Structural environment of krypton dissolved in vitreous silica

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ABSTRACT

X-ray absorption measurements on Kr dissolved homogeneously in vitreous silica (1.97 wt% Kr) have been carried out at the Kr K-edge at 4.5 K, representing the first direct determination of the sites occupied by a noble gas. The presence of EXAFS oscillations shows that the Kr atoms are surrounded by a well-defined shell of nearest neighbors, identified as oxygen atoms. The mean Kr-O distances are 3.45 ± 0.1 Å, based on a simple model of Gaussian disorder, with a Debye-Waller factor of $\sigma^2 = 0.06$ Å^2. The large Kr-O distance, which is at the upper limit of the size of the holes existing in vitreous silica, together with the existence of well-defined sites suggests a forced, densely packed environment of oxygen around Kr atoms characteristic of clathrasil surroundings.

INTRODUCTION

Because volatiles have a strong effect on the physical and chemical properties of natural magmas, the solubility behavior and dissolution mechanisms are of fundamental importance to understand igneous processes. Volatiles can be dissolved in magmas as molecules or atoms (e.g., unreacted species like H_2O, CO_2, noble gases) or as reactive species (e.g., hydroxyl or carbonate groups). Physical dissolution of neutral molecular species such as noble gases in silicate melts and glasses has been interpreted as indicating the presence of voids within the silicate polymer network (e.g., Carroll and Stolper 1993 and references therein), and provides fundamental information to understand dissolution of the more complex processes during solution of reactive species (e.g., CO_2, H_2O). The size distribution of these voids affects the porosity of a melt and is believed to control the transport properties of gas molecules. Simple models relate the distribution of the size of the interstitial holes in the frozen melt to the solubility of noble gases. Various models relying on the free-volume concept (Doremus 1966) have been applied, such as ionic porosity (Carroll and Stolper 1993), the trapped oscillator model (Studt et al. 1970), or geometrical considerations in the approximation of a random network (Shackelford 1982). All derive hole dimensions ranging from 0.5 to 4 Å.

Angell et al. (1988) simulated the environment of the noble gas in silicate melts by molecular dynamics (MD), investigating the dissolution of helium and argon in a jadeite melt at 6000 K and 72.5 and 17 kbar. Helium was found in oxygen cages with a coordination number (CN) of 10, similar to interstitial sites in cristobalite, whereas clustering was found for Ar. The possibility of a clustering of noble gases was not confirmed by recent MD simulations of the environment of noble gases in silica melt (Guillot and Guissani 1996). A cristobalite-like environment was found for helium and neon, whereas a clathrasil local structure was found around heavier noble gases.

This study presents the first direct determination of the sites occupied by a noble gas, Kr, dissolved in a supercooled silica melt at 1200 °C and 7 kbar. It should be emphasized that dissolution of Kr is performed at a temperature where the structural relaxation time (Bucaro and Dardy 1977) is much shorter (~150 s) than the run time of the experiment (24 h). Therefore, the incorporation of Kr took place in a relaxed melt. The subsequent investigation of the Kr environment was performed on a quenched supercooled silica melt (i.e., on a glass). A detailed analysis to elaborate differences in the sites occupied by Kr in the glass and melt state as well as effects of quenching is beyond the scope of this paper.

Silica was used as it represents the major oxide of silicate melts and hence serves as a first-order analogue for geologically relevant melt compositions, and Kr solubility and diffusivity in vitreous silica already has been explored (Carroll et al. 1993; Roselieb et al. 1995). Krypton is easily accessible by X-ray absorption spectroscopy (XAS) owing to the low absorption of the silica matrix at the Kr-K-absorption edge. In addition, it exhibits a high solubility in vitreous silica when compared to other silicate melt compositions (e.g., Carroll and Stolper 1993).

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EXPERIMENTAL METHODS

SiO_2 glass (Herasil 1, Heraeus Quarzschmelze, Hanau) was crushed and sieved to grain fractions smaller than 40 μm. The powder was then dried at 500 °C in Pt capsules, immediately before being filled with Kr (initial pressure ~70 bar), and welded according to the gas-loading technique described by Boettcher et al. (1989). Krypton dissolution was performed in an internally heated pressure vessel for 24 hours at 1200 ± 5 °C and 7000 ± 70 bar using Ar as a pressure medium. Finally, the samples were quenched with a cooling rate of ~200 °C/min. After the experiments, the Pt capsules were checked to eliminate the possibility of leaks and the slightly sintered samples again carefully ground in an agate mortar to eliminate undissolved Kr (see Roselieb et al. 1992). The glasses contain 1.97 wt% Kr, as indicated by gas chromatographic analysis with a Hewlett-Packard HP5890 II using the procedure described by Roselieb et al. (1992). Saturation of the sample with Kr under these *P-T-t* conditions has been shown by H. Walter (personal communication), indicating that solubilities from runs with different grain sizes and run times agree within experimental error. Electron microprobe traverses demonstrate that Kr is distributed homogeneously in grain sizes up to 40–50 μm. From X-ray powder diffraction experiments, the amount of recrystallized SiO_2 in the powder is estimated to be <4%.

EXAFS spectra were collected in transmission mode at 4.5 K at the Kr K-edge using a Si (111) monochromator on beamline D44 of the LURE-DCI synchrotron source (Orsay, France). The storage ring was operated at 1.85 GeV positron energy and 260 mA positron current. Samples were prepared by mixing the glass powder with cellulose, pressing into 1 mm thick pellets and mounting between ~10 μm thick kapton foils.

EXAFS data analysis was performed on the basis of the plane-wave single scattering approximation (Teo 1986). Background-subtracted k^3-weighted data were Fourier-filtered and fit in k-space. We tested a Gaussian distribution of the Kr-ligand distances (Bonnin et al. 1989) as well as an asymmetric lognormal distribution (Winterer, personal communication) in order to evaluate radial disorder effects. Data were reduced using theoretical amplitude and phase shift functions derived from a curved wave correction (McKale et al. 1988), as well as those obtained from FEFF 6.01 calculations (Rehr et al., personal communication). The results obtained from both methods are identical within the experimental uncertainties.

RESULTS AND DISCUSSION

The EXAFS spectrum of Kr dissolved in silica shows well-defined EXAFS oscillations (Fig. 1), in contrast to gaseous noble gases, which do not exhibit any EXAFS features. The spectrum shows a single rapidly damped frequency, and the presence of only one peak on the Fourier Transform indicates a total disorder beyond the coordination shell (Fig. 2a). The backscattering amplitude functions of Kr and O are different, as the latter is damped more rapidly than the former. The rapid damping of the EXAFS signal shows the absence of Kr neighbors, i.e., Kr occurs in silica in a well-defined environment of O atoms. The presence of ordered Kr clusters is too small to be detected and may be neglected.

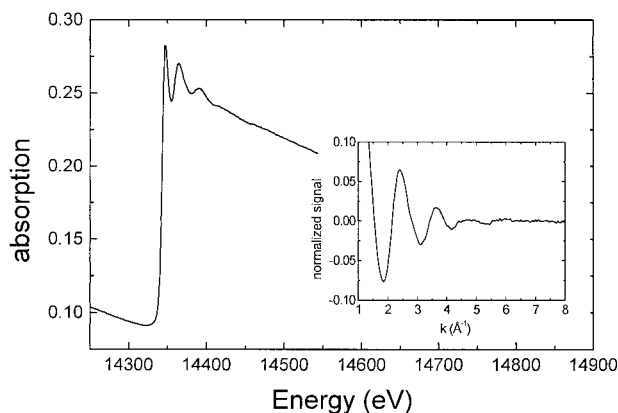The rapid damping of the EXAFS oscillations, which is also

FIGURE 1. X-ray absorption spectrum of Kr solved in vitreous silica with the normalized signal shown as inset.
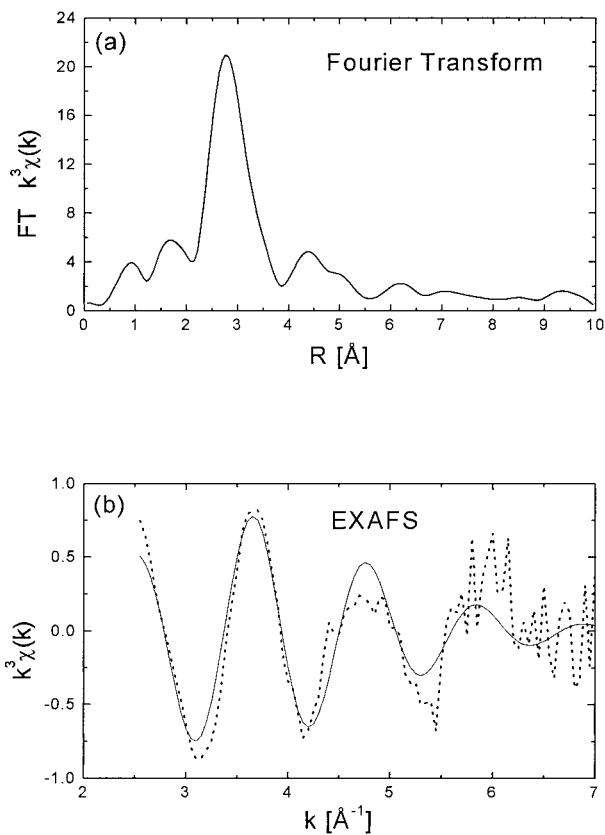

FIGURE 2. EXAFS and Fourier Transform for Kr dissolved in vitreous silica. (**a**) Fourier Transform derived from k^3 weighted $\chi(k)$ experimental data. The radial distribution function is not corrected for phase shift. The peak at 2.8 Å corresponds to a Kr-O distance of 3.45 Å. (**b**) Kr K-EXAFS k^3 weighted $\chi(k)$ function of the experimental data (dotted line) and linear least-squares fitting (solid line).

expressed by the large scatter of the $k^3 \chi(k)$ function at high k-values (Fig. 2b), limits the analysis range to kmax = 8 Å^{-1}. This results in a limitation of the number of independent parameters N to 3, according to the formula N = $2\Delta k \Delta R/\pi$, where Δk is the accessible k-range, and ΔR the region in R-space over which the fit is made (Teo 1986). This also limits the accuracy of the EXAFS-derived parameters. The number of neighbors measured by EXAFS is a minimum value, due to several factors: the high absorption coefficient, the uncertainty on the mean free path, and the radial disorder.

With a Gaussian distribution of interatomic distances (Teo 1986), the mean distance (R_{Kr-O}) is refined to 3.45 ± 0.1 Å with an associated Debye-Waller term σ^2 = 0.06 Å^2. Anharmonic effects (Eisenberger and Brown 1979) are expected because σ^2/R > 0.01, which lead to underestimated R_{Kr-O} values. Using an anharmonic distribution, the fit of the EXAFS data is slightly better with the residual decreased by ~10%. This improvement is not considered significant because of the increasing number of adjustable parameters. The experimental EXAFS value is close to that derived from MD simulations, R_{Kr-O} = 3.37 Å (Guillot and Guissani 1996). Taking the ionic radius of O^{2-} as 1.4 Å (Shannon 1976), the harmonic approximation gives a radius for Kr of 2.05 ± 0.1 Å in the investigated glass. Various sets of Kr radii have been reported in the literature. A widely used value of 1.98 Å for CN = 12 has been deduced from fcc-solid Kr. A recent set of neutral atom radii (Zhang and Xu 1995) gives radii of 1.78 Å and 1.87 Å for CN = 6 and 8, respectively. These values are associated with the effective radius set (Shannon 1976) based on an O^{2-} ionic radius of 1.4 Å. The EXAFS-derived value of 2.05 Å is consistent with the existing set of data and indicates a CN close to 12.

In the simple random glass network model (Shackelford 1982), the distribution of voids in vitreous silica is represented by a log-normal size probability function with few voids having diameters larger than 4 Å. A hole-size distribution, with a diameter ranging from 0.4 up to 5 Å, is predicted by MD simulations (Mitra 1982). The existence of well-resolved EXAFS oscillations is incompatible with a broad distribution of the available voids and a simple physical dissolution process of Kr in the voids existing in vitreous silica. This is supported by the EXAFS-derived Kr-O distance which is at the upper limit of the accessible voids in silica. Although the present data do not allow the determination of the topology of the Kr environment, the existence of specific sites may be explained by a forced, close-packed environment corresponding to a clathrasil local structure. Such an environment has been predicted recently from MD simulations in similar systems (Guillot and Guissani 1996). This finding contrasts with the generally accepted assumption that noble gases are chemically inert species and do not modify the glassy network. A similar conclusion is derived by Carroll et al. (1990) from Si K-edge XANES and EXAFS spectra of Ar and Xe-bearing SiO$_2$ glasses. The direct determination by EXAFS of the hydrophobic hydration shell of Kr in liquid H$_2$O has given a Kr-O correlation centered around 3.8 Å (Filipponi et al. 1997). These distances are close to those determined in ethanol, 3.93 Å (Bertagnolli et al. 1992). The variations observed in these Kr-O distances, although significantly larger than in our study, show the influence of the matrix on the environment of physically dis-

solved gases. Compositional effects may indeed affect the energy of formation of the clathrasil environment around heavy noble gases. Complementary information on other glasses and noble gases are needed to understand better the dissolution mechanisms of noble gases in silicate melts and glasses. Furthermore, for a more detailed analysis of the radial disorder around Kr, spectra with a better signal to noise ratio are required.

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