

Xe and Ar in high-pressure silicate liquids

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ABSTRACT

We investigated the solubility of Xe in liquids of $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{K}_2\text{Si}_4\text{O}_9$, and plagioclase ($\text{Ab}_{80}\text{An}_{20}$) compositions to pressures of 25 kbar and to temperatures of 1600 °C, complementing our previous study of Ar in a wide range of mafic and felsic silicate liquids (White et al., 1989). The solubility of Xe is about one-third that of the smaller Ar atom on an atomic basis, ranging up to 1.45 wt% in KAlSi_3O_8 liquid at 25 kbar and 1600 °C. As with Ar, the solubility of Xe increases with pressure, is independent of temperature except in $\text{K}_2\text{Si}_4\text{O}_9$ liquid, where it has a positive temperature dependence, and is strongly dependent upon the composition of the liquid, being most soluble in polymerized liquids with a high Si/Al ratio. These results shed light on the solubility mechanisms of molecular species, such as CO_2 , and they reveal that the noble gases dissolve in specific sites in the liquid, presumably as do CO_2 and some other molecular species, and not simply as microbubbles indiscriminately sequestered in interstitial sites.

Our range of calculated molar volumes for Xe at 15 kbar is 28.0–29.4 cm^3/mol , which is similar to that of solid Xe, 32–29 cm^3/mol at 89 °C between 10 and 20 kbar (Lahr and Eversole, 1962). Calculations using the Redlich-Kwong equation and corresponding states theory yield values for the volume of the vapor of 32.5 cm^3/mol for Ar and 39.4 cm^3/mol for Xe. Our calculated enthalpies of solution for Ar and Xe are within the range for Ar and Xe in magmas at 1 bar (Lux, 1987) and for CO_2 in $\text{NaAlSi}_3\text{O}_8$ at high pressures (Stolper et al., 1987).

INTRODUCTION

This is a study of the behavior of noble gases in silicate liquids at high pressures. Previously, White et al. (1989) presented results for argon silicate systems for a wide range of felsic and mafic compositions; that was the first experimental study of these systems. In this paper, we compare the behavior of Ar with that of the larger Xe atom.

An understanding of the behavior of the noble gases in silicate liquids provides insight into the solubility mechanism of other atomic and molecular components, in-

cluding CO_2 . In addition, the noble gases are significant components of the atmospheres of the terrestrial planets, but models of planetary outgassing (e.g., Zhang and Zindler, 1989) are based on solubility data of the noble gases obtained only at atmospheric pressure. Our results may also shed light on other problems involving the noble gases, such as the “missing” Xe on Earth (Wacker and Anders, 1984; Ozima and Podosek, 1983).

EXPERIMENTAL PROCEDURE

Starting materials

The albite was from the Franciscan Formation of California (Luth and Boettcher, 1986). Synthetic sanidine was prepared by crystallizing KAlSi_3O_8 glass hydrothermally at 2 kbar and 700 °C for 2 weeks. We examined the product optically to ensure complete reaction and verified our observations by X-ray diffraction. To prepare $\text{K}_2\text{Si}_4\text{O}_9$, we melted decarbonated K_2CO_3 and natural quartz at 1 bar and 1400 °C for 1 hr, followed by grinding

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and re-fusing four times to produce a bubble-free glass. The plagioclase ($\text{Ab}_{80}\text{An}_{20}$) was prepared from a gel (Luth and Ingamells, 1965) and crystallized at 1 bar and 1000 °C. We ground all starting materials and stored them in a vacuum desiccator over KOH; their compositions are tabulated in White et al. (1989, their Table 1).

Preparation of capsules

About 5 mg of starting material were loaded into a Pt capsule 2 mm in diameter and 10 mm long, with one end sealed by welding. The other end of the capsule was partly crimped, and the capsule was dried for at least 2 h. Glass starting materials were dried at 400 °C to prevent loss of alkalis; crystalline materials were dried at 900 °C.

In the previous study with Ar (White et al., 1989), we loaded the Ar as a liquid. For the present study, we loaded the Xe as a gas, using the technique developed by Boettcher et al. (1989). The advantages of this system are (1) all air is evacuated from the capsule and sample before the gases are loaded; (2) all H_2O is evacuated from the sample and capsule, and the noble gases are free of H_2O and are not exposed to air during any part of the procedure (3) the amount of gas or gases loaded into the capsule is easily controlled. To compare this procedure with that using liquid Ar, we conducted several experiments with gaseous Ar. We typically loaded ~ 0.3 mg of gas into each capsule, which was always sufficient to saturate the liquid. The Xe and Ar, obtained from Matheson Gas Products, each contained <0.5 ppm H_2O and only trace amounts of other components. Each capsule was sealed into a Pt capsule 3.5 mm in diameter with ~ 270 mg of sintered hematite. The hematite reacted to form magnetite + H_2O during the experiment and buffered the f_{H_2} at very low values.

Experimental procedure

All experiments were performed in a piston-cylinder apparatus, with 2.54-cm furnace assemblies composed of NaCl, Pyrex, graphite, BN, and MgO (Boettcher et al., 1981). The capsules were positioned horizontally in the furnace assembly, with temperature monitored by Pt-Pt₉₀Rh₁₀ thermocouples, encased in 99.8%-alumina ceramic, in contact with the top of the capsule. The hot piston-in technique was used to bring the experiments to final conditions, increasing the pressure to 90% of the final pressure, increasing the temperature to 90% of the final temperature, then increasing the pressure, and lastly the temperature, to the final values. The pressure was controlled to ~ 0.1 kbar and the temperature to ~ 3 °C. The experiments were terminated by shutting off the power to the furnace, resulting in quench rates of 150–200 °C/s.

The outer capsule was weighed, punctured, and reweighed to check if vapor had leaked from the sample capsule before or during the experiment. The buffer was removed from the sample capsule and examined optically to ensure that $>50\%$ hematite remained in the buffer. The sample capsule was then weighed, punctured, and

reweighed to demonstrate the retention of vapor and vapor saturation during the experiment.

Experimental products were examined optically to ensure that the liquid was saturated with Xe, as indicated by bubbles, and to estimate the percentage of liquid. In most cases, the products were 100% quenched liquid (glass) containing bubbles of various sizes, depending on the viscosity of the liquid. Bubbles visible in the microscope were large enough to be avoided during the microprobe analysis. Although we examined each sample with a petrographic microscope (and scanning electron microscope, in some cases), the presence of submicroscopic bubbles cannot be ruled out.

We used two methods to demonstrate the attainment of equilibrium. First, we performed experiments using different durations to ensure that similar results were obtained (e.g., compare nos. 299 and 373 with nos. 334 and 336). Second, we conducted experiments (e.g., no. 319) under conditions known from previous experiments to produce given solubilities of Xe, and then we lowered the pressures (and in some cases the temperatures) to conditions known from other experiments (e.g., no. 375R) to produce lower solubilities.

Analysis of experimental products

We determined the compositions of all of the glasses (quenched liquids), including the concentrations of dissolved Xe and Ar in the glasses, using the electron microprobe. The concentrations of the major elements are indistinguishable from those of the starting materials. There is no apparent preferential loss of K from the glass with increasing temperature, ruling out partitioning of K into the vapor phase as a reason for the temperature dependence of the solubility of Ar in $\text{K}_2\text{Si}_4\text{O}_6$. In addition, the proportion of vapor is small, precluding significant dissolution of the silicate into the vapor. Postexperimental glass compositions of $\text{K}_2\text{Si}_4\text{O}_6$ are difficult to obtain because of the hygroscopic nature of the glass and partial devitrification in some cases.

As White et al. (1989) did in their study of Ar solubility, we determined the concentrations of dissolved Xe and Ar in the glasses using calibration curves. Operating conditions were 15-kV accelerating voltage, 12-nA beam current, a 10- μm beam diameter, and 40-s counting times on peak and background positions. We determined the number of counts for the elements adjacent to Xe (or Ar) in the periodic table using standards of known composition; see White et al. for details about the determination of Ar. For Xe, we used as standards metallic Te, CsI (I), CsCl (Cs), and barite (Ba). We then calculated the normalized counts for the pure elements (Te, I, etc.) and plotted them against their atomic numbers (Fig. 1), and we determined the counting rate for 100% Xe by least-squares regression. The calibration curve is highly reproducible during the course of a day and from day to day, giving us confidence that this technique is reliable. Some of the samples were analyzed two or three times over periods of weeks, and the results were always reproduc-

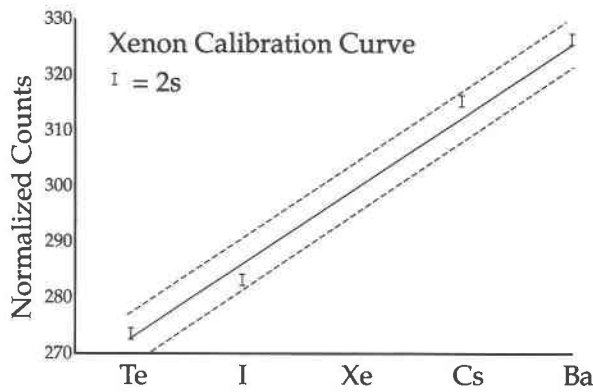


Fig. 1. Electron microprobe counting rates normalized to 100% concentrations vs. atomic number for elements adjacent to Xe in the periodic table (see text).

ible (see footnotes to Table 1; in addition, we analyzed the product of experiment G411, which contains Ar and Xe and is not listed in the tables, on September 18, September 19, and October 16, 1989, yielding 0.36% Ar and 0.64% Xe, 0.36% Ar and 0.63% Xe, and 0.36% Ar and 0.65% Xe, respectively). We ignored ZAF corrections, but the 2% error that we assigned should encompass these uncertainties. White et al. tested the calibration curve by analyzing U.S. Geological Survey standard W-1 diabase glass for K_2O . The recommended value for K_2O is 0.64 wt% (Flanagan, 1973); the value of White et al. (1989) for K_2O using the calibration curve is 0.63 ± 0.06 wt% (average of ten analyses), and their value is 0.66 ± 0.03 wt% (average of three analyses) by quantitative wavelength-dispersive analysis. It is clear that our calibration technique is a credible method of analysis for small elemental concentrations and that ignoring the matrix corrections at these low amounts does not affect the results beyond the error that we have assigned. We believe that this accuracy also applies to the measurement of low concentrations of dissolved Xe and Ar.

We determined the peak positions for Xe and Ar X-rays using a high beam current (>60 nA) on one of our glasses known to contain an appreciable amount of dissolved gas. An example of an energy-dispersive spectrum for $KAlSi_3O_8$ glass is shown in Figure 2. At least six points were analyzed in each glass. We calculated the concentration of Xe or Ar by dividing the average counts ($\pm 2\%$) by the counts for 100% Xe and Ar from the calibration curve standardization. The error was calculated by adding the 2% error on the sample counts to that determined from the calibration curve, resulting in the uncertainties listed in Table 1.

To remove all contamination from the sample capsules before they were opened, we boiled them in dilute HCl for about 1 h. To ensure that this procedure did not affect the sample, we analyzed splits of the product of experiment no. 328, one boiled and one not; the results are similar (Table 1).

As discussed by White et al. (1989), $NaAlSi_3O_8$ and

TABLE 1. Experimental results for the solubility of Xe in silicate liquids

Expt.	P (kbar)	T (°C)	t (min)	Results	Wt%Xe($\pm 2\sigma$)
$K_2Si_2O_7$					
G355	6	1000	3000	L + V	0.22(2)
G356	6	1200	1800	L + V + <i>QXL</i>	0.29(5)
G354	6	1400	8	L + V + <i>QXL</i>	0.40(10)
G338	9	1000	3000	L + V + <i>QXL</i>	0.36(5)
G339	9	1200	1810	L + V + <i>QXL</i>	0.48(5)
G340	9	1400	60	L + V	0.70(7)
G299	12	1200	720	L + V + <i>QXL</i>	0.63(9)
G373	12	1200	1800	L + V	0.67(6)
G304	12	1300	360	L + V + <i>QXL</i>	0.78(10)
G385	12	1300	360	L + V	0.99(8)
G300	12	1400	120	L + V	0.78(9)
G311	15	1200	1800	L + V + <i>QXL</i>	0.81(7)
G353	15	1400	240	L + V	1.08(8)
G357	20	1200	1440	L + V	1.19(12)
G387R*	20	1200	120	L + V	1.07(6)
G369	20	1400	180	L + V	1.50(7)
G368	25	1200	1440	L + V	1.44(9)
G370	25	1400	180	L + V	1.81(8)
$NaAlSi_3O_8$					
G367	6	1400	7	L + V	0.28(7)
G333	9	1400	13	L + V	0.39(9)
G349	9	1500	3	L + V	0.47(6)
G345	12	1400	180	L + V	0.58(5)
G346	12	1500	9	L + V	0.51(6)
G348	12	1500	23	L + V	0.63(5)
G323	15	1400	90	L + V	0.88(7)
G332	15	1500	30	L + V	0.82(5)
G375R**	15	1500	31	L + V	0.82(6)
G347	15	1600	5	L + V	0.85(5)
G320	20	1400	1020	L + V	0.97(8)
G319	20	1500	30	L + V	0.98(10)
G318	20	1600	6	L + V	0.99(7)
G374	25	1500	30	L + V	1.61(7)
G321†	25	1600	5	L + V	1.24(15)
$KAlSi_3O_8$					
G381	6	1500	2	L + V	0.29(8)
G351	9	1500	5	L + V	0.47(7)
G334	12	1400	30	L + V + <i>X1</i>	0.61(6)
G336	12	1400	87	L + V	0.58(6)
G329	12	1500	10	L + V	0.53(7)
G358	12	1500	15	L + V	0.61(7)
G352	12	1600	1	L + V	0.62(6)
G301‡	15	1500	19	L + V	0.66(7)
G359	15	1500	30	L + V	0.87(6)
G361	15	1600	5	L + V	0.89(7)
G380	20	1500	30	L + V	1.23(8)
G378	20	1600	5	L + V	1.14(6)
G328	25	1600	5	L + V	1.42(13)
G328A§	25	1600	5	L + V	1.45(17)
$Ab_{60}An_{20}$					
G330	15	1500	30	L + V	0.47(3)
G331	25	1600	10	L + V	0.83(4)

Note: phases in italics are present in trace proportions.

* The experiment was reversed from 23 kbar and 1400 °C to 20 kbar and 1200 °C. The experiment remained at 23 kbar and 1400 °C for 120 min. It took 15 min to drop the pressure to 20 kbar. After 120 min at the final conditions, the experiment was quenched.

** The experiment was held for 30 min at 20 kbar and 1500 °C. It took 10 min to drop pressure from 20 to 15 kbar, and then the experiment was held for 1 min at 15 kbar and 1500 °C.

† The sample was analyzed twice with reproducible results: on May 9, 1989, it equaled 1.24(15) and on June 14, 1989, it equaled 1.23(11).

‡ The sample was analyzed twice with reproducible results: on April 6, 1989, it equaled 0.66(7) and on July 11, 1989, it equaled 0.66(5).

§ The same experimental product as G328, but it was boiled in H_2O for 70 min.

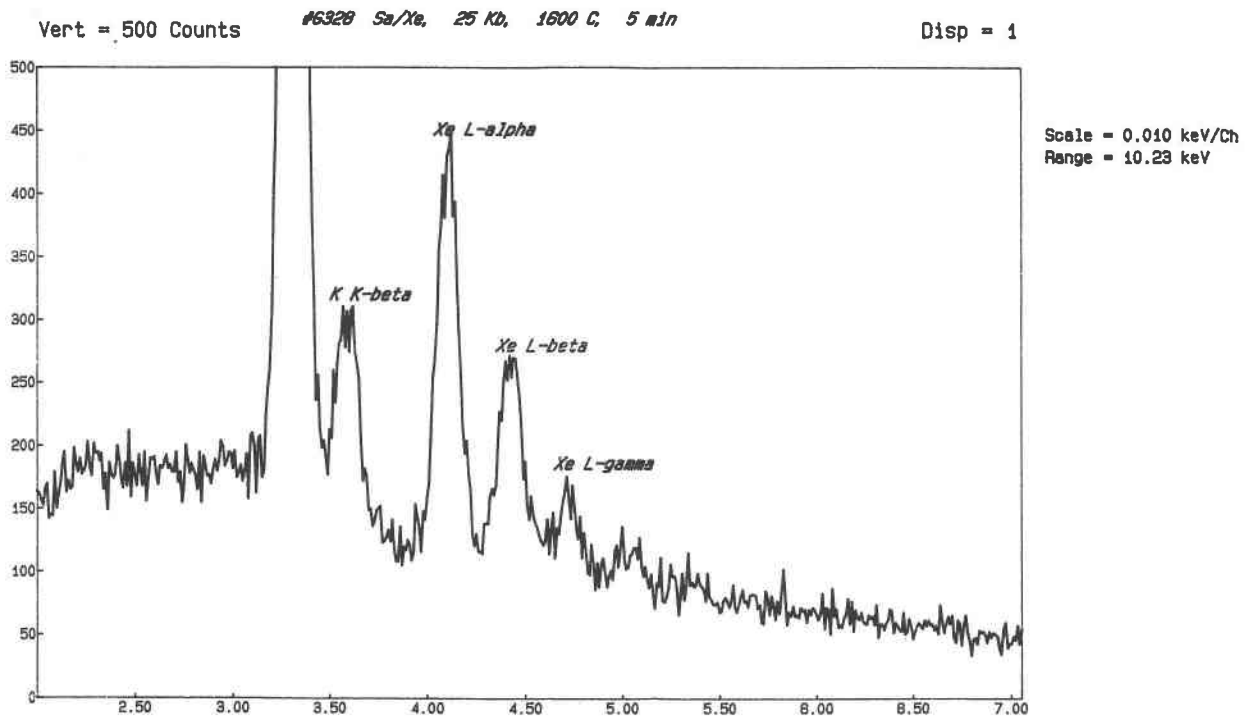


Fig. 2. Energy-dispersive spectrum of Xe-saturated KAlSi_3O_8 glass (experiment G328). The Xe peaks correspond to 1.4 wt% Xe.

KAlSi_3O_8 liquids are viscous, and the quenched Ar- and Xe-saturated glasses always contain bubbles, particularly at lower pressures, where the viscosities are higher. $\text{K}_2\text{Si}_4\text{O}_9$ is far less viscous, and there are far fewer bubbles. These bubbles result from entrapment of the gas in the interstices of the powdered starting materials when melting begins. The bubbles do not result from dissolution from the liquid, and they are easily avoided during analysis with the microprobe.

As an additional check on our analytical procedure, our colleague Mark Harrison analyzed some of our experimental products for Xe and Ar using mass spectrometry. A ~ 0.1 -mg fraction was fused for 10 min at 1550 °C in a double-vacuum resistance furnace (Harrison and Fitz Gerald, 1986), split, and expanded into a Nuclide RSS-90-4.5 mass spectrometer operated as a manometer. The ^{40}Ar peak height was compared with air-Ar aliquots before and after analyzing the unknowns, permitting accuracies of better than $\pm 3\%$. For the determination of Xe, the St. Severin meteorite was used as a standard, permitting accuracies better than $\pm 5\%$. The product of experiment no. 412 of White et al. (1989), which contained 0.77 ± 0.05 wt% Ar determined by the microprobe, yielded 0.77 wt% with mass spectrometry. Similarly for Xe, we determined by microprobe analyses that the product of experiment G317, which is not listed in Table 1, contains 0.35% Xe. Harrison's results using mass spectrometry are 0.31%.

As an additional check, we reproduced a KAlSi_3O_8 ex-

periment performed by White et al. (1989: their experiment no. 412 at 1500 °C and 15 kbar for 60 min); we loaded the Ar as a gas (our experiment no. 297 at similar conditions but for 30 min) as described above, whereas they loaded it in liquid form. Their microprobe analyses of no. 412 and ours of no. 297 both yielded 0.77 ± 0.05 wt% Ar.

We originally intended to investigate a wide range of felsic and mafic compositions, as in the earlier study of Ar, but we were unable to analyze accurately Ca-rich products (e.g., plagioclase richer in Ca than $\text{Ab}_{80}\text{An}_{20}$) on the microprobe because of interference between the Xe and Ca peaks.

RESULTS

Experimental data for $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , $\text{K}_2\text{Si}_4\text{O}_9$, and $\text{Ab}_{80}\text{An}_{20}$ compositions are presented in Table 1 and in Figures 3 and 4. The concentration of Xe increases approximately linearly with pressure for all four compositions. The solubility of Xe in $\text{NaAlSi}_3\text{O}_8$ and KAlSi_3O_8 liquids is independent of temperature within experimental uncertainty, as is true for Ar (White et al., 1989); however, the solubility of Xe in $\text{K}_2\text{Si}_4\text{O}_9$ increases isobarically with increasing temperature, as shown by the isotherms in Figure 4. These isotherms are remarkably similar to those for Ar in $\text{K}_2\text{Si}_4\text{O}_9$ at 1200 and 1400 °C. The temperature independence of the solubility of Xe and Ar in our aluminosilicate liquids at high pressure is similar to

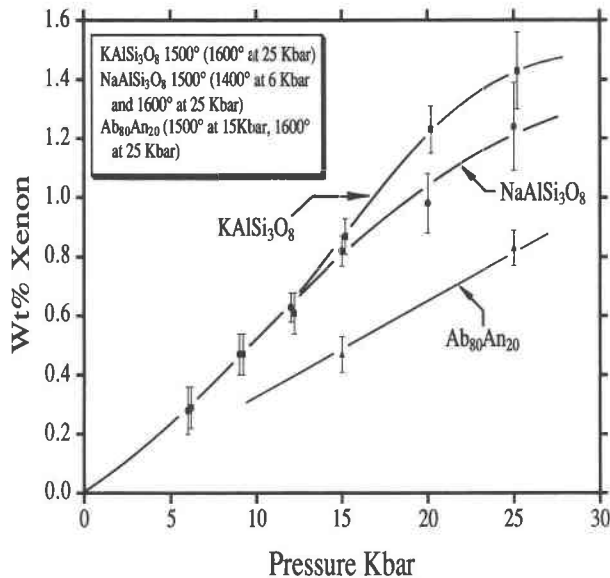


Fig. 3. Concentrations of Xe vs. pressure (polythermal).

that for He, Ne, Ar, Kr, and Xe in basaltic liquids (Jam-bon et al., 1986, their Fig. 2) at atmospheric pressure, adding credence to the applicability of our results to natural systems.

For KAISi_3O_8 -Xe (Fig. 3) and KAISi_3O_8 -Ar (White et al., 1989, their Fig. 5A), there are negative inflections in the curves just above 15 kbar. This pressure is approximately that of the singular point on the solidus of sanidine, below which it melts incongruently to leucite + liquid and above which it melts congruently (Lindsley, 1966; Boettcher et al., 1984). The SiO_2 content of the liquid decreases with increasing pressure up to the pressure of the singular point. That would be expected to decrease the solubility of Xe and Ar with increasing pressure (as discussed below), but this concept is not supported by the positive curvature of the solubility curves for Xe and Ar in that pressure region. Also, the shape of the Xe- $\text{NaAlSi}_3\text{O}_8$ curve is similar to that of Xe- KAISi_3O_8 , as are those for Ar- $\text{NaAlSi}_3\text{O}_8$ and Ar- KAISi_3O_8 . These inflections may reflect coordination changes of Al in the liquids at ~ 15 kbar, but that is not supported by our previous work on the melting of KAISi_3O_8 (Boettcher et al., 1984).

Stebbins and McMillan (1989) proposed that there is a structural change in $\text{K}_2\text{Si}_4\text{O}_9$ liquid at 15–20 kbar. Figure 4 for Xe- $\text{K}_2\text{Si}_4\text{O}_9$ and Figure 10B of White et al. (1989) for Ar- $\text{K}_2\text{Si}_4\text{O}_9$ show no radical changes in the slopes of the melting curves in this pressure interval, although the data for Xe are consistent with a change between 10 and 15 kbar. To detect structurally related changes in the liquids, it would be preferable to perform experiments closer to liquidus temperatures (e.g., at 1000 °C).

There are notable similarities between our results for Xe and previous results for Ar. The solubility of Xe is similar in $\text{K}_2\text{Si}_4\text{O}_9$ and KAISi_3O_8 liquids, especially above

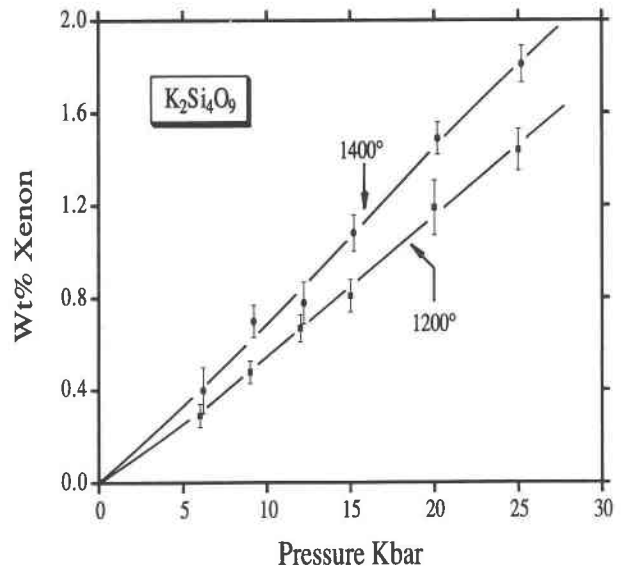


Fig. 4. Concentrations of Xe vs. pressure at 1400 and 1200 °C.

~ 15 kbar, as is the case for Ar. Also, Xe and Ar are each more soluble in KAISi_3O_8 than in $\text{NaAlSi}_3\text{O}_8$ above ~ 15 kbar. For the system Xe- KAISi_3O_8 , our data are consistent with a negative curvature above ~ 20 kbar, but we find no evidence for a maximum in the solubility of Xe above this pressure, similar to the findings of White et al. (1989) for Ar- KAISi_3O_8 . Although $\text{K}_2\text{Si}_4\text{O}_9$ is partially depolymerized (0.5 NBO/T), the absence of Al accounts for the high solubility of Xe, as well as of Ar (White et al.) in $\text{K}_2\text{Si}_4\text{O}_9$ liquid. The solubility of Xe in $\text{Ab}_{80}\text{An}_{20}$ liquid (Fig. 3) decreases markedly with an increasing $\text{CaAl}_2\text{Si}_2\text{O}_8$ component, similar to the case for Ar (White et al.). Liquids along the Ab-An join are fully polymerized, and the decrease in the solubility of Xe and Ar can be ascribed solely to the increase in $^{[4]}\text{Al}$.

An important goal of this work is to examine similarities between the solubility mechanisms in the noble gases and those of molecular species, including CO_2 and H_2O . The speciation of these components is difficult to determine and to control experimentally, and knowledge of the behavior of noble gases in silicate liquids could provide insight into that of these molecular species. For example, the results with Ar (White et al., 1989) support the conclusions of Mysen (1976) and Fine and Stolper (1986) that molecular CO_2 , like Ar, is more soluble in polymerized liquids than in depolymerized liquids.

Similarly, for compositions in the system NaAlO_2 - SiO_2 , the solubility of Ar in these liquids increases with an increasing Si-Al ratio (White et al., 1989), paralleling the trend of the proportion of molecular CO_2 (relative to total C) (Fine and Stolper, 1985). Likewise, the ratio of molecular H_2O to OH^- increases with increasing K/Na, as well as with increasing Si/Al (Silver et al., 1990), which are parameters also favoring the solubilities of the noble gases. Thus, as a general rule, the solubilities of the noble

TABLE 2. Best-fit parameters for Xe and Ar* (Eq. 2)

	P^0 (kbar)	T^0 (°C)	ΔH_{Xe}^0 (kJ/mol)	V_{Xe}^0 (cm ³ /mol)	ΔH_{Ar}^0 (kJ/mol)	V_{Ar}^0 (cm ³ /mol)
NaAlSi ₃ O ₈	15	1600	10.4	28.5	8.2	22.8
KAlSi ₃ O ₈	15	1600	10.7	28.0	7.2	20.6
K ₂ Si ₄ O ₉	15	1400	16.2	29.4	12.0	22.6

* Ar data from White et al. (1989).

gases and molecular species are strongly enhanced in highly polymerized liquids with a high Si/Al ratio.

THERMODYNAMICS

White et al. (1989) developed a thermodynamic model for Ar in a wide variety of silicate liquids. This model was based on the approach formulated by Silver and Stolper (1985) and Stolper et al. (1987) for the dissolution of H₂O and CO₂ in silicate liquids. In their models, the heterogeneous equilibria between H₂O or CO₂ molecules in the vapor and molecular H₂O or CO₂ in the liquid are considered separately from the homogeneous equilibria between the dissolved volatile components and the liquid.

Because the noble gases presumably dissolve as molecular units and do not react with silicate components in the liquid, it is instructive to compare the results for Ar and Xe with those for molecular CO₂ and H₂O. Because we are interested in the equilibrium

$$\mu_{Xe}^v = \mu_{Xe}^l \quad (1)$$

where the superscripts refer to vapor and liquid and wish to compare our results for dissolved Xe and Ar with analogous data for dissolved molecular CO₂ and H₂O, we are utilizing the equation for the heterogeneous vapor-liquid equilibrium derived in Stolper et al. (1987).

After modification, the condition of the equilibrium given in Equation 1 becomes

$$\ln(X_{Xe} f_{Xe}^0 / X_{Xe}^0 f_{Xe}) = -(\Delta H_{Xe}^0 / R)(1/T - 1/T^0) - (\Delta V_{Xe}^0 / RT)(P - P^0). \quad (2)$$

The superscript zero refers to a standard reference state arbitrarily chosen to be 15 kbar and 1600 °C for NaAlSi₃O₈ and KAlSi₃O₈, and 15 kbar and 1400 °C for K₂Si₄O₉. The mole fraction of Xe in the liquid, X_{Xe}^0 and X_{Xe} , is based on the number of moles of Xe in the liquid divided by the sum of the molar amounts of Xe + O²⁻ (Fine and Stolper, 1985). We calculated f_{Xe} in the vapor at P and T , using the modified Redlich-Kwong equation of state (Holloway, 1977; Ferry and Baumgartner, 1987) using data for the corresponding states parameters for Xe ($T_{crit} = 289.8$ K, $P_{crit} = 58.0$ atm) from Chao and Greenkorn (1975). V_{Xe}^0 is the standard-state molar volume of Xe in the liquid; ΔH_{Xe}^0 is the molar enthalpy of solution of Xe at the reference pressure and temperature. Equation 2 assumes that Xe mixes ideally in the liquid (i.e., $a_{Xe} = X_{Xe}$), that V_{Xe}^0 is independent of P and T , and that ΔH_{Xe}^0 is independent of temperature. For a more com-

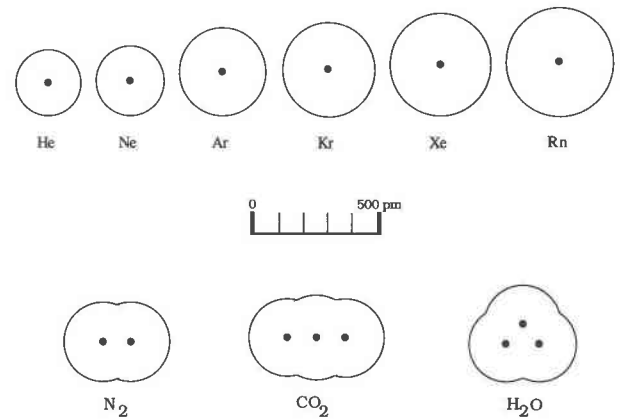


Fig. 5. Relative sizes of some atoms and molecules calculated from van der Waals radii.

plete description of the assumptions and derivations see Stolper et al. (1987).

If the concentrations of Xe in the quenched glasses are equivalent to those in the liquid at P and T , then we can calculate values for X_{Xe}^0 and X_{Xe} . Substitution of the other parameters into Equation 2 provides an equation of state to calculate the solubility of Xe at any P and T . Table 2 lists our values of V_{Xe}^0 and ΔH_{Xe}^0 for Xe in liquid NaAlSi₃O₈, KAlSi₃O₈, and K₂Si₄O₉ compositions using a multiple linear, least-squares regression program. For comparative purposes, we also list V_{Ar}^0 and ΔH_{Ar}^0 from White et al. (1989).

In the case of Ar, the calculated molar volumes are slightly larger than the volume of solid Ar extracted from shock and diamond-anvil measurements at similar pressures (19 cm³/mol, Ross et al., 1986; Zha et al., 1986). For Xe, our range of calculated volumes, 28.0–29.4 cm³/mol, is approximately that for solid Xe, 32–29 cm³/mol at 89 °C between 10 and 20 kbar, respectively, reported by Lahr and Eversole (1962). Calculations using the Redlich-Kwong equation and corresponding states theory yield values for the volume of the vapor of 32.5 cm³/mol for Ar and 39.4 cm³/mol for Xe. Our calculated enthalpies of solution for Ar and Xe are within the range for Ar and Xe in magmas at 1 bar (Lux, 1987) and CO₂ in NaAlSi₃O₈ at high pressure (Stolper et al., 1987).

CONCLUSIONS

We investigated the solubility of Xe in liquids of NaAlSi₃O₈, KAlSi₃O₈, K₂Si₄O₉, and plagioclase (Ab₈₀An₂₀) compositions to pressures of 25 kbar and temperatures to 1600 °C. The solubility of Xe is about one-third that of the smaller Ar atom on an atomic basis, ranging up to 1.45 wt% in KAlSi₃O₈ liquid at 25 kbar and 1600 °C. As with Ar (White et al., 1989), the solubility of Xe increases with pressure, is independent of temperature, except in K₂Si₄O₉ liquid where it has a positive temperature dependence, and is strongly dependent upon the composition of the liquid, being most soluble in polymerized liquids with a high Si-Al ratio. These results reveal that the

noble gases dissolve in specific sites in these liquids, presumably as do CO₂ and other molecular species, and not simply as microbubbles indiscriminately sequestered in interstitial sites.

Our results for Xe add credence to our earlier conclusion based on Ar data that the noble gases provide a useful model for the solubility and solubility mechanism of species such as molecular CO₂ and molecular H₂O and that there is a site within the liquid structure that incorporates these atomic and molecular species. Direct measurements of the solubilities of molecular CO₂ and H₂O are complicated because these components also dissolve in silicate liquids as ions, e.g., (CO₃)²⁻ and (OH)⁻. The absolute solubility of Ar in NaAlSi₃O₈ liquid (White et al., 1989) is similar to that of molecular CO₂ (Stolper et al., 1987). As shown in Figure 5, the calculated sizes of the Ar atom and the CO₂ molecule are comparable; Xe is larger, which probably explains the much lower solubility.

It is of interest that the solubility of Xe, as is the case for Ar, is similar in KAlSi₃O₈ and NaAlSi₃O₈ liquids, suggesting that the solubilities of molecular CO₂ in these liquids are also nearly equal. This is not unexpected, as both of these liquids are fully polymerized, have the same Al-Si ratio, and presumably have the same distribution of charge-balancing cations in their structures. However, because of the relatively large melting point depression of sanidine produced by CO₂ relative to that of albite, and because CO₂ is more effective in reducing the viscosity of KAlSi₃O₈ liquid than that of NaAlSi₃O₈ liquid at 25 kbar (White and Montana, 1990), we conclude that KAlSi₃O₈ liquid dissolves a larger percentage of total C as (CO₃)²⁻. Thus, it appears that KAlSi₃O₈ and NaAlSi₃O₈ liquids dissolve similar amounts of molecular or atomic species (e.g., H₂O, CO₂, and the noble gases), but KAlSi₃O₈ dissolves more (CO₃)²⁻ and, therefore, more total C.

From information in the present and previous studies, we can make the following generalizations regarding the solubilities of the noble gases and other volatile components:

1. The noble gases and molecular CO₂ are more soluble in Si-rich liquids (e.g., in NaAlSi₃O₈ vs. CaAl₂Si₂O₈) (e.g., this work; White et al., 1989; Fine and Stolper, 1985).
2. The noble gases and molecular CO₂ are more soluble in the more polymerized liquids (e.g., White et al., 1989; Mysen, 1988).
3. The solubilities of the noble gases and C [CO₂ and (CO₃)²⁻] are dependent upon the composition of the silicate liquid (e.g., this work; Mysen, 1988). This phenomenon contrasts with that of H₂O, since H₂O can occupy many structural sites regardless of the structure or the cations (e.g., Burnham, 1981). Also, H₂O is much more soluble than the noble gases and the C species (e.g., McMillan and Holloway, 1987).
4. Unlike that of the noble gases, the speciation of C in silicate liquids [CO₂ vs. (CO₃)²⁻] is a function of the composition of the liquid (e.g., Fine and Stolper, 1985); the speciation of H₂O in the liquid is relatively independent

of the composition of the liquid (e.g., Silver and Stolper, 1985), although it is more varied and complex than those of these other components.

Zhang and Zindler (1989) proposed a model for the origin of the atmosphere of the Earth in which they used a mole ratio of Ar/Xe in magma equal to 3 (based on the data of Jambon et al., 1986), which is in agreement with our values obtained using pure Xe and pure Ar. Jambon et al. used mixtures of He, Ne, Ar, Kr, and Xe, but the proportions of Xe were very small (Ar/Xe = 1.07 · 10⁵ to 1.66 · 10³). The composition of the liquid is obviously an important variable in these studies, and it would be worthwhile to continue this work using mafic composition and mixtures of the gaseous components to cast light on natural systems.

ACKNOWLEDGMENTS

We acknowledge the technical assistance of several of our colleagues: Robert Jones provided helpful advice and assistance with the operation of the electron microprobe and analyzed several of the samples; Mark Harrison determined the contents of Ar and Xe in some samples using his mass spectrometers; discussions about the noble gases with Wayne Dollage were always useful and stimulating. In addition, Jim Dickinson of Corning Glass and Dave Stewart of the U.S. Geological Survey provided us with KAlSi₃O₈ glass and albite, respectively.

Institute of Geophysics and Planetary Physics contribution no. 3430.

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MANUSCRIPT RECEIVED JUNE 9, 1993

MANUSCRIPT ACCEPTED JULY 13, 1993