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SILICATE MELTS: THEIR PROPERTIES AND STRUCTURE APPLIED  
TO PROBLEMS IN GEOCHEMISTRY, PETROLOGY  
ECONOMIC GEOLOGY AND PLANETARY GEOLOGY

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## CHAPTER 4

### VOLATILE SOLUBILITIES IN SILICATE MELTS

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#### INTRODUCTION

All naturally-occurring igneous melts contain some volatiles. The nature and amounts of volatiles dissolved in igneous melts influence virtually all of the physical and chemical properties of silicate melts discussed in this volume. The physical and chemical properties of silicate melts, in turn, determine the behavior of an igneous melt in response to the state of the system (e.g. pressure, temperature, stress field, etc.). Thus an adequate understanding of the solution of volatiles in silicate melts is essential for an understanding of the petrogenesis of igneous rocks.

The solubility of volatiles in natural geologic melts has been a subject of experimental investigation by petrologists since the work of Goranson (1931) on the solubility of water in the Stone Mountain Granite. In the past ten years, more experimental determinations of volatile solubilities in geologic melts have been published than were available in the previous half-century. Much of the recent work has resulted from the development of new methods for volatile analysis [e.g., water by vacuum fusion manometry (Harris, 1981); carbon by beta-track mapping (Mysen and Seitz, 1975)] and much interest in the mechanisms of volatile solution in silicate melts has been generated by the success of vibrational spectroscopy in observing the speciation of dissolved volatiles (Stolper, 1982a) and their effects on melt structure (Mysen *et al.*, 1980). Finally, due to the advent of analytical techniques for observing the natural concentrations of several light elements in igneous rocks and fluid inclusions, the data base for volatile element geochemistry is growing rapidly.

This chapter is divided into two sections. The first section deals with the techniques of solubility determination that have been used by experimental petrologists and highlights the advantages and drawbacks associated with each method. The second section is a review of solubility determinations and melt-fluid partitioning data for volatile species. The solubility relationships of volatile compounds of H, C, O, S, Cl, F, N, and B are considered. In the summary, suggestions are made for expanding the knowledge of volatile interactions in geologic melts.

## METHODS

## Chemography

The determination of volatile solubility by chemographic methods involves the construction of a portion of the phase diagram of the system of interest. Phase relations of binary and ternary volatile-silicate systems have been discussed by several workers (Ricci, 1951; Morey, 1956; Wyllie and Tuttle, 1960; Pichavant, 1983). The following discussion is an evaluation of the phase relations in a two-component system with no binary compounds or liquid immiscibility. Isobaric projections of this type of system (T-X or "rock-water" diagrams) have been used to derive volatile solubilities from phase equilibrium experiments.

For the general case of a binary system with no binary compounds or liquid immiscibility, two types of phase behavior are possible, depending on whether or not the solubility curve joining the triple points of silicate and volatile intersects the critical curve ( $L = V$ ) that connects the critical points of silicate and volatile. The system  $\text{NaCl-H}_2\text{O}$  is an example of the case (Type I) where the solubility curve ( $S + L + V$ ) and the critical curve ( $L = V$ ) do not intersect (Sourirajan and Kennedy, 1962). Figure 4-1a illustrates a projection of phase relations in a type I binary system onto the pressure-temperature (P-T) plane. The system  $\text{SiO}_2\text{-H}_2\text{O}$  is an example of the second type of behavior (Kennedy *et al.*, 1962). Figure 4-1b illustrates the phase relationships of a binary system exhibiting this type of behavior (Type II), projected onto the P-T plane. In this case the pressures required to saturate intermediate liquid solutions with the solid silicate phase (Ss) are so high that the solubility curve actually interrupts the critical curve (dashed line, Fig. 4-1b). The two segments of the critical curve are terminated by the original two unary critical points ( $C_w$  and  $C_s$ ) and by two binary critical end points, the upper and lower critical end points (UC and LC, respectively). It should be emphasized here that Figs. 1a and 1b are strictly applicable only when the silicate phase of interest behaves as a single component (i.e., congruent melting, boiling, and sublimation are observed for the volatile-free silicate). Albite composition melt will probably dissociate by vaporization of Na before the P-T conditions of  $C_s$  are reached.

Figure 4-1b is, however, the source of information for the construction of isobaric T-X or "rock-water" diagrams. The circled numbers in Fig. 4-1b indicate the relative temperatures of phase boundaries that were used to construct the isobaric section illustrated in Fig. 4-2. For a pressure above the triple point of the volatile, but below the critical point of the silicate, the isobaric T-X diagram is as represented in Fig. 4-2. The location of the  $L_1 = L_1 + V$  univariant equilibrium curve in Fig. 4-2 is one method of determination of volatile solubility. The volatile content of any melt along this curve (point 7 to point 5 in Fig. 4-2) corresponds to the solubility value at the temperature of interest. The temperature dependence of volatile solubility is

given by the slope of this line that may be either positive or negative near the  $L_1 + Ss + V$  point. For pressures below  $Cs$  this curve must eventually yield a negative slope and close out the divariant  $L_1$  field on the left (dry) side of the diagram.

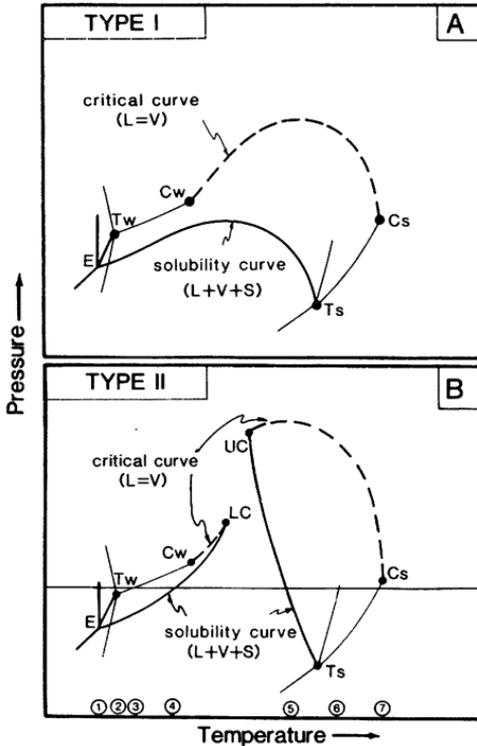


Figure 4-1. Pressure-temperature projections in binary systems with no liquid immiscibility or binary compounds. The light lines represent phase relations in the single-component systems and the heavy lines represent phase relations in the two-component system. (a) = Type I behavior and (b) = Type II behavior. ( $T_w$  and  $T_s$  are the triple points of water and silicate;  $C_w$  and  $C_s$  are the critical points of water and silicate;  $E$  is the silicate-water eutectic;  $UC$  and  $LC$  are the upper and lower critical end points of the silicate-water system.) (the circled numbers indicate construction points for Fig. 4-2.)

Physically, this method of solubility determination involves the optical inspection of quenched experimental runs to observe the presence or absence of fluid-filled vesicles in the glass or dimples on the surface of the glass slug. This technique is restricted to melt compositions that quench to a glass. Some high-pressure, gas-media apparatuses have relatively slow quench rates and inspection of experimental charges from these runs often reveals the

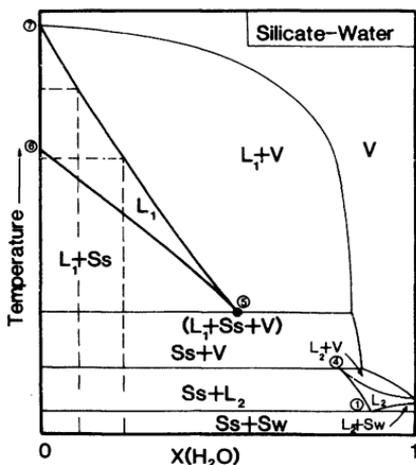


Figure 4-2. An isobaric section of Fig. 4-1b between the triple point pressure ( $T_w$ ) and the critical point pressure ( $C_s$ ). [Redrawn from Ricci (1951)].

presence of small (1 micron) single-phase fluid inclusions that have been interpreted as quench vesiculation (Voigt *et al.*, 1981). The nucleation and growth of vesicles should occur, theoretically, at very small oversaturation of the volatile [less than 10 bars (Sparks, 1978)]; however, Day and Fenn (1982) reported that formation of dimples on the surface of viscous melts may be delayed until oversaturation reaches levels of up to one weight percent water.

The second chemographic technique that may be applied to the isobaric projection of a binary silicate-volatile system is the location of the equilibrium  $L_1 + Ss + V$ . In isobaric projection, this point (Fig. 4-2) lies at the intersection of the water-undersaturated silicate liquidus ( $L_1 = L_1 + Ss$ ) and the water-saturated melting point ( $Ss + V = L_1 + V$ ). Determination of these two lines is an experimental method for locating the  $L_1 + Ss + V$  point. This equilibrium occurs at a total water content equal to the solubility of water at the water-saturated melting point of the silicate. This technique has the advantage that crystal-liquid relationships in relatively viscous systems such as albite-water are usually more easily quenched than liquid-vapor relationships (as above). The disadvantages of this technique are that a large number of vapor-undersaturated experiments are required for one solubility determination and equilibrium reversals can be difficult to achieve in low-temperature, volatile-undersaturated systems.

In ternary systems containing two volatiles and one silicate phase, the chemographic approach may be used to obtain the

compositions of coexisting liquid and vapor compositions. Egglar and Kadik (1979) used the following technique to obtain such information in the system albite-H<sub>2</sub>O-CO<sub>2</sub>.

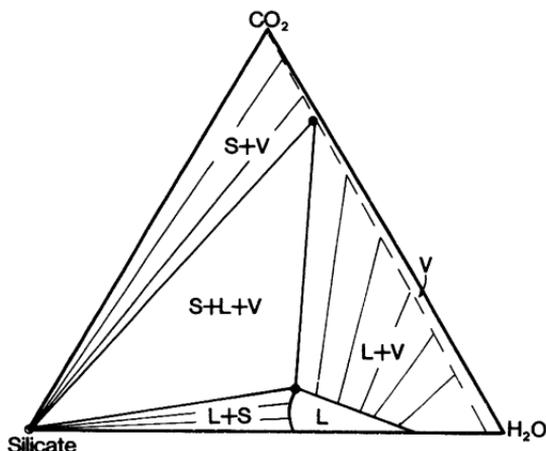


Figure 4-3. An isobaric, isothermal section of the system silicate-H<sub>2</sub>O-CO<sub>2</sub>. Heavy lines represent phase field boundaries, light lines represent tie-lines for the compositions of coexisting phases. [Redrawn from Egglar and Kadik (1979)].

Figure 4-3 is a ternary, isobaric, isothermal projection of phase relations in a system silicate-H<sub>2</sub>O-CO<sub>2</sub>. The phase topology includes two single-phase fields (L and V). Bulk compositions in these fields would form a single fluid phase of silicate liquid or H<sub>2</sub>O-CO<sub>2</sub> vapor, respectively, at the temperature and pressure portrayed. There are three two-phase fields, labelled L + S, S + V, and L + V. The compositions of coexisting phases are schematically indicated by tie lines in Fig. 4-3. There is one three-phase assemblage where the compositions of crystal, liquid, and vapor are indicated by the corners of the three phase triangle in Fig. 4-3. One corner of this triangle is essentially pure silicate. A second corner, that of the vapor phase composition, is close to the binary join H<sub>2</sub>O-CO<sub>2</sub>. If the silicate solute content of the vapor is negligibly small then the H<sub>2</sub>O-CO<sub>2</sub> ratio of the fluid may be determined by experimental determination of the S + L + V = L + V equilibrium (i.e., the volatile-saturated liquidus of the system). Alternatively, the position and thus the H<sub>2</sub>O-CO<sub>2</sub> ratio is determined as the intersection of the vapor-saturated liquidus and the vapor-saturated solidus (S + V = S + L + V).

The third corner of the three-phase triangle may be determined by experimental determination of the saturated liquidus and the L + S = L + S + V. Alternatively, if the CO<sub>2</sub> contents are known by another technique, then only the vapor-saturated liquidus need be determined to complete the construction of the three-phase triangle.

In practice, Egglar and Kadik (1979) determined the  $\text{CO}_2$  contents of quenched samples by an analytical technique (beta-track autoradiography, see below) and then located chemographically the positions of the vapor-saturated liquidus. Although the experiments locating the  $S + L + V = L + V$  curve are performed at near liquidus temperatures for the compositions used, the resulting data is the volatile solubility for a solidus point (see Fig. 4-3).

Sakuyama and Kushiro (1979) performed a series of polybaric, isothermal decompression experiments in order to determine the vesiculation behavior of a hydrous andesite during eruption. Theoretically, the isothermal decompression experiment may be used to bracket the pressure of volatile saturation for a given silicate-volatile system. Sorapure (1981) has used this technique to determine the solubility of water in albite melt. This method requires that the nucleation of vesicles is rapid and that the overall process approximates the equilibrium phase assemblage at the low-pressure end point of each experiment.

Chemographic techniques all provide direct determinations of volatile solubility in the sense that the information is obtained at the pressure and temperature of interest. The first application of a chemographic determination of volatile solubility was by Yoder et al. (1957) in the system  $\text{NaAlSi}_3\text{O}_8\text{-KAlSi}_3\text{O}_8\text{-H}_2\text{O}$ .

#### Differential Thermal Analysis

One other technique that relies on measurements made at the pressure and temperature of interest is differential thermal analysis. Egglar and Rosenhauer (1978) used this technique to determine volatile solubilities in diopside melt. Figure 4-4 illustrates the principles of the differential thermal analysis (DTA) method of volatile solubility determination. Physically, two thermocouples are placed within the experimental hot zone. One thermocouple is in intimate contact with the capsule containing the silicate-volatile system and another thermocouple is placed in the hot zone in an inert material (e.g.,  $\text{Al}_2\text{O}_3$ ). The difference in temperature between the two thermocouples is recorded during a linear heating cycle. A representative trace of the temperature difference  $\Delta T$  is illustrated in inset b of Fig. 4-4. For experiments which experience volatile-undersaturated melting at the pressure of interest, two peaks are resolved in the DTA trace. The first peak,  $T_{p1}$ , corresponds to the initiation of endothermic melting of the silicate at the volatile-undersaturated solidus (Fig. 4-4, inset a). The linear segment of the DTA trace between  $T_{p1}$  and  $T_{p2}$  corresponds to the volatile-undersaturated melting region (i.e., the  $L + S$  field of inset a). The position of the volatile-undersaturated liquidus is bracketed by the temperatures of  $T_{p2}$  and  $T_e$  (where the system has thermally reequilibrated). By performing a polybaric series of DTA runs, the loci of  $T_{p1}$ ,  $T_{p2}$  and  $T_e$  temperatures may be plotted as in Fig. 4-4. The intersections of the  $T_{p2}$  and  $T_e$  curves with the  $T_{p1}$  curve provide maximum and minimum saturation pressures for the volatile content of the experiments.

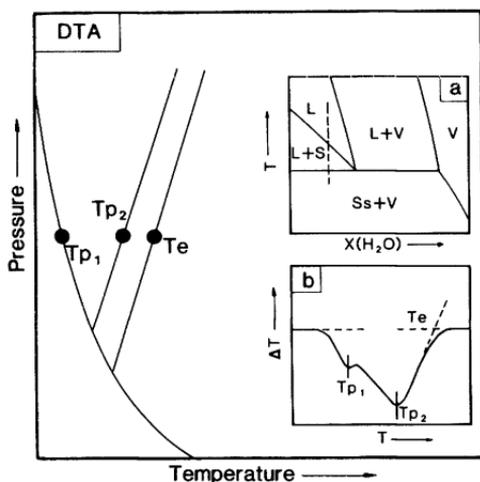


Figure 4-4. The determination of volatile solubility by differential thermal analysis (DTA). [Modified from Egger and Rosenhauer (1978)].

The use of DTA methods for volatile solubility determinations requires that the system under investigation respond rapidly enough, for the heating rate chosen, for resolution of the two peaks  $T_{p1}$  and  $T_{p2}$ , on the DTA trace.

#### Direct Analysis

Direct analysis methods of volatile solubility determination involve analysis of volatile concentrations in quenched samples. Therefore, all the analytical methods discussed below require that the volatile contents of equilibrium-saturated melts are unaffected by the quench. Generally, due to the positive pressure dependence of volatile solubility, isobaric quenching is required. Quenching behavior varies strongly as a function of quench rate, melt composition, and the nature and amount of included volatiles. The relatively rapid quench rate of the solid-media type of pressure apparatus is adequate for preserving run volatile contents in viscous, siliceous melt compositions. As noted above, some internally-heated, gas-media pressure vessels have much slower quench rates and siliceous melts such as albite and orthoclase may exhibit evidence of quench reequilibration (Burnham and Jahns, 1962; Oxtoby and Hamilton, 1978; Voigt *et al.*, 1981). One way to evaluate the effects of quenching on the volatile content of siliceous melts is to inspect optically the glass slug for the presence of quench vesicles. The loss of volatiles from a siliceous melt during slow quenching results in the formation of small (1-2 micron)

single-phase fluid inclusions. These fluid inclusions are easily distinguished from inclusions which stabilize and grow during the experimental run, at pressure and temperature. These latter, equilibrium vesicles are typically larger (10-50 micron), commonly contain two fluid phases, grow in size with increasing experimental duration, and are often deformed during the quench. If the melt is more fluid, due to either its chemical composition (Hamilton *et al.*, 1964) or the temperature of the run (Oxtoby and Hamilton, 1978), then the experiments may yield vesicle-free glasses at volatile saturation. Any direct analysis study must contain documentation of the details of run duration and quench procedure and should include a description of the physical appearance of the run products.

Several analytical techniques have been used to determine volatile contents of experimental run products. Beta-track autoradiography (Mysen and Seitz, 1975) is a microanalytical technique that has been applied to the investigation of C and S solubilities in a range of melt compositions. This method consists of doping the starting material with an isotope of the volatile element that spontaneously decays by emission of beta particles. The beta radiation of the quenched runs is recorded on a nuclear emulsion and the beta tracks are counted under reflected light magnification from a photographically-developed emulsion. Beta-track autoradiography has an advantage over some other techniques because sample homogeneity may be easily inspected under the microscope.

Vacuum fusion manometry (Harris, 1981) is a microanalytical technique that has been used for the volatile analysis of both natural and synthetic melt samples. Dingwell *et al.* (1984) used this technique to investigate water solubility in haplogranitic melts. The method involves the fusion of a sample under vacuum to liberate volatile species that are subsequently collected in a cold trap. The LN<sub>2</sub> cold trap is then heated slowly past the sublimation temperatures of the volatile species present. The amount of each volatile is determined by measuring the pressure of the gas in a known volume, with a capacitance manometer. In the study by Dingwell *et al.* (1984) the glass samples analyzed had been polished down to 50-100 microns thickness. These samples could be investigated under a transmitted light microscope to ensure the absence of unbreached vesicles in the relatively viscous melts investigated. This technique may be used to determine more than one volatile species with a single analytic run.

Other positive analysis techniques that have been borrowed from standard analytical procedures in the earth sciences included gas chromatography for CO<sub>2</sub> (Brey, 1976; Brey and Green, 1976), high temperature mass spectrometry for CO<sub>2</sub> (Rai *et al.*, 1983), Infrared spectroscopy for CO<sub>2</sub> (Johnson *et al.*, 1985) and H<sub>2</sub>O (Silver and Stolper, 1985a), and electron microprobe analysis for sulfur [e.g., Carroll and Rutherford (1985)]. Microanalytical techniques such as vacuum fusion manometry, focussing infrared spectroscopy and beta-track autoradiography are amenable to careful visual inspection and avoidance of equilibrium vesicles during analysis. Bulk techniques require careful documentation of the methods used to

## DINGWELL - Volatile Solubility

account for the source of a measured volatiles evolved from run products.

### Analysis by Difference

The analysis of volatile content by difference from 100% has been attempted in the past. Assigning the difference from 100% in microprobe analyses to H<sub>2</sub>O or CO<sub>2</sub> contents in experimentally quenched run products is unsatisfactory. Typical values obtained by this technique overestimate volatile contents by 50% to 100% in natural and experimental samples (Mysen *et al.*, 1976). Appropriate standards for volatile-containing glasses are difficult to establish. Such glasses are very fragile under the electron beam and ZAF corrections for light elements may be significantly affected by volatile content.

The analysis of water by weight loss is based on the principle that the difference in weight of the final run product before and after piercing of the noble metal capsule and drying of the contents is a measure of the excess water that was originally added to the experimental run and remained undissolved in the melt. There are several possible difficulties arising from this method of volatile solubility determination. Firstly, the nature and amount of any vesicles in the glass slug must be evaluated (preferably for each run). Any occluded water in the capsule that survives the sample drying process will invalidate the procedure. Secondly, at relatively high pressures (greater than 5 kbar) or in the presence of complexing agents (e.g., F, Cl), the silicate solute content of the fluid phase will be significant. This material, deposited during the quench or during the drying process, will obstruct proper determination of the weight of the excess fluid phase. Despite these considerations, which may account for the high results of Goranson (1931, 1936) on albite and Stone Mountain Granite, Oxtoby and Hamilton (1978) report a good reproducibility of weight-loss determinations on vesicle-free glasses of very silicic composition. The experiments of Oxtoby and Hamilton (1978) were performed at 1200°C to enhance escape of equilibrium vesicles from their charges. If the temperature dependence of volatile solubility is significant, however, this technique is of limited use in siliceous water-saturated systems where the temperatures of interest are 400 to 600°C lower (e.g., Burnham and Jahns, 1962).

## HYDROGEN

### Gas Species

Water is the most abundant H-bearing gas species in equilibrium with most igneous melts. Other H-bearing gas species, such as CH<sub>4</sub> and H<sub>2</sub>S, may be stabilized under relatively reducing conditions and will be discussed in the sections on carbon and sulfur, respectively. Hydrogen gas, H<sub>2</sub>, is a principal component of solar nebulae and its effects on the phase relations of simple silicate systems at extremely low pressures have been investigated by Mysen

et al. (1985). In addition,  $H_2$  may be a significant component of an O-H or C-O-H fluid phase in equilibrium with mantle melts under very reducing conditions (Eggler and Baker, 1982; Luth and Boettcher, 1986a).

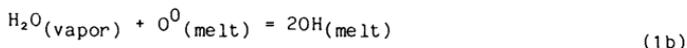
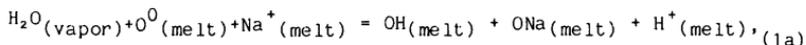
#### Solution Mechanisms- $H_2$

The mechanism of  $H_2$  solution in silicate melts is unknown at present. Two possibilities are molecular hydrogen and Si-H (hydride) complexes. Infrared spectra of a  $SiO_2$  glass containing 2 mole %  $H_2$  which was subjected to gamma rays and a neutron flux indicates the presence of Si-H bonds (Faile and Roy, 1970) whereas Faile and Roy (1971) observed that most of the  $H_2$  dissolved in  $SiO_2$  glass at 3 kbar and less than 800°C was present in these glasses as molecular  $H_2$ . Finally, Bell et al. (1962) have outlined the possibility of  $H_2$  reducing  $Si^{4+}$  to  $Si^{3+}$  or  $Si^{2+}$  to yield dissolved  $OH^-$ .

#### Solution Mechanisms- $H_2O$

One of the earliest discussions of the structural role of water in silicate melts of geological interest was by Wasserburg (1957). Three distinct mechanisms for water solution were proposed by Wasserburg (1957). In current terminology, these mechanisms would be described as (1) replacement of bridging oxygens [i.e., hydroxylation to form two silanol (Si-OH) groups]; (2) replacement of nonbridging oxygens (via alkali exchange) and (3) molecular solution. Wasserburg chose to treat mechanisms (1) and (2) as energetically equivalent and then proceeded to develop a statistical thermodynamic, ideal solution, mixing model for water in silicate melts that matched the available water solubility data for albite melt (Goranson, 1936). Shaw (1964, 1968) extended the solution modelling of water-silicate mixtures using a simple regular solution approximation that successfully modelled the pressure and temperature dependence of albite-water mixtures but was incapable of accounting for the critical behavior that had been reported by Kennedy et al. (1962) for the system  $SiO_2-H_2O$ . Spera (1974) presented a binary asymmetric solution model based on the water solubility data available for andesite, basalt and pegmatite (Burnham and Jahns, 1962; Hamilton et al., 1964) to generate activity coefficients for silicate-water mixtures. Calculations performed by Spera (1974) indicated that the silicate-water miscibility gap remained in the systems basalt-water and andesite-water over the entire range of geologically plausible temperatures and pressures. Complete miscibility was predicted for the system Harding pegmatite - water at 26.1 kbars and 700°C.

Burnham (1974, 1975, 1979a, 1979b, 1981) developed a model for the solution of water in silicate melts, based on the solubility determinations of Burnham and Jahns (1962) and the P-V-T data of Burnham and Davis (1971, 1974). The principle silicate-water interactions envisioned by Burnham (1975) are included in Fig. 4-5 [a modification of Burnham (1979a, Fig. 16-2)] and are represented by the following reactions:



where  $\text{O}^0$  refers to a bridging oxygen (Mysen, this volume).

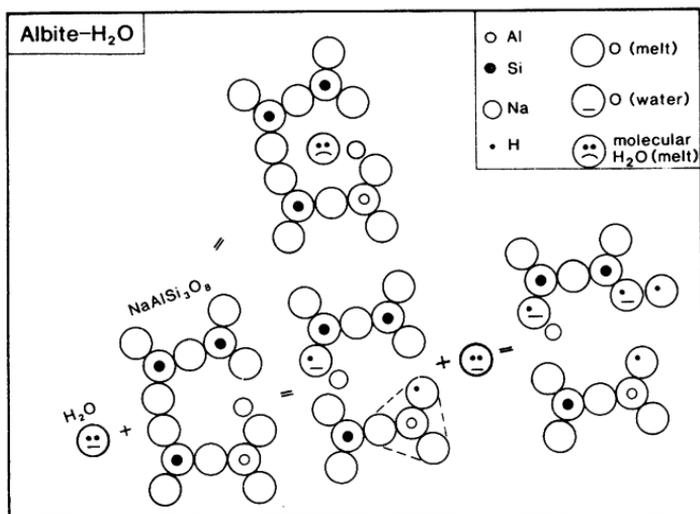


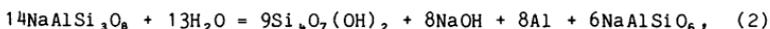
Figure 4-5. The solution of water in albite melt. [Modified from Burnham (1979b)].

The mechanism for water solution in albite melts was split into two sequential steps. The first step is breakage of an oxygen bridging bond and creation of two terminal bonds in its place, a Si-OH bond and a Si-O-Na complex. The Na atom has been transported from its network stabilizing position near the aluminate tetrahedra to the site of the broken bridging bond. The aluminate tetrahedron is now stabilized by an H<sup>+</sup> ion which has, in effect, exchanged with the Na atom illustrating Burnham's (1975, 1979a,b) concept of exchangeable cations. In subsequent calculation schemes (Burnham, 1979a,b) the number of exchangeable cations per molecule of melt is an important parameter in estimating water solubility. The second stage of Burnham's (1975) two-stage scheme is also presented in Fig. 4-5. At a mole fraction of water equal to 0.5, all exchangeable cations (in NaAlSi<sub>3</sub>O<sub>8</sub> composition melt) have been exchanged. Thus the cation exchange mechanism of water solubility is no longer possible and a second mechanism occurs with further water dissolution. The second mechanism of water solution involves the dissociation of an incoming water molecule to form two Si-OH complexes.

Burnham (1979a,b) was successful in rationalizing the solubility determinations of Hamilton *et al.* (1964) and Burnham and

Jahns (1962) in terms of this albite-water model. Casting the anhydrous compositions of Mt. Hood andesite, Columbia River basalt, and Harding pegmatite into molecules (based on 8 oxygen atoms per molecule) Burnham (1975) brought the solubilities of water in these melts into equivalence.

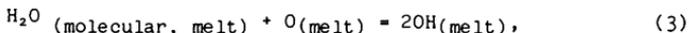
Mysen *et al.* (1980) obtained Raman spectra for hydrous silicate glasses and did not observe any evidence for the presence of tetrahedrally-coordinated Al bonded to a hydroxyl group. If the aluminate tetrahedron in Fig. 4-5 is not stabilized by the exchanged  $H^+$  (to form an Al-OH bond) then the aluminum atom would be unstable in tetrahedral coordination. Mysen *et al.* (1980) proposed that a reaction of the type;



which includes the production of network-modifying Al, (8Al), a Si-enriched network structure, ( $9Si_4O_7(OH)_2$ ), anhydrous metasilicate-like units, ( $6NaAlSiO_6$ ) and OH associated with network modifying Na, (NaOH).

Eggler and Rosenhauer (1978) and Mysen and Virgo (1980b) proposed that in relatively depolymerized melts such as diopside and sodium disilicate, respectively, water may dissolve by replacement of nonbridging oxygens.

Stolper (1982a,b) returned to a model of molecular water solution in silicate melts proposed by Wasserburg (1957). Stolper (1982b) presented infrared spectra of natural and synthetic hydrous glasses that clearly indicated the presence of molecular water in these samples. Orlova (1964) had previously presented similar spectra but there was (and is) controversy concerning the sensitivity of water speciation to natural and experimental quenches. Stolper contended that the infrared spectra accurately reflected the nature of dissolved water (rather than occluded fluid inclusions) that was quantitatively quenched in from high pressure and temperature. (Stolper *et al.* (1983) presented preliminary evidence that the OH/H<sub>2</sub>O concentration ratios of albite + 4-5wt% total water are independent of quench rate in the range of 0.3 to 160°C/sec.) Next, Stolper (1982b) quantified the proportions of OH and H<sub>2</sub>O in the investigated samples by calibrated integral molar absorptivities with glasses of known water content. (Stolper's (1982a,b) estimate of composition-independent molar absorptivities has been revised recently to include composition-dependence (Stolper and Silver, 1985). The proportions of hydroxyl and molecular water were rationalized in terms of the homogeneous equilibria;



where the mass action term;  $K_1$ , defined as;

$$K_1 = a_{OH}^2, \text{ melt} / [(a_{H_2O, \text{molecular}})(a_{O, \text{melt}})] \quad (4)$$

is independent of temperature and anhydrous silicate melt

composition and equal to 0.2. Figure 4-6 shows the proportions of molecular water and hydroxyl groups obtained by Stolper (1982b). Solution of the first few weight percent of water in silicate melts proceeds predominantly by formation of dissociated hydroxyl groups; however, there is a small but finite proportion of molecular water created at the start of water solution. The proportions of dissolved molecular water and hydroxyl groups cross over near 4.5 wt. % total dissolved water; and at higher water contents, water dissolves dominantly as molecular species.

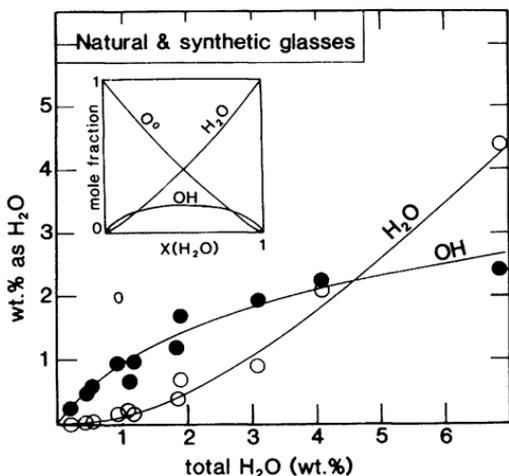


Figure 4-6. The proportions of molecular water and hydroxyl groups in natural and synthetic glasses. [Redrawn from Stolper (1982b)]. [Inset: the proportions of OH, H<sub>2</sub>O and melt oxygens (O<sup>o</sup>) predicted from an ideal silicate-water solution with  $K_1=0.2$ ].

Silver and Stolper (1985b) have cast the freezing point depression and water solubility data for the systems albite-water, diopside-water, and silica-water in terms of an ideal mixing model similar to that of Wasserburg (1957) for the mixing of melt oxygens, water molecules, and hydroxyl groups. Given the assumptions of their formulation, Silver and Stolper (1985b) use the agreement between the observed and calculated pressure-dependences of (1) melting and (2) water solubility in the systems albite- and silica-water to confirm independently the value of  $K_1=0.2$  observed in the infrared spectra.

It should be noted that, at present, the thermodynamics of albite-water and diopside-water may be adequately modelled by formulations that include (Silver and Stolper, 1985) and exclude (Burnham, 1981; Eggler and Burnham, 1984) the presence of molecular water in these melts.

Finally, the dissociated proportion of dissolved water in silicate melts, whether it be equal to or less than 100 percent of the total dissolved water, must be structurally bonded to one or more cations. The molar absorptivities of different X-OH bonds may vary considerably (Paterson, 1982) despite Stolper's (1982b) choice of a single molar absorptivity for all hydroxyl species. The relative stabilities of various cation-hydroxyl complexes is being investigated by Mysen and Virgo (1986a) who report that studies in binary silica-hydroxide systems such as  $\text{SiO}_2\text{-Al(OH)}_3$ ,  $\text{SiO}_2\text{-Ca(OH)}_2$  and  $\text{SiO}_2\text{-NaOH}$  indicate the following order of complex stability;  $\text{Ca-OH} > \text{Na-OH} > \text{Al-OH} > \text{Si-OH}$ . The resolution of hydrous speciation in geologic melts will be greatly aided by development of the capability for high pressure, high temperature spectroscopic measurements on hydrous molten silicates.

## SOLUBILITY DETERMINATIONS

### Hydrogen

No quantitative data are available on the solubility of  $\text{H}_2$  in silicate melts of geologic interest. Luth and Boettcher (1986a,b), however, have investigated the melting behavior of albite, diopside and  $\text{SiO}_2$  in the presence of an O-H fluid phase at the iron-wustite- $\text{H}_2\text{O}$  and hematite-magnetite- $\text{H}_2\text{O}$  buffers. Luth and Boettcher (1986b) have investigated the melting of albite and diopside in the presence of a pure  $\text{H}_2$  fluid phase. Increasing  $\text{H}_2$  concentration relative to  $\text{H}_2\text{O}$  in the fluid phase results in increasing melting temperatures in all systems and the solidus depression in the  $\text{H}_2$ -bearing systems is larger than that observed for the equivalent silicate- $\text{H}_2\text{O-CO}_2$  systems at an equivalent (calculated) mole fraction of  $\text{H}_2\text{O}$ . The implication of such behavior is that  $\text{H}_2$  is more soluble than  $\text{CO}_2$  in  $\text{H}_2\text{O}$ -bearing albite, diopside and  $\text{SiO}_2$  melts. Finally, the difference in the solidi of silicate- $\text{H}_2\text{O-H}_2$  (hematite-magnetite- $\text{H}_2\text{O}$  buffer) and  $\text{SiO}_2\text{-H}_2\text{O}$  systems is larger than that which would result from simple dilution of  $\text{H}_2\text{O}$  by  $\text{H}_2$ , implying that the solution of  $\text{H}_2$  in these melts inhibits  $\text{H}_2\text{O}$  solution at low concentrations of  $\text{H}_2$  in the vapor.

### $\text{H}_2\text{O}$

#### Pressure Dependence

The solubility of water in silicate melts is a positive function of pressure. More specifically, the pressure dependence of water solubility up to 0.5 mole fraction (albite-equivalent moles of anhydrous melt) describes a square root dependence on water fugacity. At greater water contents, the pressure dependence of water solubility is a logarithmic function of water fugacity (Burnham, 1975).

## Temperature Dependence

The solubility of water in silicate melts is a negative function of temperature (Goranson, 1931; Khitarov *et al.*, 1959; Burnham and Jahns, 1962; Oxtoby and Hamilton, 1978). The negative temperature dependence of water solubility in granitic melts is approximately 0.2-0.3 wt. % water per 100°C in the pressure range of 1 to 3 kbar.

## Precision of Determinations: Albite-water

The most extensively investigated silicate-volatile system is albite-water. The results of several investigations of water solubility in this system are useful for comparison of many of the techniques of solubility determination discussed above such as weight loss (Goranson, 1936; Orlova, 1964; Oxtoby and Hamilton, 1978), chemography (Burnham and Jahns, 1962; Fenn, 1973), isothermal decompression (Sorapure, 1981) and direct analysis (Khitarov *et al.* 1959)

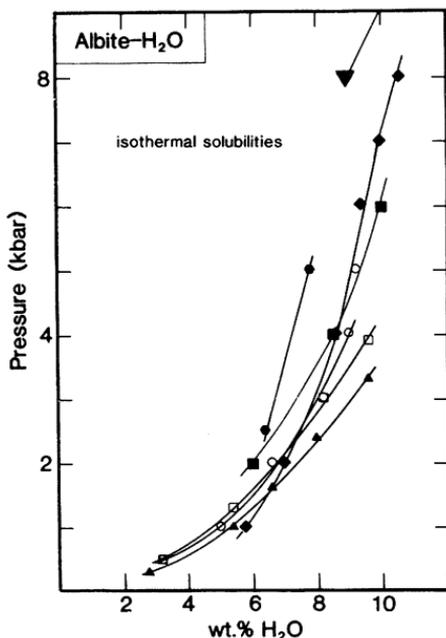


Figure 4-7. The solubility of water in albite melt. [open circles, Khitarov *et al.* (1959); diamonds, Oxtoby and Hamilton, (1978); solid squares, Burnham and Jahns (1962); open squares, Orlova (1964); triangles, Goranson (1936); hexagons, Fenn (1973); inverted triangles, Sorapure (1981)].

Data for the isothermal pressure dependence of water solubility in albite melt are presented in Fig. 4-7. The weight loss determinations of Goranson (1936) may be too high due to incomplete extraction of occluded, undissolved water during drying. The data of Fenn (1973) and Sorapure (1981) are substantially lower than other determinations but the reasons for this discrepancy are not clear. The determinations of Khitarov *et al.* (1959) (positive analysis), Burnham and Jahns (1962) (chemography), and Orlova (1964); Oxtoby and Hamilton (1978) (weight loss) are in reasonable agreement.

## Geologic Melts

Figure 4-8 summarizes water solubility data for natural silicate melts.

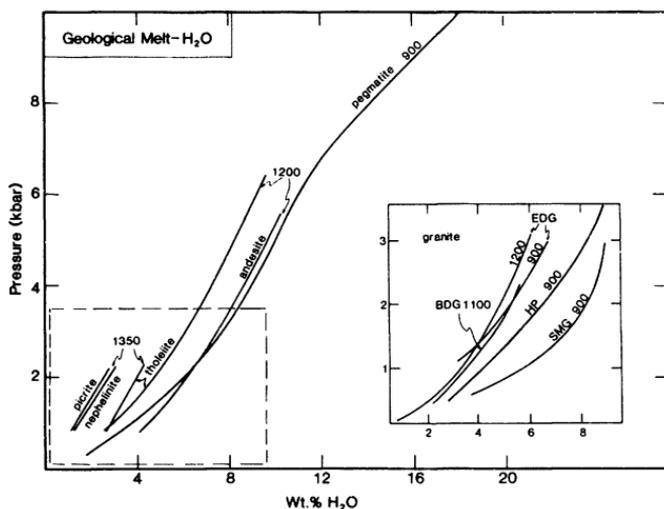


Figure 4-8. The solubility of water in natural melts. [numbers on curves refer to temperature ( $^{\circ}\text{C}$ ): Data from Scarfe (1973), picrite, nephelinite and tholeiite; Hamilton *et al.* (1964), tholeiite, and andesite; Burnham and Jahns (1962), Harding pegmatite (HP); Khitarov *et al.* (1959), El'Dzurtinskii granite (EDG); Oxtoby and Hamilton (1978), Beinn an Dubhaich granite (BDG); Goranson (1931), Stone Mountain granite (SMG)].

Water solubility increases with increasing silica content from picrite and nephelinite melts through basalt and andesite to granitic pegmatite. The solubility of water in granitic melts at low pressure (1 to 3 kbar) has been studied extensively [Goranson (1931); Khitarov *et al.* (1959); Burnham and Jahns (1962); Oxtoby and Hamilton (1978)] and isothermal solubilities are presented in the inset of Fig. 4-8.

The effect of aluminum saturation on the solubility of water in melts close to the 1 kbar haplogranite minimum melt was investigated recently by Dingwell *et al.* (1984). Both Al-oversaturated (peraluminous) and Al-undersaturated (peralkaline) melts have higher water solubilities than the 1 kbar thermal minimum (Al-saturated) melt composition (Fig. 4-9).

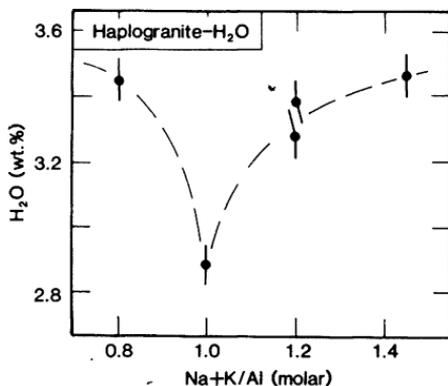


Figure 4-9. The effect of aluminum saturation on the solubility of water in haplogranitic melts. [Data from Dingwell *et al.* (1984)].

In contrast with the strong influence of aluminum saturation on water solubility, the effect of exchanging K for Na in melts of granitic and feldspathic composition is insignificant over the Na/K range of most granitic magmas [Voigt *et al.* (1981); Dingwell *et al.* (1984)].

Finally, the solubility of water in phonolitic melts was investigated by Kogarko *et al.* (1977) (natural melt) and Dingwell *et al.* (1984) (synthetic melt). Both studies indicated that the solubility of water in phonolite melts is significantly higher than in granitic melts.

## CARBON

### Gas Species

The most important carbon-bearing gas species in equilibrium with most magmas is CO<sub>2</sub> but there are two possible exceptions. Firstly, anhydrous magmas in equilibrium with graphite/diamond and a C-O vapor phase will be buffered by the reaction:

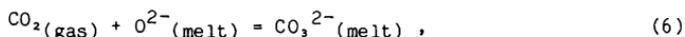


This buffer yields vapor compositions with a significant proportion of CO at upper mantle temperatures and pressures (Egler *et al.*,

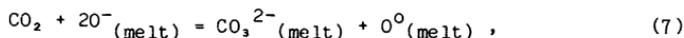
1979). Secondly, magmas coexisting with a C-O-H vapor phase at oxygen fugacities below the magnetite-wustite solid-solid oxygen buffer will contain significant amounts of CH<sub>4</sub> and H<sub>2</sub> (Eggler and Baker, 1982) with CH<sub>4</sub> becoming dominant below the iron-wustite solid-solid oxygen buffer.

#### Solubility Mechanisms

The 1 atmosphere solution of CO<sub>2</sub> in basic silicate melts was proposed by Pearce (1964) to be a carbonation reaction of the type:



where O<sup>2-</sup> represents "free oxygens" in the silicate melt (i.e., those not bonded to tetrahedral cations) and CO<sub>3</sub><sup>2-</sup> represents a carbonate complex associated with an alkali or alkaline earth cation in the melt. The occurrence of free oxygens in silicate melts is probably restricted to melts more basic than those found in nature (Mysen, this volume). In geological melts the oxygens are coordinated by one or two tetrahedral cations (i.e., nonbridging and bridging oxygens, respectively (Mysen, this volume) and CO<sub>2</sub> may react with nonbridging oxygens in these melts via a reaction of the type:



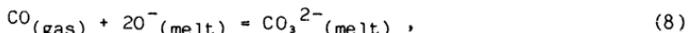
where O<sup>-</sup> represents a nonbridging oxygen and O<sup>0</sup> represents a bridging oxygen. CO<sub>2</sub> solution via Eqn. 7 results in the formation of a carbonate complex and a bridging oxygen in the melt. Formation of the bridging oxygen, in effect, polymerizes the silicate melt. The observation that CO<sub>2</sub> is more soluble in more depolymerized melts supports the contention that carbonation is the solution mechanism dominant in most melts of geologic interest.

Molecular solution of CO<sub>2</sub> in silicate melts is supported by vibrational spectra of carbon-bearing glasses on the join NaAlO<sub>2</sub>-SiO<sub>2</sub> although the specific temperature-, pressure- and composition dependence of the CO<sub>2</sub>/CO<sub>3</sub><sup>2-</sup> ratio in this system is under discussion [Mysen (1976); Fine and Stolper (1983,1986a,b) and Mysen (pers. comm., 1985)]. Mysen and Virgo (1980a) have proposed that in Ca-Mg- and Ca-Na-bearing silicate melts, dissolved carbon is present as CaCO<sub>3</sub><sup>0</sup> complexes whereas NaCO<sub>3</sub><sup>0</sup> complexes have been proposed for albite melt (Mysen and Virgo, 1980c). Fine and Stolper (1986a) have shown that the CO<sub>2</sub>/CO<sub>3</sub> ratio of dissolved carbon is a strong function of glass composition in the system Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>; increasing with decreasing Na content along the join NaAlO<sub>2</sub>-SiO<sub>2</sub> and with the addition of excess Al<sub>2</sub>O<sub>3</sub> to albite melt. Natural basaltic and synthetic Ca,Mg-silicate glasses contain no molecular CO<sub>2</sub> (Fine and Stolper, 1986b). Finally, Boettcher (1984) has proposed that the increase in carbon solubility in SiO<sub>2</sub> melt at high pressure may be due to the solution of carbon as tetrahedral cations.

Eggler et al. (1979) observed that the infrared spectra of melts saturated with a CO-CO<sub>2</sub> vapor phase consisting of 30-40 mol %

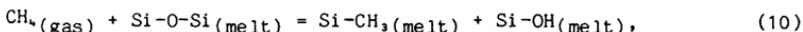
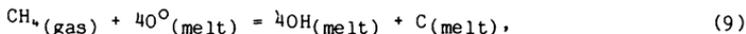
## DINGWELL - Volatile Solubility

CO showed only one carbonate absorption band in their infrared absorption spectra and proposed, therefore, that CO dissolved in silicate melts via the reaction:



Note that in Eqn. 8 no bridging oxygens are produced, and, therefore, the melt will not be polymerized by CO solution.

Eggler and Baker (1982) have proposed that  $\text{CH}_4$  dissolves in silicate melts by one or both of the following reactions:



In both of these reactions,  $\text{CH}_4$  acts as a depolymerizer of the silicate melt by replacing bridging oxygens with nonbridging complexes.

## SOLUBILITY DETERMINATIONS

### Composition Dependence

Fig. 4-10 contains high-pressure determinations of  $\text{CO}_2$  solubility in synthetic melts. Mysen (1976) observed that  $\text{CO}_2$  solubility increases with increasing melt basicity on the join  $\text{SiO}_2$ - $\text{NaAlO}_2$  from albite to nepheline composition. Holloway *et al.* (1976) also observed an increase in  $\text{CO}_2$  solubility with increasing melt basicity from  $(\text{Ca},\text{Mg})_{3.2}\text{Si}_{2.4}\text{O}_8$  to  $(\text{Ca}_{.68}\text{Mg}_{.32})_4\text{Si}_2\text{O}_8$ .

The  $\text{CO}_2$  solubility determinations of Mysen *et al.* (1975) for andesite, tholeiite, and olivine melilite nephelinite are presented in Fig. 4-11. The  $\text{CO}_2$  solubility is a strong positive function of melt basicity.

### Temperature Dependence

The temperature dependence of  $\text{CO}_2$  solubility in silicate melts appears to depend strongly on pressure and melt composition. Figure 12 illustrates the observed temperature dependence of  $\text{CO}_2$  solubility in various synthetic silicate melts which have been equilibrated with an essentially pure  $\text{CO}_2$  vapor phase. Insets a, b and c of Fig. 4-12 indicate three possible types of temperature-dependence of solubility. As can be seen from Fig. 4-12, simple negative (inset a), positive becoming negative with increasing temperature (inset b), and negative becoming positive with increasing temperature (inset c) are three trends of the temperature-dependence of  $\text{CO}_2$  solubility that have been experimentally observed. At pressures below the critical point of the  $\text{CO}_2$ -free silicate melt (insets a, b)

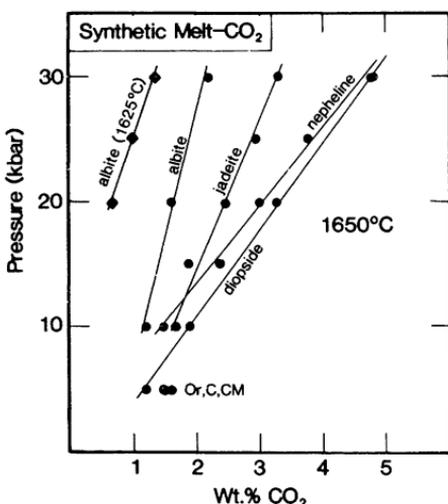


Figure 4-10. The solubility of carbon dioxide in some synthetic melts. [Data from Mysen (1976), Mysen *et al.* (1976) and Johnson *et al.* (1985); closed circles = beta track, closed diamonds = infrared spectroscopy; Or = orthoclase, CM = Ca<sub>0.5</sub>AlSi<sub>3</sub>O<sub>8</sub>, CM = Ca<sub>0.25</sub>Mg<sub>0.25</sub>AlSi<sub>3</sub>O<sub>8</sub>].

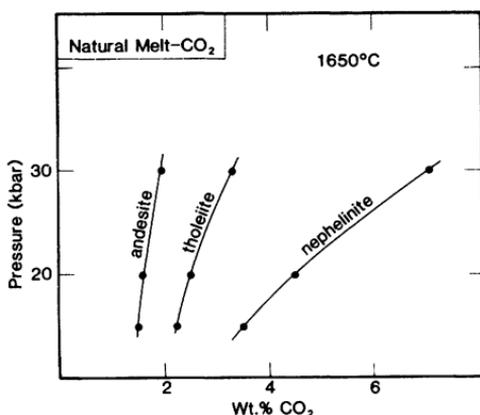


Figure 4-11. The solubility of carbon dioxide in melts of andesite, tholeiite and nephelinite. [Data from Mysen *et al.* (1975)].

the solubility of water may exhibit either a negative (inset a) or a positive (inset b) temperature-dependence but the temperature-dependence near the L + S + V point must become negative at higher temperatures to close out the L and L + V fields on the CO<sub>2</sub>-free side of the diagram. At pressures above the critical point

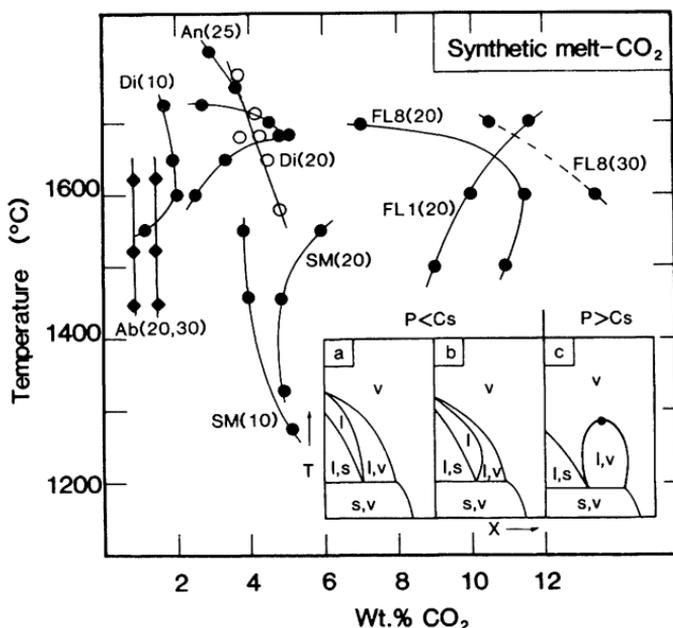


Figure 4-12. The temperature dependence of carbon dioxide solubility in synthetic melts. [Data from Holloway et al. (1976), Mysen (1976), Mysen et al. (1976), Mysen and Virgo (1980a,b), Rai et al. (1983), Johnson et al. (1985)]. Numbers in brackets refer to pressure (in kbar). (Ab = albite, Di = diopside, An = anorthite, SM =  $\text{NaCaAlSi}_2\text{O}_7$ , FL8 =  $(\text{Ca}_{0.67}\text{Mg}_{0.33})_2\text{SiO}_4$ , FL1 =  $\text{CaMgSiO}_4$ .; closed circles = beta track, open circles = mass spectrometry, closed diamonds = infrared spectroscopy.)

of the pure silicate, the  $V = L + V$  curve forms a closed loop which does not intersect  $\text{CO}_2$ -free compositions. The temperature-dependence of solubility in this case may be negative near the  $L + S + V$  invariant assemblage and become positive with increasing temperature or be positive at all temperatures. A major point made by Rai et al. (1983) is that  $\text{H}_2$  diffusion into single Pt capsules may produce complex C-O-H fluid equilibria in nominally anhydrous  $\text{CO}_2$  solubility studies.  $\text{H}_2$  diffusion could explain some of the apparent discrepancies in  $\text{CO}_2$  solubility determinations because the experiments in such studies have been performed in different types of pressure vessels and therefore under differing conditions of  $p\text{H}_2$ . As noted by Boettcher et al. (1982) and discussed at length by Luth and Boettcher (1986a), experiments performed under conditions of unbuffered  $p\text{H}_2$  are only nominally anhydrous. The presence of a C-O fluid phase aggravates the problem of  $\text{H}_2$  diffusion into single Pt capsules because the fluid phase

contains oxygen which can react with the diffusing  $H_2$  to form  $H_2O$  for dissolution in the melt (e.g. Rai et al. (1983)). The complexity of temperature dependence observed in Fig. 4-12 means that extrapolation of  $CO_2$  solubility data to lower, subliquidus temperatures is not advised.



Mysen (1976) and Holloway and Lewis (1974) have investigated the solubility of  $CO_2$  in hydrous melts. Data for synthetic and natural melts are presented in Fig. 4-13.

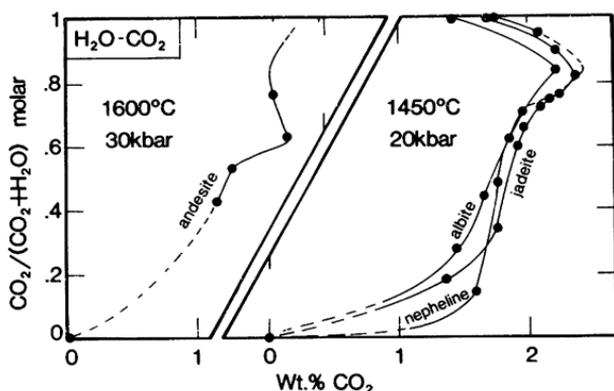


Figure 4-13. The  $CO_2$  contents of natural and synthetic melts saturated with an  $H_2O-CO_2$  vapor phase. [Data from Mysen *et al.* (1975,1976)].

The solubility of  $CO_2$  increases with the addition of up to 0.2 mole fraction of  $H_2O/(H_2O + CO_2)$  in the vapor phase. The increase in  $CO_2$  solubility was interpreted by Mysen (1976) as follows. The solution of water in these melts results in the creation of nonbridging oxygens. Therefore, the carbonation reaction (Eqn. 7) for  $CO_2$  solution, which consumes nonbridging oxygens, proceeds further in hydrous melts due to the increased proportion of nonbridging oxygens available. Beyond approximately 0.2 mole fraction of  $H_2O$ , the solubility of  $CO_2$  decreases with increasing water content, presumably due to the rapidly decreasing fugacity of  $CO_2$  in the vapor phase.

#### CO

The solubility of  $CO-CO_2$  vapor in silicate melts equilibrated with graphite has been investigated by Egger *et al.* (1979). The  $CO-CO_2$  vapor (containing 30-40 mol %  $CO$ ) was more soluble than pure  $CO_2$  vapor in melts of albite and diopside composition. Egger *et al.* (1979) inferred, by comparison of  $CO-CO_2$  and  $CO_2$  solubilities, that  $CO$  was appreciably soluble in silicate melts and that the

temperature dependence of CO solubility was negative.

#### CH<sub>4</sub>

The solubility of CH<sub>4</sub> in silicate melts has not been systematically investigated at high pressure. Rai et al. (1983) reported the solution of 0.18 to 0.51 wt. % CH<sub>4</sub> in diopside melt at 20 kbars and 1600°-1700°C. These experiments were performed in the presence of a complex, CO<sub>2</sub>-CO-CH<sub>4</sub>-H<sub>2</sub>O-bearing vapor phase. Also, Egglar and Baker (1982) reported a significant (~ 150°C) liquidus depression of diopside in the presence of a CH<sub>4</sub>-H<sub>2</sub> vapor phase containing approximately 85-90 mol % of CH<sub>4</sub>.

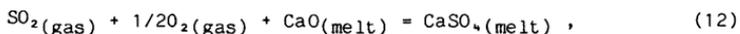
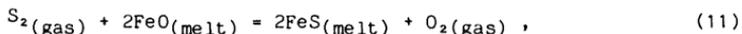
### SULFUR

#### Gas Species

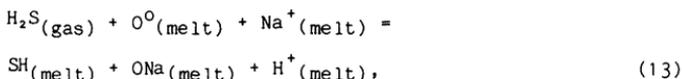
Gas samples from active basaltic volcanoes (Gerlach and Nordlie, 1975a,b,c) and gas speciation calculations based on coexisting oxide-sulfide pairs and independent estimates of H<sub>2</sub>O fugacity (Whitney, 1984,1985) indicated that the most abundant sulfur-bearing gas species in equilibrium with terrestrial magmas were SO<sub>2</sub> and H<sub>2</sub>S. Gerlach and Nordlie (1975b) calculated that minor concentrations of S<sub>2</sub> and COS may occur in equilibrium with some basaltic liquids.

#### Solubility Mechanisms

An important parameter controlling the solution mechanism of sulfur in silicate melts is oxygen fugacity (Fincham and Richardson, 1954). Solubility determinations at 1 atmosphere, discussed below, clearly indicate two distinct fO<sub>2</sub> ranges of sulfur solution behavior. At low fO<sub>2</sub>, the sulfur dissolves in dry silicate melts as the sulfide ion, S<sup>-</sup> and there is strong evidence that in the range of fO<sub>2</sub> corresponding to sulfide solution, iron is the melt component associated with dissolved sulfide (e.g., Haughton et al., 1974). At high fO<sub>2</sub> the sulfur dissolves as the sulfate complex, SO<sub>4</sub><sup>2-</sup> and the magnitude of sulfate solubility is strongly related to the amount of calcium in the silicate melt (e.g., Katsura and Nagashima, 1974). These two solution mechanisms may be represented by the following reactions:



In hydrous systems, Burnham (1979a) proposed that sulfur may dissolve via the reaction:



(i.e., analogous to equation 1a for water solubility).

#### Solubility Determinations

Figure 4-14 contains the results of several determinations of the sulfur content of natural silicate melts at constant  $f\text{S}_2$  and varying  $f\text{O}_2$  (Shima and Naldrett, 1973; Katsura and Nagashima, 1974; Buchanan and Nolan, 1979).

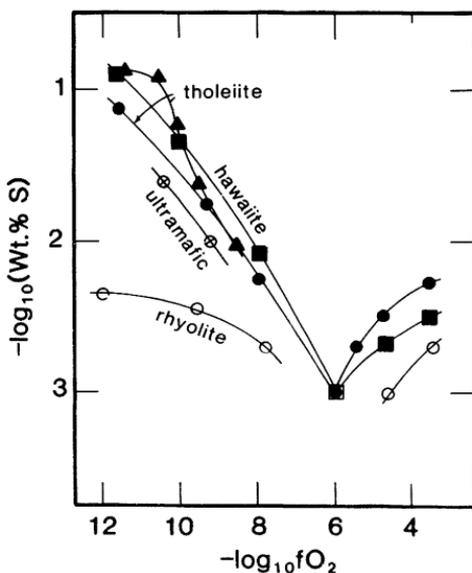


Figure 4-14. The  $f\text{O}_2$ -dependence of sulfur solubility in natural melts at 1 atm. [Data from Katsura and Nagashima (1974), squares, open and closed circles; Shima and Naldrett (1973), circles with crosses; Buchanan and Nolan (1979), triangles].

It is apparent that the  $f\text{O}_2$  dependence of sulfur content describes a minimum near  $\log(f\text{O}_2)$  equal to  $-6$ . At higher oxygen fugacity the sulfur content of the silicate melts increases with increasing oxygen fugacity, presumably due to solution of sulfur as the sulfate ( $\text{SO}_4^{2-}$ ) complex. At lower oxygen fugacities, sulfur contents increase with decreasing oxygen fugacity due to the increasing stability and solution of sulfur as the sulfide ion ( $\text{S}^{2-}$ ). In the

sulfide solution range, sulfur content is positively correlated with iron content, and, in the sulfate solution range, sulfur content is positively correlated with melt calcium content. At sulfur saturation, melts in the sulfide solution range are saturated with an immiscible FeS liquid whereas in the sulfate solution range anhydrite is the saturating phase.

The sulfur contents of a silicate melt in equilibrium with either anhydrite or an immiscible FeS liquid, and an H-O-S fluid phase were recently investigated by Carroll and Rutherford (1985) in the system dacite-FeO-H-O-S. The equilibrium sulfur content of the dacite melt was controlled by iron content at constant  $f_{S_2}$ ,  $f_{O_2}$ , temperature and pressure. The saturation surface of FeS is a positive function of pressure in this system. These liquids were saturated with a hydrogen-bearing vapor phase over a range of oxygen fugacities from the graphite-methane to the quartz-fayalite-magnetite solid-solid buffers; however, Fig. 4-15 indicates that iron content controls sulfur solubility and sulfur is, therefore, probably dissolved as FeS complexes rather than  $HS^-$  in these melts.

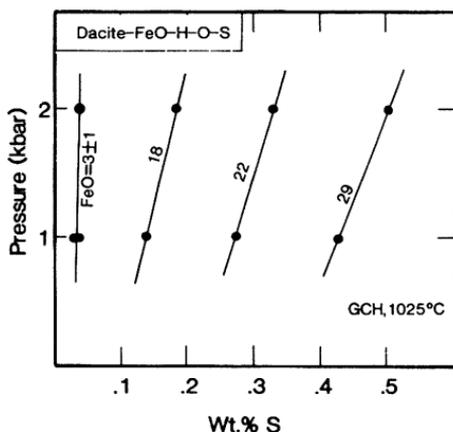


Figure 4-15. The sulfur content of Dacite + FeO melts equilibrated with an H-O-S buffer at the graphite-methane ( $f_{H_2}$ ) buffer (GCH). [Data from Carroll and Rutherford (1985)].

The pressure- and temperature-dependence of the FeS saturation surface of anhydrous andesite and basalts has been investigated by Wendlandt (1982) who showed a positive temperature dependence and a negative pressure dependence for these melts (Fig. 4-16). The positive temperature dependence of the FeS saturation surface has been confirmed by Buchanan et al. (1983) for an anhydrous, synthetic tholeiite melt. The FeS saturation surface is at higher melt sulfur contents in basalt than in andesite.

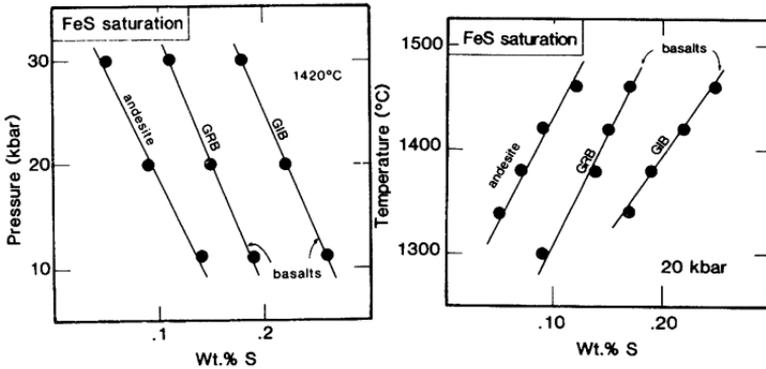


Figure 4-16. The pressure- and temperature-dependence of the FeS saturation surface of natural andesite and tholeiite melts. [Data from Wendlandt (1982); GRB = Grande Ronde Basalt, GIB = Galapagos Island Basalt].

Mysen and Popp (1980) have investigated the pressure dependence of the sulfur contents of albite and diopside melt at the Ag, Cu, and Pt metal-sulfide buffers. Both Fe-free melts show a positive pressure dependence of sulfur content (Fig. 4-17). Diopside dissolves significantly more sulfur than albite, suggesting that sulfur reacts preferentially with nonbridging oxygens in these Fe-free melts.

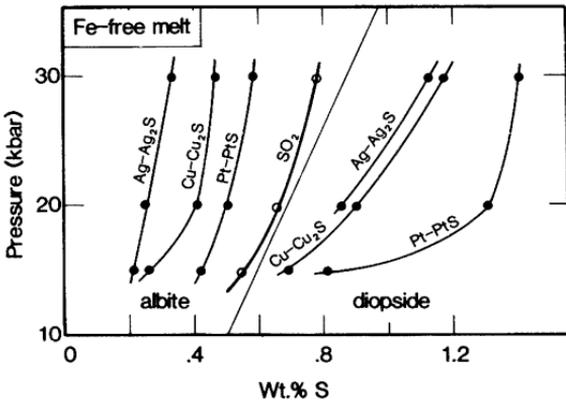


Figure 4-17. The sulfur contents of albite and diopside melts equilibrated with Ag, Cu and Pt metal-sulfide buffers at high pressure. [Data from Mysen and Popp (1980)]. Also, the solubility of SO<sub>2</sub> in albite melt (added as Na<sub>2</sub>SO<sub>3</sub>, Mysen (pers. comm. 1985)). [Data from Mysen (1977)].

## CHLORINE

Chlorine is dissolved in aqueous fluids coexisting with magmas as chlorides of Na, K, Ca, Mg, Fe and H (Roedder, 1984). Burnham (1979a,b) has suggested that the solution of chlorine in hydrous silicate melts proceeds via the following reaction:



Koster van Groos (1966) has determined the NaCl liquid saturation surface in the system albite-NaCl-H<sub>2</sub>O. At 1 kbar, albite melt dissolved approximately 3 wt. % NaCl. The addition of water decreased the solubility of NaCl in albite melt.

The solubility of HCl in melts of basalt, andesite and rhyolite composition has been investigated at 1 atm by Iwasaki and Katsura (1967). The solubility of HCl increased with decreasing temperature and decreasing silica content.

The partitioning of chlorine between granitic and trondjemitic melts and an aqueous vapor phase has been investigated by Kilinc and Burnham (1972). Chlorine partitioned strongly in favor of the aqueous phase. The melt-vapor partition coefficient of chlorine ranged from 0.023 at 2 kbar to 0.012 at 6 kbar and then increased to 0.077 at 8 kbar.

## FLUORINE

The speciation of fluorine in aqueous fluids equilibrated with magmas is uninvestigated, but evidence from melt-vapor partition experiments indicates that the Al, Na, K and Si solute contents of an aqueous vapor phase increase with fluorine addition (Hards, 1978; Dingwell, 1984). Fluorine is highly soluble in silicate melts (Manning, 1981; Dingwell, 1985). The melt-vapor partition coefficient of fluorine is in the range of 3 to 10 (Burnham, 1967; Hards, 1978).

The solution mechanisms of fluorine in dry silicate melts have been investigated with Raman spectroscopy by Mysen and Virgo (1985a,b,c). Melts of albite and albite(15 wt. %)silica(85 wt. %) dissolve fluorine by formation of Al-F and, to a lesser extent, Na-F complexes.

Koster van Groos and Wyllie (1968) determined the saturation surface of NaF in the system albite-NaF-H<sub>2</sub>O. At 1 kbar, albite melt dissolved 17 wt. % NaF. The addition of water slightly decreases this value.

Textures interpreted as silicate-fluoride liquid immiscibility have been observed in some experimental studies on natural granitic

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melts [Anfilogov *et al.*, (1973); Glyuk and Anfilogov (1973a,b); Kovalenko (1978)] but not in other studies [Danckwerth (1981); Manning (1981)], and, therefore, the importance of silicate-fluoride-liquid immiscibility in nature is difficult to ascertain.

### NITROGEN

Nitrogen is present as  $N_2$  and  $NH_4$  in the system C-O-H-N under magmatic conditions. Holloway and Reese (1974) and Reese and Holloway (1974) have determined the nitrogen contents of albite glass equilibrated with C-O-H-N fluid to be 0.015 wt. % at  $P(\text{tot}) = 2.1$  kbar and  $P(N_2) = 1$  kbar and 0.045 wt. % at  $P(\text{tot}) = 4.6$  kbar and  $P(N_2) = 2$  kbar.

### BORON

Boron is highly soluble in silicate melts. Pichavant (1981) has determined a melt-vapor partition coefficient of 0.33 in the system haplogranite- $H_2O$ - $B_2O_3$  at 1 kbar and 800°C.

### SUMMARY

In this chapter, attention has been focused on the methods of determination of volatile solubility in silicate melts. It is emphasized that all methods have drawbacks that limit their usefulness. All direct analysis techniques rely on quenching to preserve the volatile contents of interest. Thus all direct analysis methods must evaluate the effects of quenching (i.e., by varying quench rate or by comparison with DTA and chemographic determinations.). Also, direct analysis methods must confirm that the volatile contents being measured are derived solely from the phase of interest. Direct analysis methods, successfully employed, yield extremely precise solubility determinations and are thus amenable to analysis of low volatile (e.g., low pressure) contents and small differences in solubility due to melt compositional variation. Differential thermal analysis has the advantage that no quench is required.

The solution of water in silicate melts has been investigated for 50 years yet there is still disagreement on the mechanism of solution. Thermodynamic formulations have been constructed to account for the temperature- and pressure-dependence of water solubility and liquidus-depression with either complete or partial dissociation. The resolution of this subject awaits the technology for high-pressure, high-temperature spectroscopic investigation of hydrous silicate melts. Water does depolymerize silicate melts and the solubility of water increases with increasing melt polymerization. Recent work on the low-pressure solubility of water in granitic melts indicates melt-compositional variations that require further investigation in order to enhance understanding of boiling phenomena in late-stage silicic systems.

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The solubility of carbon dioxide in silicate melts appears to be a considerably more complex function of melt composition and temperature than is the case for water. Discrepancies in different methods of carbon dioxide analysis of experimental products must be resolved before much progress can be expected to occur in this area. The data presently available for carbon dioxide indicate that the mechanisms of solution are carbonation and molecular solution. Carbon dioxide solubility increases with melt basicity.

The solubility of sulfur in silicate melts is a strong function of oxygen fugacity. Low oxygen fugacity stabilizes sulfide solution in melts that is positively correlated with iron content. High oxygen fugacity stabilizes sulfate solution that is positively correlated with calcium content. In iron-free melts, sulfur is more soluble (as a sulfide) in more depolymerized melts.

The partitioning of elements that are often enriched in hydrothermal fluids requires more investigation. The melt-fluid partitioning of Li and Be is uninvestigated. Boron and chlorine partition in favor of the aqueous fluid whereas fluorine partitions in favor of silicate melts. Partitioning of these and other elements into a carbon dioxide-dominated fluid remains uninvestigated. Finally, the speciation of volatile elements such as B, Cl and F in hydrothermal fluids at magmatic conditions of pressure and temperature will be understood more clearly as vibrational spectra of hydrothermal solutions are collected.

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