfate phase (anhydrite). The low S solubility is caused by a combination of low melt FeO content and the low temperature of silicic magmas. The former is an important factor at relatively low magmatic oxygen fugacity where dissolved S is dominantly sulfide, whereas decreasing temperature significantly decreases both sulfide and sulfate solubilities (see Fig. 5).

Fluorine and chlorine abundances are relatively low in metaluminous dacites and rhyolites (F, 200–1500 ppm; Cl, 600–2700 ppm). In the Bishop Tuff melt inclusions, F varies from 160 to 460 ppm and Cl varies from 550 to ~800 ppm. Both elements are more abundant in the most highly differentiated, early erupted Bishop Tuff whereas lower concentrations occur in the least differentiated magma that erupted later. Melt inclusions from the 1991 Mt. Pinatubo dacite contain ~1000 ppm Cl. In contrast to halogen abundances in metaluminous magmas, peralkaline rhyolites (pantellerites) contain as much as 1.3 wt% Cl and 1.5 wt% F. These high concentrations reflect the highly differentiated nature of these magmas, which causes Cl and F to increase like other incompatible trace elements, and to the effects of alkalies in increasing Cl and F solubilities in silicate melts. Peraluminous tin and topaz rhyolites of the western Unites States and central Mexico also contain high halogen concentrations, with Cl reaching 0.5 wt% and F as great as 5 wt%.

C. Gradients in Volatile Abundances and Vapor Saturation in Magmas

Gradients in dissolved volatiles, especially H_2O, within individual silicic magma bodies have been inferred from (1) variations in phenocryst assemblages and compositions; (2) variations in whole-rock abundances of F and Cl; and (3) the observation that many volcanic eruptions evolve with time from high-energy Plinian columns to pyroclastic flows, or culminate with quiescent dome extrusion. Gradients in dissolved H_2O in silicic magma bodies have more recently been confirmed using ion probe and infrared spectroscopic techniques on melt inclusions in phenocrysts. However, changes in eruptive style from Plinian column to pyroclastic flow often do not appear to be related to differences in pre-eruptive dissolved water, insofar as this is recorded by melt inclusions in phenocrysts. Even effusive (nonexplosive) eruptions of silicic magma appear to involve magma with initially high dissolved H_2O concentrations. That such magmas are erupted nonexplosively requires that water be lost prior to extrusion. This probably occurs when magma decompression induces sufficient vesicularity to form a magmatic foam that is highly permeable to gas loss.

It has commonly been thought that magmas of intermediate to silicic composition only become gas-saturated during shallow ascent and emplacement, during eruptive decompression, or during advanced (pegmatitic) stages of plutonic crystallization. However, studies of eruptive dynamics, CO_2 and SO_2 emissions, and melt compositional features all suggest that many magmas in subvolcanic reservoirs are saturated with a multicomponent vapor. Volcanoes could be viewed primarily as gas vents. In particular, the small but finite solubility of CO_2 in silicic magmas at crustal pressures could result in saturation with H_2O-CO_2 vapor during partial melting as well as during ascent, emplacement, and crystallization. High-temperature fluid inclusions in phenocrysts from some silicic volcanic rocks provide direct evidence of pre-eruptive vapor saturation. Gradients in alkali and trace element abundances might result in part from upward flux of exsolved gas in a large magma body.

Correlations between CO_2 and trace elements in melt inclusions from the Bishop Tuff indicate that the magma was gas saturated during pre-eruptive crystallization. Quantitative models of gas exsolution during crystallization of the Bishop magma are consistent with exsolved gas contents varying from about 1 wt% in the deeper regions of the magma body to nearly 6 wt% near the top (Fig. 13). Thus the data and models suggest that there was a gradient in exsolved gas, with mass fractions of gas increasing upward toward the roof of the magma body. Because the exsolved gas phase would be H_2O rich, such large exsolved gas contents imply that the early erupted Bishop magma had a bulk (dissolved + exsolved) H_2O content of ~10 wt%. However, these interpretations assume that gas traveled with and remained in the magma during most of its evolution. The presence of significant mass fractions of exsolved gas in Bishop magma is consistent with H_2O and CO_2 dissolved in minimally degassed rhyolitic obsidians at Mono Craters, California. Similar mass fractions of pre-eruptive exsolved gas have been inferred for the magma bodies of the 1982 El Chichón and 1991 Mount Pinatubo eruptions by assuming that all SO_2 released (measured by remote sensing techniques) was stored in the erupted volume of magma.

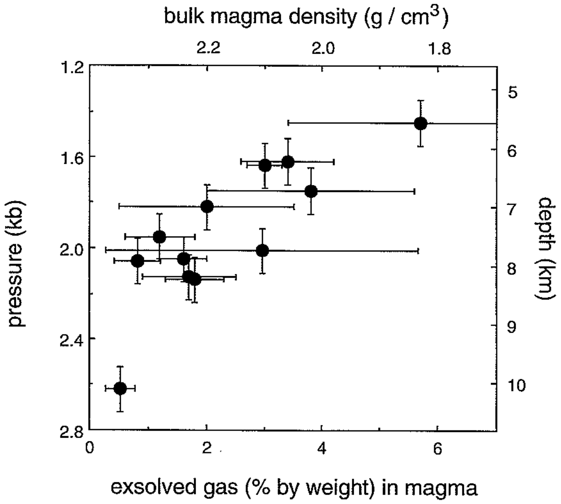

FIGURE 13 Exsolved gas content in the crystallizing Bishop rhyolitic magma as inferred from volatile and trace element analyses of melt inclusions. The bulk magma (melt + crystals + gas) density is given along the top of the diagram. (Modified from Wallace *et al.,* 1995, *Nature.*)

D. Volcanic Gases, SO_2 Emissions, and Pre-Eruptive Vapor Saturation in Magmas

One of the most important constraints on bulk (dissolved + exsolved) magmatic volatile contents comes from studies of the fluxes of SO_2 from erupting volcanoes. During the last several decades, scientists have discovered that SO_2 gas injected into the stratosphere by explosive eruptions is converted in a matter of days into aerosols rich in H_2SO_4 (sulfuric acid) that can affect both climate and atmospheric chemistry. Measurements of the amounts and fluxes of SO_2 emitted from erupting volcanoes can be made with remote sensing techniques, including both ground- and air-based use of the ultraviolet correlation spectrometer (COSPEC) and the satellite-based total ozone mapping spectrometer (TOMS). Comparison of SO_2 emissions with petrologic estimates of dissolved S in volcanic magmas has led to a conundrum, known as the "excess" sulfur problem. Inclusions of melt in erupted phenocrysts indicate dissolved sulfur contents that are far too low (by a factor of 10–100) for the melt to exsolve the total mass of SO_2 erupted. Excess eruptive S is observed in most eruptions for which remote sensing and melt inclusion data are available. Exceptions to this general pattern are eruptions of basaltic magma from the Hawaiian volcanoes, Kilauea and Mauna Loa. Most SO_2 emission estimates that are based on melt inclusions in volcanic phenocrysts assume that the only source of sulfur released during an eruption is that which was originally dissolved in the silicate liquid (melt) portion of the magma shortly before eruption. However, there is a large body of evidence, based on petrologic, remote sensing, and volcanic gas data, that nearly all of the SO_2 released during many explosive eruptions was actually contained in pre-eruptive exsolved gas. As a result, eruptions of exsolved-gas-rich silicic magmas can release large amounts of SO_2 derived from pre-eruptive exsolved gas, notwithstanding very low concentrations of dissolved S.

VII. IMPORTANCE OF VOLATILES IN VOLCANIC ERUPTIONS

A main goal of volcanology is to understand volcanic eruptions. Decompression of volatile-rich, viscous magmas can result in explosive eruptions because of the thousand-fold volumetric expansion of gas with decompression from 1000 to 1 bar. Gas that occupied 1 vol% of the magma at 1000 bars occupies 91 vol% at 1 bar, and the latter corresponds to a dilute spray of particles in a gas jet. Importantly, gas exsolution generally begins at depth with small amounts of relatively CO_2-rich gas followed by increasing proportions and amounts of H_2O-rich gas nearer the surface. Some stiff (high viscosity) magmas may have internal pressures approaching 100 bars only a few meters below the surface, because gas has been slow to escape from the magma. Theoretical modeling reveals that magmatic volatile contents largely govern the explosivity of eruptions. Conversely, plume height and tephra dispersal can be used to infer pre-eruptive volatile contents. Modeled and observed volatile concentrations have been partly at odds, and this has led to critical reassesments and model improvements. In some cases, reconciliation has tended to increase the amount of volatiles needed for specific effects, implicating the presence of significant exsolved pre-eruptive gas.

Modeling of explosive silicic eruptions shows that the velocity of erupting material is strongly dependent on the amount of exsolved gas. Eruption velocities at the vent, estimated from the maximum size of blocks deposited near the vent, are as much as 400–600 m/s for the most powerful Plinian eruptions. Such velocities are estimated to require 3–6 wt% exsolved H_2O, an amount that is consistent with dissolved concentrations indicated by experimental work and measured in melt inclusions. In many eruptions, there is an observed or inferred transition from a Plinian eruption column to a collapsing column, resulting in a transition from pumice-fall to ash-flow deposition. Lower magmatic H_2O concentrations, or increased mass flux of erupting magma with the same H_2O concentration due to widening of the vent can, theoretically, cause the Plinian column to become unstable and collapse to form pyroclastic flows. Interpretations of the Bishop eruption based on tephra characteristics, however, suggest synchronous eruption of one or more sustained jets that fed both a buoyant (Plinian) column, from which pumice-fall material was deposited, and collapsing clouds, which deposited ash-flows. As the eruption continued, the proportion of ash-flow material increased, the amount of H_2O in melt inclusions increased slightly (Fig. 12), and the amount of pre-eruptive exsolved gas decreased (Fig. 13). Thus the amount of pre-eruptive exsolved gas may be especially important in regulating eruptive style.

The height of basaltic lava fountains is also controlled largely by the amount of exsolved gas in the erupting magma. The initial (pre-eruption) amounts of H_2O that are necessary to propel lava fountains to 200- and 800-m heights are about 0.3 and 0.6 wt%, respectively. These estimates have been revised upward in light of the fact that much of the magma in typical Hawaiian-style fountains falls back into a bowl-shaped crater surrounding the vent, forming a pond of relatively dense, degassed magma. Newly vesiculating magma from depth loses some of its kinetic energy as it fountains through this degassed magma pond. After accounting for this effect, the resulting estimates of H_2O concentration based on observed fountain heights are consistent with both dissolved H_2O contents determined from analyses of melt inclusions trapped in olivine phenocrysts and with estimates based on the composition and fluxes of volcanic gases. Modeling also suggests that the transition from lava fountaining to intermittent Strombolian explosions is not likely to be related to a decrease in volatile content but rather is caused by a reduction in the ascent velocity of magma, which results in more time for bubble coalescence to occur. In contrast, a decrease in magmatic volatile content is predicted to result in a transition to passive effusion of vesicular basaltic lava.

VIII. EFFECTS OF VOLATILES ON PHYSICAL PROPERTIES OF SILICATE MELTS

Small amounts of dissolved volatiles have important effects on the density, viscosity, and crystallization of melts and magmas, and these can influence magma ascent, eruption, and differentiation. Experimental data are available concerning the effects of H_2O, CO_2, and F on melt density and viscosity, but comparable data for Cl and S do not exist.

A. Density

The partial molar volume of H_2O dissolved in melt of albite composition ($NaAlSi_3O_8$) has been directly measured by experiment as 14–20 cm^3/mol over the temperature range from 750 to 950°C. Partial molar volumes of dissolved H_2O in rhyolitic and basaltic melts estimated indirectly from solubility data are generally similar to the low end of the range for albite melt. In detail, however, determinations from solubility data can be complex because of the concentration-dependent speciation of dissolved H_2O into both OH^- groups and molecular H_2O. Given the molecular weight of H_2O (18 g/mol) and a partial molar volume of ~14 cm^3/mol, addition of dissolved H_2O to a melt represents a component with a density slightly greater than 1 g/cm^3 compared with densities for anhydrous basaltic and rhyolitic melts of ~2.7 and ~2.3 g/cm^3, respectively. Thus addition of dissolved water to a melt decreases the melt density. The effect of adding 6 wt% dissolved H_2O to a rhyolitic melt is to decrease the density by about 5%, whereas addition of 2 wt% H_2O to a typical basaltic melt decreases its density by 2–3% relative to anhydrous values.

The best estimates for the partial molar volume of dissolved molecular CO_2 (rhyolitic melt) and carbonate (basaltic melt) derived from solubility data are between 21 and 28 cm^3/mol. The low solubility of CO_2 results in relatively low concentrations in magmas at crustal depths, such that CO_2 is not expected to have a strong effect on the densities of magmas stored in the Earth's crust. At mantle depths, especially in silica poor magmas in which CO_2 solubility (dissolved as carbonate) is relatively high, CO_2 can have significant effects on melt densities. The molecular weight of CO_2 (44 g/mol) and the range of partial molar volumes given earlier indicate that dissolved carbonate represents a component with a density of ~2 g/cm^3. The effect of adding 3 wt% CO_2 to an alkali basaltic melt is to decrease the melt density by ~3%. For comparison, addition of 3 wt% dissolved H_2O to the same melt decreases melt density by ~5%.

Determining the effects of dissolved F on silicate liquid density is complex, but available data clearly indicate that addition of F decreases melt density.

B. Viscosity

Experimental studies of viscosity demonstrate three important features of the viscosities of silicate melts. The first is that silicate melts exhibit Newtonian behavior, defined as a liquid in which the rate of shear in the liquid is linearly proportional to the magnitude of the applied shear stress. The second important feature is that silicate melt viscosity increases rapidly with decreasing temperature. Thirdly, silicate liquid viscosities are also strongly dependent on melt composition, the most important component being SiO_2. With increasing SiO_2 content in a melt, viscosity also increases. The combination of the inverse dependence of viscosity on temperature and the positive covariation with SiO_2 content results in low-temperature rhyolitic melts having a viscosity that is as much as 8 orders of magnitude (10^8 times) greater than that of a high-temperature basaltic melt.

Addition of dissolved H_2O to a melt decreases the viscosity, probably because H_2O weakens or breaks apart the aluminosilicate framework of the melt, which makes it flow more readily. Experimental studies have shown a nonlinear effect of H_2O in decreasing viscosity (Fig. 14). Over the range from 0 to 3 wt% H_2O, water has

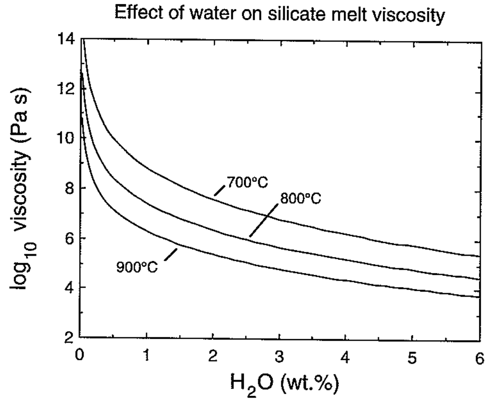

FIGURE 14 Effect of dissolved water on the isothermal viscosity of a granitic (rhyolitic) melt. Note that at low water concentrations, the 700 and 800°C curves are for supercooled melt, because the temperatures are below the solidus temperature for melting of dry granite (900°C for H_2O-free granite). Calculated from Hess and Dingwell (1996).

a very strong effect in reducing viscosity. In the case of siliceous melts, addition of 3 wt% H_2O to a dry melt may reduce the viscosity by as much as 5 orders of magnitude. For dissolved H_2O greater than 3 wt%, addition of more water has a much smaller effect on the viscosity. The reason for the change in the effect of H_2O is plausibly related to the speciation of dissolved water. From 0 to 3 wt% H_2O, water is dissolved predominantly as OH^- groups bound to the aluminosilicate framework—thus in this concentration range, dissolved water has a relatively large effect on viscosity. Above 3 wt% H_2O, the amount of water that is present as OH^- reaches a maximum value, and additional dissolved water is mostly present as H_2O molecules that do not cause weakening or breaking of aluminosilicate bonds. Thus at higher concentrations water has a smaller effect on silicate melt viscosity.

Determining the effects of dissolved CO_2 on melt viscosity is difficult. Available experimental data suggest that dissolved CO_2 reduces the viscosity of silicate melts, but the effect is much smaller than for H_2O. Experimental studies show that F has a relatively large effect in reducing the viscosity of SiO_2-rich melts. Although the concentration of F in most natural magmas is low enough to preclude it having a significant effect, F-rich topaz rhyolites have sufficient F to reduce magma viscosity by as much as 3 orders of magnitude. A manifestation of this effect is the eruption of topaz rhyolites to form unusually long lava flows with little associated explosive tephra.

IX. ORIGIN OF VOLATILES, EARTH DEGASSING, AND VOLATILE RECYCLING VIA SUBDUCTION

Studies of both inert and reactive volatile elements help scientists evaluate the origin and evolution of the Earth. This chapter has as its primary focus the reactive volatiles that mostly become chemically bound into either minerals or molecules in air, water, oil, and ice. In this section, we give an elementary overview of some of the inert volatile elements (usually termed *noble gases*): helium, neon, argon, krypton, xenon, and radon. Studies of inert gases, particularly helium and argon, help constrain ideas about Earth's origin and evolution. The noble gases readily enter the Earth's atmosphere, and they comprise both radiogenic and nonradiogenic isotopes. Thus certain isotopic ratios change in time and may reflect ratios of radioactive parent nuclides and nonradiogenic inert gas in compositionally distinct and physically separate parts of the Earth. Helium and argon are especially interesting in this regard. Helium has two isotopes: ^{3}He and ^{4}He. Radioactive decay of uranium and thorium yield ^{4}He, whereas radiogenic production of ^{3}He is negligible in virtually all Earth environments. Furthermore, helium escapes from the atmosphere because in the upper stratosphere, the pressure is low, atoms are far apart, and the average speed of low mass atoms may exceed the threshold value at which Earth's gravitational field can slow outward-moving atoms and return them to the Earth. The more helium there is in the air, the greater the outgoing escaping flux (number of atoms of helium escaping per year, for example). At some point the amount of helium in air is just right for the escaping flux to be balanced by the rate of supply from the interior of the Earth.

Geological processes such as ocean circulation, seafloor spreading, and continental erosion affect the fluxes of helium from various storage reservoirs within the earth. As a result, the ratio of nonradiogenic ^{3}He to radiogenic ^{4}He in different rocks and water bodies characterizes various sources of He: Helium in air is relatively poor in ^{3}He compared to helium in oceanic ridge basalts and basalts associated with hot spots such as Hawaii. Thus it is likely that most of the helium in air comes from continental rocks, which are rich in uranium and thorium, and have therefore produced significant ^{4}He from radioactive decay. Such rocks have evolved near the Earth's surface for geologically long periods of time and probably their original ^{3}He was lost from the Earth's atmosphere long ago. Only deeply buried sources plausibly retain ^{3}He that was initially present in the Earth when it formed from objects in the solar nebula. Thus comparatively high ^{3}He/^{4}He ratios of basalts from Hawaii suggest that Hawaiian basalts are derived, at least in part, from deep within the mantle, possibly from an undegassed remnant of lower mantle material left over from early in Earth's history.

Similarly, investigations of radiogenic ^{40}Ar (produced from the radioactive decay of ^{40}K) compared with nonradiogenic ^{36}Ar in both terrestrial and meteoritic rocks support the view that the mantle consists of at least two parts. One part has largely lost its argon and presumably most of its other volatiles, including reactive ones such as H_2O, which readily dissolve in silicate melts and are carried toward the surface in magmas. A second part seems to still have much of its nonradiogenic argon (^{36}Ar) and evidently is relatively primordial. An atom of argon is 10 times more massive than one of helium and nearly all argon is retained in the atmosphere by Earth's gravitational field. Nearly all argon in air is ^{40}Ar, but there is less ^{40}Ar than the amount expected based on the ^{40}K content of the Earth, which is independently reasonably well known. Thus there must be a significant part of the Earth that contains much of the ^{40}Ar that has been produced by decay of ^{40}K during the history of the Earth and which has not yet reached the atmosphere. If an incompletely degassed mantle reservoir contains the missing radiogenic ^{40}Ar, then this reservoir would likely also contain a significant amount of reactive volatiles such as H_2O and CO_2.

Studies of inert gases are consistent with the theory that early in its history, the Earth was covered by a deep magma ocean, caused by conversion into heat of some of the gravitational potential energy of accreting material. Inert volatiles would have become predominantly degassed and concentrated in the atmosphere during the Earth's formation. Such an early atmosphere could have been largely lost from the Earth as a result of solar activity or violent impacts. Significant amounts of reactive volatiles such as H_2O could have dissolved in the magma ocean. Subsequent crystallization of the magma ocean and formation of minerals poor in H_2O would promote degassing by concentrating the reactive volatiles in a diminishing residue of liquid, thereby leading to the formation, rise, and escape of bubbles of gas.

It is conceptually important that present degassing rates of primordial, nonradiogenic inert gas from ocean ridge magmatism (based on the ^{3}He rate and ratios of other inert gases to ^{3}He), when multiplied by the age of the Earth, yield much less total nonradiogenic neon and argon than is presently in Earth's atmosphere. Thus it is inferred that the rate of degassing from the Earth either was much greater in the past, or that significant inert gas has been separately added to the outermost Earth by meteoritic infall. The present-day isotopic composition of nonradiogenic inert gases being degassed from the Earth is noticeably different from that in air, and intermediate between that of inert gases from the Sun and from meteorites. The discrepancy can therefore be reconciled with either a mixture of sources for the Earth's inert gases or preferential loss from Earth's atmosphere of less massive isotopes.

Subduction provides a mechanism by which sediments and altered oceanic crust are recycled back into the mantle. The sediments and altered crust are relatively rich in the two major reactive volatiles: carbon dioxide stored as carbonates, and water, both as pore water and as water bound in hydrous minerals such as clays. Most of the hydrous minerals break down to anhydrous minerals and release water vapor as the subducting rock heats up. The pore water and the water released from hydrous minerals are buoyant, and increasing pressure from the weight of overlying rocks collapses pores and forces water out of deeply buried rocks. Some deep storage of water is possible, however, in view of experimental studies which show that some dense hydrous magnesian silicates are stable to very high pressures and temperatures. Also, small concentrations of water occur as structurally bound OH^- in nominally water-free minerals such as olivine and pyroxene. Subduction-related basaltic magmas are notably more water-rich than midocean ridge and ocean island basaltic magmas, and such magmas may return most or all of the subducted water to the surface. A small fraction of the subducted water may be cycled into the deeper mantle, but this is unconstrained.

The isotopic composition of water is unaffected by radioactive decay (except for bomb tritium) and has probably been negligibly affected by preferential escape from Earth of hydrogen compared to more massive deuterium. Ratios of hydrogen to deuterium in various water reservoirs mainly reflect the geologic processes that partition water into these reservoirs. Water initially released from magmas at igneous temperatures is eventually redistributed by formation of new low-temperature minerals in the reservoirs of altered rocks, seawater, freshwater, and ice. Isotopic fractionation during this redistribution causes the oxygen and hydrogen isotopic composition of seawater to differ from that dissolved in parental basaltic magmas; the balance is made up mainly by the isotopically light water bound in altered rocks. There is no isotopic evidence for a significant source of surface water beyond that which degasses from basaltic magmas. Nor is there evidence for preferential subduction and hidden storage of water that is isotopically distinct from that which is in parental basaltic magmas.

The isotopic composition of carbon in parental basaltic magmas and various terrestrial reservoirs is not certain. There may be a significant isotopic shift upon degassing and this makes it difficult to assess the isotopic composition of carbon in parental basaltic magmas. The predominant recognized reservoir of terrestrial carbon is in sedimentary limestones and dolomites and it differs significantly from that which degasses from basaltic magmas at igneous temperatures. Photosynthesis yields reduced carbon in biological tissues that is relatively poor in ^{13}C and this affects the isotopic composition of carbon in surficial reservoirs. Existing knowledge permits the amount and isotopic composition of buried organic matter (mainly reduced C in shales and coals) to balance the amount and isotopic composition of carbon in carbonate rocks, yielding a sedimentary average that is consistent with igneous gas. However, significant additions of isotopically distinctive carbon to Earth's early atmosphere during the final stages of accretion as well as storage of carbon in Earth's core are possible. Furthermore, it is possible that the isotopic composition of carbon now released from magmas reflects a recycling steady state, and it may have differed in the remote past, reflecting a smaller proportion of recycled carbon.

Carbonate rocks, if mixed with quartzose rocks will undergo decarbonation reactions during subduction into the deep crust and shallow upper mantle, and carbon dioxide-bearing gas will form and return to the surface. This may be a source of some carbon dioxide in gas reservoirs and hot springs, but most carbon dioxide in such environments is derived from superficial sources like heated groundwater. Carbonate rocks alone or with silica-poor minerals are refractory and may remain stable to great depths in the mantle. Thus subduction of limestones can potentially introduce carbon dioxide as carbonate rocks into the deep mantle where it may persist. Subduction of carbonate rocks plausibly increased during the past 180 million years owing to biological evolution of pelagic foraminifera and formation of abundant, subductable deep oceanic carbonates, possibly reversing the net flux of carbon dioxide back into the mantle from the crust. The flux of carbon dioxide associated with subduction zone volcanism is poorly known, and this topic could benefit greatly from further study.

The downgoing view of carbon dioxide is illuminated by the fact that at fairly shallow mantle depths the carbonate mineral dolomite becomes stable in a typical assemblage of mantle silicates. Thus a deep residence of mineralogically bound carbon dioxide is feasible. Under the conditions of pressure and temperature where dolomite is stable in the mantle, carbon dioxide is quite soluble in silicate melts and can flux partial melting at comparatively low temperatures. The upgoing view of ascending carbonate-rich magmas is marked by the expected release of carbon dioxide gas at shallow upper mantle pressures. Plausibly this pressure-sensitive effervescence of carbon dioxide gas is partially responsible for the explosive nature of rare magmas, bringing diamonds and fragments of the mantle to the upper crust.

Yearly amounts of reactive volatiles H_2O and Cl that are subducted are in the range of rough estimates of what is returned surfaceward by arc magmatism. If there were no surfaceward return of subducted H_2O and Cl, then the formation, alteration, and subduction of oceanic crust would comprise a net drain on the water and salt in the oceans. The geologic record and understanding of tectonism reveal that continental crust and ocean water have existed for most of Earth's history; subduction has not caused the oceans to dry up. Thus water lost to altered oceanic crust is probably largely returned to the oceans via dewatering of subducted crust and subduction-related magmatism.

X. FUTURE DIRECTIONS

The study of magmatic volatiles lies at the interface of igneous petrology and volcanology. Much of our present state of knowledge has been derived relatively recently due to major advances in techniques of microanalysis. Improvements that are under way will soon make it possible to measure the isotopic composition of volatile and nonvolatile species in silicate melt inclusions, as well as the determination of some volatile trace metals in trapped fluid or vapor + melt inclusions in volcanic phenocrysts. Combined analyses of volatile species, trace elements, and isotope ratios (e.g., H, O, S, C, He, Sr) will contribute to a better understanding of volatile recycling in the Earth, melting processes, magmatic differentiation, and magma degassing.

The pressure-dependent solubilities of the major volatiles H_2O and CO_2 in silicate melts make it possible to use melt inclusions as geobarometers. Combined with major, trace, and isotopic data, and detailed knowledge of time–volume–compositional variations in eruptive deposits, melt inclusions can be used to place constraints on magma chamber configurations, and magmatic and eruption processes. In this context, petrologic techniques for estimating the bulk (dissolved + exsolved) volatiles in magma bodies need to be further developed and refined in order to better understand volcanic gas fluxes, low-pressure degassing, and the relationship between volatiles and eruption dynamics. Although the interpretation of melt inclusion data is frequently complex due to effects of magma mixing, crystallization, and volatile leakage, the ability to sample melt inclusions from different stratigraphic levels of an eruptive deposit makes it possible to get an unprecedented look at the workings of magma bodies.

It is increasingly being recognized that magmatic volatiles, including volatile trace metals, make important contributions to magmatic-hydrothermal ore deposits. Future analytical developments that make it possible to measure the stable and radiogenic isotope ratios of melt inclusions will significantly add to our knowledge of magmatic inputs to ore-forming systems. Another important area of future research will be the relationship between volatile abundances in volcanic rocks and their plutonic equivalents. The goal of such work will be to gain a better understanding of the relationship between plutonic and volcanic rocks and, in particular, whether volcanic eruptions tap the volatile-enriched upper portions of larger crustal magma reservoirs, leaving behind less volatile-rich, uneruptable material that eventually solidifies as a pluton.

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