SOLUTION AND SHOCK-INDUCED EVOLUTION OF ARGON IN VITREOUS CARBON

C. Gary Zuss and Thomas J. Ahrens

ABSTRACT

Vitreous carbon has been shown to be the main noble-gas carrier in chondritic meteorites. To add to our knowledge of noble gas solutions and vacancies in carbonaceous material, experiments were performed on vitreous carbon, a type of amorphous carbon. Argon in vitreous carbon samples were prepared under high-temperature conditions using argon as the pressurizing medium. Solubility data were obtained for temperatures of 773 to 773 K and pressures of 350 to 250 bars. Up to 7 wt. % Ar was dissolved in the carbon. The solubility data were compared to a thermodynamic model of argon atoms dissolving into a fluid population of "holes" in the carbon. Two variables of the model yielded estimates of the enthalpy of solution of Ar in vitreous carbon (ΔHsol) of -4700±400 cal/mole.

Preliminary shock experiments showed that 28% of the total argon was released by driving a 4 GPa ± shock into the argon-rich carbon. It was demonstrated that shock-induced major loss is not simply caused by the impact-induced dissolution of grains. The present values of shock pressure required for partial liquid devolatilization of Ar from carbon is below the range (5-30 GPa) that H2O is released from pyrolysis.

1. Introduction

Noble gases are important tracer compositions of the planets because their relative abundances places constraints on early solar system processes such as accretion. The noble gases in the atmospheres of Earth, Venus, and Mars and the bulk of the noble gases in meteorites all have a similar elemental abundance pattern which has been labelled "planetary." This planetary component of the noble gases is of particular interest as we try to understand the accretion of terrestrial planets. On a broad scale, it is isotopically similar to solar noble gases but it is elementally fractionated with respect to solar abundances. In chondrites, most of the planetary noble gas is located in the fine-grained matrix. The noble gas content(s) have been a subject of research. Originally, the carrier of the isotopic component was thought to be a discrete phase and labelled "phase C." A series of studies over the last 25 years led by a group in Chicago [1-8] have revealed that the planetary noble gas component in chondrites is actually quite complex but that carbonaceous carbon is the main carrier. Tong and Anders [8] suggested a classification scheme for the "planetary" component, with at least five subcomponents, labelled P1 through P5. The first of the five subcomponents, P1, is the well-known "O-gas" and is thought to be carried by some form of amorphous carbon. P2 and P3 are carried in carbonaceous polymers. P4 is a uranium component and P5 is carried in a refractory oxide [9].

Since carbon was recognized as the probable carrier of planetary noble gas, several researchers have focused on conducting experiments with noble gases and carbon. Prick et al. [10] examined noble gas entrainment during syntheses of carbonaceous macromolecular, kerogen-like substances. Wacker et al. [11] and Zarchuk et al. [12] studied the sorption of xenon in amorphous carbon. Later, Walker [13] studied the sorption of Ne, Ar, Kr, and Xe in carbon black, acesine carbon, and diamond. These last three studies resulted in a model in which gases are physically adsorbed on interior surfaces of carbon grains. These surfaces are formed by the "hysteresis"
micropores present in amorphous carbon [13-15]. However, all of these studies have failed to find a carbon whose experimentally determined distribution coefficients are high enough to account for the amounts of trapped noble gases in meteorites based on current estimates of the conditions under which the meteorites were formed and assuming that the noble gases were trapped in a nebular-like environment.

In this paper, we present the results of studies of the sorption of argon in vitreous carbon, a glass-like form of amorphous carbon. The vitreous carbon samples which we prepared at high pressure and temperature have Ar concentrations of up to 7 w.t.%. If these concentrations are assumed to represent equilibrium solubility values, the data can be fit with simple thermodynamic models and we can compare our results with distribution coefficients to previous sorption studies at lower pressures and temperatures. The present data are fit with one such model and we briefly discuss the implications.

Using argon-rich vitreous carbon as a target, we also conducted two preliminary impact-induced devolatilization experiments. Impact-induced devolatilization experiments are a relatively new type of shock experiment in which a volatile-rich sample is shocked and the shocked sample (solid recovery experiment) and/or the released gas (gas recovery experiment) are recovered and analyzed. In this way, one can determine what fraction of a given gas is released and what fraction is retained upon impact.

Earlier impact-induced devolatilization experiments examined minerals containing H$_2$O and CO$_2$ upon impact at different velocities [16-21]. Lange and coworkers [17-19] found that serpentine and calcite begin to lose H$_2$O and CO$_2$ respectively at initial shock pressures of 10-15 GPa. Complete devolatilization occurs at shock pressures of 30-40 GPa. Tyburczy et al. [20] found similar results for shock-induced H$_2$O loss from carbonaceous chondrite (incipient devolatilization at 11 GPa and complete devolatilization at about 30 GPa). Later, Tyburczy et al. [21] refined the pressure of incipient devolatilization of serpentine to 5 GPa and also noted an impact-induced hydrogen isotopic fractionation that varied depending on the shock pressure.

Earlier experiments of a different type were performed to study the behavior of noble gases during shock. Several workers [22-23] studied the shock implantation of argon and other noble gases. Others [24-26] performed experiments to examine argon loss during shock, specifically addressing the question of how the $^{36}$Ar/$^{40}$Ar ratio (and thus the apparent age) is affected by shock. Still others [27] looked at the disturbance of the L-Ne system caused by shocks. The experiments reported here are the first shock-induced devolatilization experiments conducted on a noble gas aimed at determining the absolute loss of gas at various shock pressures.

2. Experimental method

2.1. Starting material

Vitreous carbon is a low density (1.30-1.55 g/cm$^3$), glass-like form of amorphous carbon. It differs from graphite in that it has a lower density, lower porosity and higher hardness and strength. The structure of glass-like carbon is very disordered with many micropores. Constraints on the structure and some proposed models are discussed in Noda et al. [28] and Jenkins et al. [29]. There are a number of different methods of preparation of glass-like carbon, among them slow aging and slow carbonization of carbonaceous material, carbonization under pressure [28] and combustion [30]. During the carbonization process, a carbonaceous substance (such as cellulose, polylurfuryl alcohol or polyvinyl chloride) is destructively disintegrated out of contact with air, forming carbon along with liquid and gaseous products. The carbon used in this study was purchased from ATOMIC INCORPORATED who have not published their method of preparation. They report in their catalogue that this vitreous carbon is "obtained by carbonization and subsequent thermal treatment of carbonaceous materials with strong molecular bonds which, after carbonization, leave a coke in crystallographic disorder."

2.2. High-pressure experiments

Argon-rich samples were prepared by placing 3-mm diameter vitreous carbon cylinders contained in unsealed Au-Pd capsules in cold seal furnaces under argon pressures of 0.25-1.5 kbar at
773-973K for 13 days or more. The unsealed capsules prevented any contact between the carbon and the high-temperature walls of the metal pressure vessel but allowed for free exposure between the carbon and the argon pressure medium. The exposure time scale was chosen based on the experience of Carroll and Stolper [31] who prepared Ar-rich silica glass by a similar method. Pressures were measured with 0.1-100,000 psi bourdon-tube gauges that were calibrated against a Heise 0-5000 bar gauge. Temperatures were measured and controlled with internal chromel-alumel thermocouples which were placed through a drilled out filler tubes to within several millimeters of the samples. Run conditions are listed in Table 1. The samples were quenched with a stream of compressed air. Quench to room temperature took approximately five minutes and pressure drops during quench never exceeded 19% of the original pressure.

2.3. Analytical techniques

Internal disks were cut from each sample perpendicular to the long axis of the cylinder, set in epoxy which was heated to 373K, and then polished with alumina sandpaper and alumina powder. Mounted samples were analyzed for argon.

| Sample # | T (K) | Time (days) | Ar (%)
|----------|-------|-------------|------
| CG-VCA-1 | 973±10 | 18.0 | 6.45±0.30
| CG-VCA-2A | 973±10 | 13.3 | 2.71±0.10
| CG-VCA-2B | 973±10 | 13.3 | 4.15±0.20
| CG-VCA-2C | 973±10 | 13.3 | 4.87±0.19
| CG-VCA-2D | 973±10 | 13.3 | 5.71±0.31
| CG-VCA-3B | 973±10 | 19.4 | 1.83±0.07
| CG-VCA-4C | 973±10 | 19.4 | 1.83±0.07
| CG-VCA-4D | 973±10 | 19.4 | 1.83±0.07
| CG-VCA-5A | 973±10 | 36.8 | 2.75±0.21
| CG-VCA-5B | 973±10 | 36.8 | 2.75±0.21
| CG-VCA-5C | 973±10 | 36.8 | 2.75±0.21
| CG-VCA-6A | 973±10 | 68.1 | 5.85±0.19

Values represent the mean of twenty analyses in the center of each sample. Errors are one standard deviation for these analyses.

The experimental datum at 973K has been excluded from the thermodynamic fits. The sample was considered cracked when it was removed from the furnace and this is considered suspect.

SOLUBILITY AND FISSION-PROMPTED EXTRUSION OF ARGON IN VEMON CARBON 339

content using the JEOL 733 electron microprobe at Caltech. All samples were analyzed within forty-eight hours of the time they were quenched. Typically, a profile was measured from the circular edge to the center of each disk for example, see Fig. 1.

The microprobe was operated with an accelerating potential of 15 keV, a beam current of 50 nA and a spot diameter of 20 µm. Since mobility of volatile elements was a concern, the stability of the argon content under the electron beam was checked in some samples. This check involved repeat analyses on a single point at twenty second intervals for five minutes or more. The count rates on the argon peak for each analysis were then compared. Points at the center of a disc had a steady count rate while the count rate of two points within 60 µm of the edge of the disc dropped as much as 41% in five minutes, indicating that argon is being mobilized from these sites. However, after 40 seconds, the count rate near the edge was within 2% of the value after the first twenty second interval and so a 30 second counting time was chosen for argon analyses.

The standard used in these electron microprobe analyses was an Ar-doped silica glass that had been analyzed by isotope dilution mass spectrometry by Dr. G.B. Dylampl of the U.S. Geological Survey. The isotope dilution technique is described in Dylampl and Lamphere [2]. The standard contains 0.63 wt. % argon and is one of the standards used by Carroll and Stolper [31] in their experiments on argon solubility in silica glass. The standard is estimated to be homogenous with respect to argon with at most 5% variation [31].

The precision of our analytical technique was assessed by repeat analysis of individual points. Multiple analyses were performed on several points and for points in the center of the disk these varied by only 1.7% in a single day. Similar profiles were measured across the same cut surface of one sample at weekly to monthly intervals. They show that argon is slowly diffusing from the sample, especially at the edge, but that in the center of the circular cross-section, the argon content decreases by no more than 10% in four months. Errors due to counting statistics are very small (< 18%) since there are large concentrations of argon and thus high count rates.

It is more difficult to assess the accuracy of
those analyses as this depends largely on our knowledge of our standard and the isotope dilution analysis. Carroll and Steiper [3] compared electron microprobe results to Rutherford back-scattering analyses and concluded that there was no serious problem with the accuracy of the microprobe calculation. A test of the accuracy of our microprobe analyses, an argon-rich carbon sample was analyzed by isotope dilution mass spectrometry (again by Dr. Dabney) for comparison with our microprobe results. The outer edge of this sample was sanded away with alumina sandpaper after it had been equilibrated with argon at high pressure. The remaining portion of the sample was homogeneous with respect to argon to within 15% based on electron microprobe measurements. One disc from this sample was analyzed on the electron microprobe while two smaller fragments were clipped from another disc for measurement on the mass spectrometer. Argon was extracted from these fragments using a conventional argon extraction line and analyzed by conventional isotope dilution techniques (except that the sample was not baked). The results of these two analyses are 5 and 21% lower than the microprobe analysis of the same sample. However, as we will discuss in the next section, argon is slowly diffusing from these carbon samples so this discrepancy may in part reflect more rapid diffusion of argon from the small fragments analyzed by mass spectrometry than from the larger disk analyzed by electron microprobe. In any case, we conclude that our microprobe analyses are not seriously inaccurate and conservatively estimate the accuracy of our analyses to be 20%. Note, however, that the error bars for Ar concentration in Figs. 1, 2 and 7 represent 1σ estimates for precision based on repeat analyses of single samples.

2.4. Shock experiments

Two 3-mm diameter, 0.5 mm thick disk-shaped samples of the Ar-rich morphous carbon were cut from cylinders and polished on their flat faces with alumina powder. These were placed in rented stainless steel containers, like those described by Bodough et al. [3]; Lange and Ahrens [17] and Tykocki et al. [21]. Sintered steel flyer plates were used to impact the sample assemblies at velocities of 0.9 and 0.87 km/s with the Caltech 20 mm pellrat gun. The assemblies were machined open and the two powdered samples were recovered. Recovered samples were analyzed on the electron microprobe (see section 2.5 for details) alongside unshocked samples from the same cylinder. In the second shock experiment (shot #979), a second disk from the same cylinder was ground to a grain size similar to that of the shocked sample and analyzed with the shocked and the unshocked sample. Conditions for our two shock experiments are listed in Table 2.

In order to estimate the initial and peak shock pressure of these experiments, the Impulse Match solution method described in Ahrens [14] was used. This required a knowledge of the Hugoniot of vitreous carbon. An estimate was made using the particle velocity ($u_p$), shock velocity ($v_s$) data of Mavko [35] for vitreous carbon of density 1.492 g/cm$^3$ in the range of $u_p < 3.3$ km/s. A linear fit to these data gives the relation $v_s (\text{km/s}) = 2728 + 1.081 u_p$. The initial density of the present samples, 1.470 ± 0.001 g/cm$^3$, were determined using the Archimedes method. Temperature-controlled, high-purity toluene was used for this determination. Uncertainties for shock pressures are estimated using errors in measuring impact velocity and sample density.
TABLE 3
Shock recovery experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Initial sample density (g/cm³)</th>
<th>Proportional velocity (km/s)</th>
<th>Initial shock pressure (GPa)</th>
<th>Peak shock pressure (GPa)</th>
<th>Unshocked Ar content (wt %)</th>
<th>Shocked Ar content (wt %)</th>
<th>Impact-indicating Ar loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>992</td>
<td>1.98 ± 0.05</td>
<td>6.90 ± 0.03</td>
<td>4.23 ± 0.11</td>
<td>18.62 ± 0.63</td>
<td>5.77</td>
<td>3.8</td>
<td>27.9</td>
</tr>
<tr>
<td>997</td>
<td>1.50 ± 0.05</td>
<td>8.67 ± 0.03</td>
<td>4.06 ± 0.11</td>
<td>17.92 ± 0.63</td>
<td>164-sunground</td>
<td>1.17</td>
<td>28.7</td>
</tr>
</tbody>
</table>

* Unshocked, ground sample lost 0% of its argon while shocked sample lost 28.7%.

and uncertainties in the Hugoniot of vitreous carbon. However, we point out that our estimates of shock pressure are based on an assumption of uniaxial loading. These 1-D estimates and the computed errors are good for internal comparisons of experiments but they may be a good deal in error from the actual shock pressures.

3. Results

3.1. Analysis of argon-rich carbon

Up to 7 wt.% argon was dissolved in these vitreous carbon cylinders, but its distribution is not homogeneous. Profiles across cylindrical discs show higher argon concentrations in the center of the cylinder than on the edges (Fig. 1). Profiles from different discs cut from a single sample along its length were similar, indicating that the argon content does not vary longitudinally in the cylinder. In order to determine whether the variation in argon content from the edge to the center of the cylinders was a quench effect, a diffusion effect, or an artifact of sample preparation (e.g., heating of sample in epoxy for microprobe mount), or a structural inhomogeneity within the cylinder, several additional experiments were performed. Repeat profiles across the same cut, polished surface of a single sample revealed that argon is slowly diffusing from the polished surface of the sample but that it is diffusing more rapidly from the edge than from the center. This result agrees with our test for stability under the electron beam which also indicated that the argon near the circular edge of the cylinder is more mobile than in the center. On one sample (CG-VCAR-4A, see Fig. 1) the outer 500 μm of the circular edge were removed with alumina sandpaper prior to high-pressure equilibration with argon and then it was prepared similarly to other samples. Its argon content does not decrease as dramatically at the edges as in other samples (Fig. 1), implying that the inhomogeneity of argon content is due at least in part to some radial variation in the structure of these samples. This is not surprising if one realizes that these cylinders were machined or molded by manufacturers into their shapes and structural variation could be an artifact of this process.

Each argon weight percent listed in Table 1 is the average of 20 points from the center of the given sample where the argon content is relatively homogeneous. Errors are one standard deviation for these twenty analyses. In our thermodynamic fits and discussion, we assume that these concentrations represent equilibrium solubilities. This assumption has not yet been rigorously proven but two observations support this view: Diffusion coefficients for Ar in silica glass determined by Carroll and Stolper [31] imply that argon would not diffuse to the center of a 3-mm diameter silica glass cylinder in time periods of two to three weeks. Based on this result, we expect to see cylindrical diffusion profiles in our vitreous carbon samples with higher concentrations at the edges of the cylinder. When we saw the highest concentrations in the centers of the cylinder, this suggested that we were much closer to equilibrium solubility than expected. Secondly, two samples (CG-VCAR-2A and CG-VCAR-6A) were prepared at the same pressure and temperature but for very different exposure times (13.1 and 68.1 days, respectively). Their argon concentration profiles and Ar concentrations are the same within error.

Figures 2 and 3 show the temperature and pressure dependence of argon solubility using concentrations in the centers of the cylinders. All data are from samples measured one day after quench. On these figures, we have fit the data with two
measurements were made one day after the shock experiment. Both experiments involved an initial shock pressure of \( \approx 4 \) GPa and a peak reverberated shock pressure of \( \approx 18 \) GPa. It is noteworthy that, though the two experiments were performed on samples with different concentrations of argon, they resulted in the same impact induced argon loss, \( \approx 28\% \) of their total argon. In shot \#907, the unshocked, ground sample lost no argon while the shocked sample (which was reduced to a similar fine grain size by the impact) lost 28\% of its argon. This result indicates that the shock-induced argon loss is not caused by the impact-induced diminution of grain size.

4. Discussion

4.1. Analysis of argon-rich carbon

In Appendix A, we compare our data to two cases of a general thermodynamic model of argon atoms occupying a fixed population of "holes" in vitreous carbon. In doing so, we assume that the argon concentration measured at the center of each cylinder is the equilibrium value for a vapor–glass interface at the \( P \) and \( T \) of preparation and thus represents true solubility data. Here we use the term "solubility" to mean that the argon is incorporated in the carbon structure in a thermodynamically equilibrated state—this could actually mean that argon atoms are "adsorbed" on the surfaces of the many micropores of the structure. In this sense, we have not differentiated between solubility and adsorption. The assumption of equilibrium solubility is difficult to rigorously prove. It is possible that the argon is present in the carbon as \( \text{Ar}_2 \) or \( \text{Ar}_3 \) clusters, but we deem this unlikely because of the nature of the isothermal curve we obtained (Fig. 2).

Comparing the fits for the two cases of the model (Figs. 2 and 5, Table 3), one sees that the pressure data do not allow us to constrain \( P^* \) (for definition of symbols, see Table 4). Higher-pressure data is necessary to choose the better of the two models. However, the temperature \( T_{\text{iso}} \) both suggest a \( \Delta H_{\text{iso}} \) of approximately \( \approx 4000 \) cal/mole Ar.

Fits to thermodynamic models enable us to compare our solubility data from samples prepared at high temperatures and pressures to the

![Figure 2](http://example.com/fig2.png)  
Fig. 2. Pressure dependence of argon solubility at \( T = 973 \) K. All measurements are from the centers of cylinders, measured one day after quench. Aron concentration error bars are one standard deviation for multiple analyses of single sample. Pressure error bars are estimates of uncertainties of the gauge combined with uncertainties due to any changes in pressure (i.e., leaks) during the experiments. Curves are explained in Appendix A. Aron fugacity was calculated using a Redlich–Kwong equation of state [34]. We have adjusted from the more familiar wt % units for argon concentration to the more thermodynamically useful units cm\(^3\) STP/g. For reference, 1 wt % Ar = 5.7 cm\(^3\) STP/g and 10 wt % Ar = 22.4 cm\(^3\) STP/g.

![Figure 3](http://example.com/fig3.png)  
Fig. 3. Temperature dependence of argon solubility at \( P = 250 \) bars. All measurements are from the centers of cylinders, measured one day after quench. Curves are explained in Appendix A. Aron concentration error bars, as in Fig. 2, are one standard deviation for multiple analyses of single samples.

![Figure 4](http://example.com/fig4.png)  
C. GAZIS and T.J. AURENS

variations of a thermodynamic model discussed in Appendix A. Note that the experiments' data at \( T = 1073 \) K has been excluded from our fits. That sample was considerably cracked when it was removed from the furnace and this may be responsible for the unexpectedly low Ar concentration.

3.2. Shock deconsolidation experiments

The conditions and results of our two shock experiments are shown in Table 2. All microprobe
data of other workers [10,15,36,37,43] whose samples were prepared at lower temperatures and pressures. Table 3 lists the distribution coefficients for argon in these studies. With the exception of the results of Cole et al. [37], the distribution coefficient for Ar in vitreous carbon is at least fifty times higher than any of the other synthetic carbonaceous samples. Cole et al. [37] studied the sorption of nitrogen and the noble gases on Saran type porous carbon at temperatures of 273–398K and pressures of 1 bar and less Saran carbon, like some forms of vitreous carbon, is prepared by the slow heat treatment and carbonization of polyvinylidene chloride and its copolymers with vinyl chloride. Despite the lower temperatures and much lower pressures of Cole’s study, their distribution coefficient for argon is very similar to our extrapolated value, suggesting that the structure of Saran carbon and the vitreous carbon of the present study may be similar.

We can also use the fits to these models to extrapolate our data to nebular pressures and temperatures. These are very large extrapolations but they allow us to compare the equilibrium solubility concentrations of Ar in vitreous carbon to the inferred concentration of argon in “phase Q” in carbonaceous chondrites. We will compare our data with 60Ar to avoid confusion between primordial and radiogenic components. We will assume a range of nebular conditions for the region where carbonaceous chondrites formed since there are a range of estimates in the literature. The partial pressure of argon is usually estimated assuming that the total nebular pressure is within an order of magnitude of 10^{-4} bars [38,39]. Since the solar H/Ar ratio is approximately 3 x 10^{10} and H is over an order of magnitude more abundant than any other volatile, the partial pressure of Ar is estimated at 6 x 10^{-11} bars. Temperature estimates vary according to meteorite class and model calculations but generally fall in the range of 300–500K [40]. Here we assume a pressure range of 10^{-12} to 10^{-11} bars and we extend the range of estimated temperatures to 200 to 500K. For this range of conditions, we obtain concentrations ranging from 3.9 x 10^{-12} to 9.9 x 10^{-7} cm^3 STP/g from our model extrapolations. In carbonaceous chondrites, a typical 60Ar concentration is 5 x 10^{-7} cm^3 STP/g [41] and that argon is carried by < 0.5% by weight of the meteorite [3] giving a concentration of 60Ar in the carrier of > 1 x 10^{-4} cm^3 STP/g. Despite the high concentrations of argon

<table>
<thead>
<tr>
<th>TABLE 2:</th>
<th>Arsenic distribution coefficients for various synthetic carbonaceous samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Distribution coefficient (cm^3 STP/g atm^{-1})</td>
</tr>
<tr>
<td>Paper</td>
<td>0.02</td>
</tr>
<tr>
<td>Arsenic “polymer” (Melanodine)</td>
<td>0.041 *</td>
</tr>
<tr>
<td>Laser pulse condensed carbon</td>
<td>0.016</td>
</tr>
<tr>
<td>Catalyst carbon</td>
<td>0.15 x 10^{-4}</td>
</tr>
<tr>
<td>Precipitated carbon</td>
<td>from sugar</td>
</tr>
<tr>
<td>from paper</td>
<td>4 x 10^{-4}</td>
</tr>
<tr>
<td>Carbon black</td>
<td>6 x 10^{-4}</td>
</tr>
<tr>
<td>Diamond</td>
<td>2.7 x 10^{-4}</td>
</tr>
<tr>
<td>Acetate carbon</td>
<td>0.013</td>
</tr>
<tr>
<td>Saran carbon 786</td>
<td>13.84 to 14.12</td>
</tr>
<tr>
<td>Vitreous carbon 5</td>
<td>12.0</td>
</tr>
<tr>
<td>General model</td>
<td>8.4</td>
</tr>
</tbody>
</table>

* Note that is the conversion in noble gas literature to express noble gas concentrations in condensed phases in units of cm^3 STP/g. When these are normalized to a gas phase, described by partial pressure, the units of distribution coefficients are cm^3 STP/g atm^{-1}.

* Computed based on argon solubility in equilibrated water at 323K [56].

* Extrapolated from high-temperature pressure data.
in vitro carbon, the extrapolated nebular concentra-
tions are still at least two orders of magni-
tude lower than those observed in carbonaceous chondrites.

Though in vitro carbon may not be the carrier of "Q-gas," it probably represents an upper limit in solubility-controlled noble gas concentrations in carbon. In order to explain the observed meteoritic noble gas concentrations by solubility, one must invoke either higher pressures ($P_n > 10^{-5}$ bars) or lower temperatures ($T \leq 135$ K), or a combination of the two. Partial pressures of argon of $10^{-5}$ bars imply a total nebular pressure of $= 3$ bars. Pressures such as this could be achieved within small planetary bodies in the early solar system. Pepin [42] presents a related explanation for noble gas abundances in planetary atmos-
pheres: he suggests that noble gases adsorbed on "planetary cores" and were subsequently out-
gassed from planetary interiors to form the pre-
sent-day atmospheres. Zones of high pressure could also have produced the necessary noble gas concentrations in meteorites. The problem with this model is that these high noble gas concentra-
tions would then be confined to localized zones.

Yang and Anders [43] and Wacker [11] suggest that there may be a pressure-independent process by which noble gases are incorporated into meteorites. Yang and Anders [43] postulate that noble gases may exchange with either adsorbed species and fill more than their share of active sites provided that the activation energy of ex-
change is present. In an extreme case, all active sites would be occupied by noble gases. Wacker [11] suggests that when noble gases enter the pore labyrinth of carbon, they may no longer effec-
tively communicate with other atoms in the grain or the gas outside the grain. Thus, the distribution coefficient, in the limit of long exposure time, would be independent of pressure.

The low-temperature hypothesis is supported by Fanale and Canyon [44] who suggest that the solid material of carbonaceous chondrites may have cooled to temperatures as low as $120$ K before the gasuose portion of the nebula disper-
sed. One problem with this hypothesis is that this temperature would produce chemistries with major elements less which might interfere with the trap-
ping of noble gases [40]. Also, the Fanale and Canyon model refers to adsorption of noble gases

en carbon, a process which would alone not pro-
duce the noble gas retentivities observed in chondrites.

If noble gases are not incorporated by equi-
librium solubility, one must invoke other more effi-
tient trapping mechanisms to explain the high concentra-
tions of noble gases in meteorites.

The arguments above assume that planetary noble gases were trapped in the solar nebula under meteorite formation conditions. However, the pos-
sibility exists that the planetary gas resides in pre-solar carriers as several authors have suggested [7,45-46]. Hasso and Alexander [46] present a model in which "normal planetary" noble gas is trapped in carbonaceous matrices on pre-solar dust grains. The pre-solar dust grains and their mantles were later incorporated into pristine chondritic meteorites. The model explains many of the charac-
teristics of "normal planetary" noble gas and eliminates the distribution coefficient problem be-
cause the dust temperature in dense molecular clouds is very low (10-30 K).

Clearly, further experiments are necessary to test the thermodynamic models we have set forth her and to assess the importance of in vitro carbon as a noble-gas carrier. One simple test would be to compare the retentivity of Ar in its carrier phase in meteorites to the retentivity of Ar in in vitro carbon. The carrier phase of "normal planetary" noble gases is concentrated in the re-
sidue of HF/HCl demineralization of bulk meteorite samples [3,4]. Most of the noble gases can be removed from this HF/HCl residue by treat-
ment with femming HNO3 or other strong oxy-
clasts [3]. During stepwise heating of this residue, Ar is released over a range of fairly high tempera-
tures (1073-1673 K) [47-49]. At present, our knowledge concerning the retentivity of Ar in in vitro carbon is that in the centers of these cylinders Ar is not volatilized or mobilized by electron bombardment (on a 20-μm-diameter spot with a 50 nA beam current and a 15 keV accelerat-
ing potential). Acid etching experiments and step-
wise heating experiments would be of interest. In addition, the pressure and temperature ranges of our experiments could be extended, particularly to lower pressures such as those relevant to the nebula. Similar experiments on in vitro carbon using other noble gases could also be carried out to see whether the elemental fractionation pattern
in vitreous carbon matches those of the terrestrial atmospheres. Other forms of glassy carbon could also be studied.

4.2. Shock devolatilization experiments

Though these shock experiments are preliminary, we believe that the results are promising since two samples with different pre-shock argon contents gave the same result: at an initial shock pressure of 4 GPa, 20% of the total argon is released. We have also shown that this argon release is not due simply to the reduction in grain size which the impact caused. Another aspect of the shock must have caused the argon loss. Possibly relevant is Tyburczy et al.'s [21] isotopic evidence that devolatilization initiates at sites of greater than average energy deposition (i.e., shear bands). Thus they suggest that higher temperatures at these sites cause devolatilization. A second possibility is that diffusion rates are enhanced after the release of shock pressure as the sample anneals after shock heating. Stepwise heating experiments would be of interest to determine the activation energies for shocked samples. Thirdly, microcracks may be formed which would explain the argon loss since they would decrease the effective grain size and thus may enhance diffusion and argon loss. A fourth possibility is that the short-lived volume change caused by the shock pressure drives the argon from the carbon much as water is driven from a saturated sponge when it is impacted. Further experiments such as microscopic studies of shocked samples and more controlled shock experiments may elucidate dominant devolatilization mechanisms.

A main thrust of these shock-induced devolatilization studies has been to determine their implications for planetary accretion. Since devolatilization of H$_2$O begins at a finite shock pressure, Ahrens [50] suggests a model in which a volatile-rich primitive accretion core forms in the early stages of planetary accretion. At this time, the proto-Earth is still small and impact velocities and thus shock pressures are low enough that volatiles are retained upon impact. The volatile-rich core may later be dispersed into the (lower?) mantle and could be the source of the primordial $^3$He which is being emitted over mantle plumes (e.g., Hawaii) and mid-ocean ridges today. This model was based on earlier shock-devolatilization experiments [16–21] which indicated that the release of H$_2$O begins at shock pressures of 5 GPa and complete devolatilization occurs at shock pressures of $\sim$30 GPa. Our shock experiments show partial devolatilization at a lower shock pressure than water and imply incipient devolatilization at still lower pressures. When verified by further experiments and viewed in the context of this model, these results might explain the fact that a relatively small amount of primordial argon is apparently being emitted from the mantle today [31].

Clearly, shock devolatilization is only one of the processes by which volatiles are released from a growing planet. The relative importance of shock devolatilization versus other outgassing mechanisms, such as accretional-induced heating on longer time scales or volcanic outgassing, is as yet unknown and we have not addressed that problem here.

Finally, we emphasize that these shock experiments are not complete. Any inference of implications for planetary accretion assumes that the amorphous carbon we are using is a valid analogue for the noble-gas bearing component in meteorites. This assumption could be tested by further experiments on the vitreous carbon and by comparison with gas recovery experiments on meteorites.

Acknowledgments

This work has profited greatly from the sound technical advice and generous use of laboratory facilities proffered by Professors E.M. Stolper and P.J. Wyllie. We also appreciate the generous assistance of Dr. Brent Dalyrmpile in his running standard samples in his U.S.G.S. laboratory. Research was supported by NASA under NAGW 1941, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, Contribution No. 4087.

Appendix A—Thermodynamic models

In this appendix, the solubility data are fit with a thermodynamic model of argon dissolving in vitreous carbon. Notation is defined in Table 4 and the equations and fit parameters for the ex-
Experimental data are summarized in Table 5. Here we consider two cases of a model in which Ar atoms occupy a fixed population of "holes" or sites in the carbon. The first is a general case in which the argon atoms dictate the holes in which they reside. The resulting molar volume change is the molar volume of Ar in the sorbed state, i.e., $V_{Na} - V_{Na}^{(0)} - V_{Na}^{(0)}$, where $V_{Na}^{(0)}$ and $V_{Na}^{(0)}$ are the molar volumes of filled and empty holes respectively. In the second case, the familiar Lang
mum adsorption model [52], the argon atoms occupy sites passively, causing no volume change in the hole site.

The high pressures of these experiments necessitated the use of fugacities rather than pressures for thermodynamic calculations. Fugacities for argon were calculated using the Redlich-Kwong equation of state. Redlich and Kwong [53] proposed the following equation of state with two adjustable parameters:

$$P = \frac{RT}{V} - b - \frac{a}{V^2 + bV}$$

where a is a measure of the cohesion between molecules and b is a measure of the volume of the molecules. For argon, a = 16.9 x 10^6 bar cm^3 K mole^{-1} and b = 22.3 cm^3 mole^{-1}. The use of the Redlich-Kwong equation of state to determine fugacities and activities for geologically relevant fluid mixtures and P-T conditions is described in Holloway [54,55].

In general, the equilibrium between argon in the sorbed state and the sorbed phase and argon vapor can be described thermodynamically by the equation:

$$\ln f_{\text{Ar, sorb}}(P, T) = \frac{\Delta H_{\text{Ar, sorb}}(T_0)}{RT_0} - \frac{\Delta H_{\text{Ar, sorb}}(T_0)}{RT} + \int_{T_0}^{T} \frac{\Delta H_{\text{Ar, sorb}}(T)}{RT^2} dT$$

(1)

where $$\Delta H_{\text{Ar, sorb}}(P, T)$$, $$P$$, $$T$$, $$f_{\text{Ar, sorb}}(P, T)$$, $$\Delta H_{\text{Ar, sorb}}(P, T)$$, and $$\Delta H_{\text{Ar, sorb}}(T_0)$$ are defined in Table 4. This equation describes both the general case of this model and the Langmuir model. In each case, the activity of Ar is defined as the ratio of filled to empty sites. That is, the concentration is related to the activity by the relationship:

$$x = x/(1 - x)$$

(2)

where x = m/M is the fraction of filled sites, M = total number of sites, and m = number of filled sites (concentration). This definition of activity follows from the derivation of the entropy term in the Langmuir model (see Denbigh [52]).

General case—Ar atoms in fixed population of "holes" causing volume change

In the general case of this model, $$V_{\text{Ar, sorb}}(P, T)$$ is not assumed to be equal to zero and thus the holes are allowed to dilate when Ar atoms are sorbed. Assuming $$\Delta H_{\text{Ar, sorb}}$$ and $$\Delta H_{\text{Ar, sorb}}$$ are constant, equation (1) can be written:

$$\ln f_{\text{Ar, sorb}}(P, T) = \ln f_{\text{Ar, sorb}}(P_0, T_0) - \frac{\Delta H_{\text{Ar, sorb}}}{RT} \left( \frac{1}{P} - \frac{1}{P_0} \right)$$

(3)

If we use the activity-concentration relationship of equation (2) and choose an arbitrary $$P_0$$ and $$T_0$$, equation (3) has three unknowns: $$\ln f_{\text{Ar, sorb}}(P_0, T_0)$$, $$V_{\text{Ar, sorb}}$$, and $$\Delta H_{\text{Ar, sorb}}$$. If we know the solubility of argon at three or more pressures-temperature conditions, we can perform a multiple regression on our data to obtain values for these unknowns. In using the activity-concentration relationship of equation (2), one must choose a value for $$M$$, the total number of sites. We employed a range of values and found that for all $$M = 1 	imes 10^{24}$$ Ar atoms/cm^3 C, the fits to our data were similar with $P^2$ values of 0.994 and that the values of $$m_0$$ (the concentration at $$P_0$$ and $$T_0$$), $$V_{\text{Ar, sorb}}$$, and $$\Delta H_{\text{Ar, sorb}}$$ were nearly identical. The fit is shown in Figs. 3 and 4 and the resulting values of $$\Delta H_{\text{Ar, sorb}}$$ and $$\Delta H_{\text{Ar, sorb}}$$ are listed in Table 5. Although

---

**Fig. 4.** Least squares fit to temperature data. Squares represent data. Activity (x) is calculated assuming the activity-concentration relationship of equation (2) in the appendix. The maximum number of sites (M) and in this relationship is that obtained with a best fit of the Langmuir model to the pressure data (see Table 5). Fugacity (f) is composed of a Redlich-Kwong equation of state [54]. Line drawn by: ln(x)/f = -9.570 + 2.490x x 10^{-1}. This fit has a regression coefficient of 0.992.
the fit is good, this model does not appear realistic because the total number of sites is equivalent to 13 argon atoms per carbon atom and the derived molar volume of Ar in vitreous carbon (51.6 cm³/mol) is quite large compared to the derived molar volume of Ar in silica glass [31].

Langmuir model—Ar atoms cause no volume change of "holes".

The Langmuir adsorption model is a specific case of the general thermodynamic model described above, the case where \( v_\infty, P, T = 0 \) for all \( P, T \) (there is no volume change of the "holes"). Equation (3) at constant \( T \) reduces to:

\[
\ln \left( \frac{a(P, T)}{a(P_0, T)} \right) = \frac{\Delta H_{\text{ads}}}{RT}
\]

(4)

So \( \ln(a/P) \) is independent of pressure at any given \( T \). Using our activity–concentration relationship (equation (2)), this becomes:

\[
\frac{m/M}{m_0} = K(T)
\]

(5)

Isothermal data can be fit to this equation with a least squares fit to obtain values for the maximum number of sites \( M \) and an equilibrium constant \( K(T) \). Such a fit is shown in Figure 4 with the resulting values for \( M \) and \( K(T) \) listed in Table 5.

Though the Langmuir model is usually expressed as a monolayer, it can be extended into multilayer space. At constant pressure, assuming \( \Delta H_{\text{ads}} \) is constant with respect to temperature, equation (3) with \( v_\infty, P, T = 0 \) can be written:

\[
\ln \left( \frac{a(P, T)}{a(P_0, T)} \right) = \ln \left( \frac{m/M}{m_0} \right) + \frac{\Delta H_{\text{ads}}}{RT} = \text{constant} + \frac{\Delta H_{\text{ads}}}{RT}
\]

(6)

Thus, if we plot \( \ln(a/P) \) against \( 1/T \), we can extract \( \Delta H_{\text{ads}} \) from the slope of the resultant line (Figure 4). The results of the fit to our temperature data are shown in Figure 4 and the value of \( \Delta H_{\text{ads}} \) is listed in Table 5.

References
