

## Trapping of noble gases in proton-irradiated silicate smokes

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**Abstract**—We have measured Ne, Ar, Kr and Xe in Si<sub>2</sub>O<sub>3</sub> “smokes” that were condensed on Al substrates, vapor-deposited with various mixtures of CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O and noble gases at 10 K and subsequently irradiated with 1 MeV protons to simulate conditions during grain mantle formation in interstellar clouds. The noble gases were analyzed using conventional stepwise heating and static noble gas mass spectrometry. Neither Ne nor Ar is retained by the samples upon warming to room temperature, but Xe is very efficiently trapped and retained. Kr is somewhat less effectively retained, typically depleted by factors of about 10–20 relative to Xe. Isotopic fractionation favoring the heavy isotopes of Xe and Kr of about 5–10‰/amu is observed. Correlations between the specific chemistry of the vapor deposition and heavy noble gas retention are most likely the result of competition by the various species for irradiation-produced trapping sites. The concentration of Xe retained by some of these smokes exceeds that observed in phase Q of meteorites and, like phase Q, they do not seem to be carriers of the light noble gases. Such artificially prepared material may, therefore, offer clues concerning the incorporation of the heavy planetary noble gases in meteoritic material and the nature of phase Q.

### INTRODUCTION

PLANETARY NOBLE GASES ARE KNOWN TO BE MIXTURES of several isotopically distinct components. A pre-solar origin is ascribed to the less abundant “exotic” components, such as Ne-E, s-process Kr and Xe, and Xe-HL, while the remainder, the “normal” components carried in the “Q”-phase, are most likely of solar system origin (*cf.* Anders, 1988). It is now widely accepted that most of the carriers of these components are carbonaceous (*cf.* Huss and Alexander, 1987). In contrast, silicate phases carry little or no trapped planetary noble gases, yet such phases comprise >50–90% of meteoritic material (For the few exceptions see, for example, Jentsch and Schultz (1987) and Hintenberger *et al.* (1969). The reader is also referred to Schultz and Kruse (1989) and references therein.) That no distinct silicate phases have been found with an abundance of trapped noble gases leads the authors to question whether pristine silicate grains can carry measurable quantities of trapped noble gases or whether such grains can be modified by interstellar processes to enhance trapping. If the former, then either meteoritic silicates did not form in the presence of noble gases or they were preferentially destroyed in the interstellar environment leaving only carbonaceous noble gas carriers. Nuth and Donn (1984) have argued that Si<sub>2</sub>O<sub>3</sub> smokes are good analogs to the condensates in oxygen-rich circumstellar environments. To explore the possibility that noble gases can be incorporated into high-energy (retentive) sites in amorphous silicate grains, or in icy organic mantles deposited on these grains, we have measured the isotopic and elemental composition of Ne, Ar, Kr and Xe trapped in artificially-prepared silicate condensates (smokes). For a review of noble gases trapped in other artificially-prepared carbonaceous material, we refer the reader to Wacker (1989).

A motivation for this work is the scenario whereby interstellar grains encounter molecular clouds at low temperatures (<50 K) resulting in the formation of icy mantles on the surfaces of the grains (*cf.* Huss and Alexander, 1987). These icy mantles would consist of various condensed gases, including CH<sub>4</sub> + NH<sub>3</sub> + H<sub>2</sub>O (MAW) and the heavier noble gases. Irradiation of molecular grain mantles at low temperatures followed by gradual warming in the interstellar medium can result in more refractory

organic coatings which could serve to trap noble gases (Greenberg *et al.*, 1983). The mechanism for the incorporation of noble gases on the grains would most likely be quite complex and be driven by a variety of factors. Physical adsorption of the noble gases on porous silicate surfaces or on processed grain mantles could dominate the incorporation process, but simple adsorption alone is probably not sufficient to account for the high surface concentrations apparently required by phase “Q.” Energetic particle irradiation may enhance the bonding of the heavy noble gases by providing high energy trapping sites through broken bonds (chem-adsorption, sometimes referred to as “anomalous adsorption,” *cf.* Garrison *et al.*, 1988). Refractory organic coatings may themselves provide the actual trapping sites or protect the heavy noble gases trapped at high energy sites from replacement by more chemically active species.

The elemental and isotopic compositions of the noble gases in these smokes do offer clues concerning the incorporation of the noble gases in amorphous interstellar silicate grains. Our results show that extremely large quantities of Xe and lesser amounts of Kr can be incorporated and retained in many of these smokes; severe isotopic fractionation of Kr and Xe can also occur on surfaces of freshly condensed silicate material irradiated by energetic protons. The lighter noble gases (Ne and Ar) are not effectively retained by these smokes.

### SAMPLES AND EXPERIMENTAL PROCEDURE

The samples analyzed in this study (seven silicate and two non-silicate) were prepared at Goddard Space Flight Center. We (J.N. and M.M.) collected vapor-condensed Si<sub>2</sub>O<sub>3</sub> smokes on Al substrates and then vapor-deposited ice mixtures of CH<sub>4</sub> + NH<sub>3</sub> + H<sub>2</sub>O (MAW) and noble gases (NG) on these grains. The substrates were maintained at ~10 K during the deposition of the ice and NG mixtures (assuring total condensation of the noble gases), and during the subsequent irradiation with 1 MeV protons. As the samples were warmed to room temperature the molecular ice mixtures polymerized and became varnish coatings on the silicate grains. For the seven silicate-base samples, the silicate grains were initially vapor-condensed on Al substrates in one apparatus and then transferred (exposed to the atmosphere) to the apparatus where the ice and NG deposition and the irradiation occurred for all of the grains. The silicate grains averaged approximately 20–30 nm in diameter, based on SEM analysis. A more detailed description of the preparation of similar silicate smokes is given by Nuth *et al.* (1988).

TABLE 1. Silicate smoke composition and noble gas results.

Sample	Composition <sup>a</sup>	<sup>84</sup> Kr (10 <sup>-8</sup> ccSTP/g)	<sup>132</sup> Xe	<sup>84</sup> Kr/ <sup>132</sup> Xe	Isotopic fractionation <sup>f</sup>	
					Kr (‰/amu)	Xe (‰/amu)
9	Si <sub>2</sub> O <sub>3</sub>	e	e	—	—	—
15	Si <sub>2</sub> O <sub>3</sub> → MAW <sup>b</sup>	76.3	668.6	0.114	3.6	1.0
14	Si <sub>2</sub> O <sub>3</sub> → NG <sup>c</sup>	359.8	6568.8	0.055	5.9	3.7
12	Si <sub>2</sub> O <sub>3</sub> → NG → MAW	76.3	2537.1	0.030	5.9	1.9
10	Si <sub>2</sub> O <sub>3</sub> → (MAW + NG) <sub>mix</sub> <sup>d</sup>	3.4	2032.3	0.002	f	3.5
13	Si <sub>2</sub> O <sub>3</sub> → (MAW + NG) <sub>mix</sub>	43.9	142.7	0.307	13.3	1.6
2	(MAW + NG) <sub>mix</sub>	28.1	270.2	0.104	14.7	0.4
6	(MAW + NG) <sub>mix</sub>	12.2	162.3	0.075	10.8	0.9
1	Fe(CO) <sub>5</sub> :SiH <sub>4</sub> :H <sub>2</sub> O → NG	e	0.7	—	—	8.3

<sup>a</sup> All samples were irradiated with  $1.5 \times 10^{15}$  p/cm<sup>2</sup> except #1 ( $5 \times 10^{14}$  p/cm<sup>2</sup>); Arrows indicate that components were deposited sequentially; '+' indicates co-deposition; See text for sample preparation details.

<sup>b</sup> MAW = CH<sub>4</sub> + NH<sub>3</sub> + H<sub>2</sub>O.

<sup>c</sup> NG = noble gases: Ne:Ar:Kr:Xe = (49:49:1:1 mixture).

<sup>d</sup> (M:A:W:NG)<sub>mix</sub> = (25:25:25:25) except #6, (12.5:12.5:62.5:12.5).

<sup>e</sup> Kr or Xe not detectable above spectrometer blank.

<sup>f</sup> Error weighted linear fractionation based on total compositions given in Table 2 relative to air composition (Oziřna and Podosek, 1983); isotopes <sup>78</sup>Kr and <sup>80</sup>Kr excluded for Kr.

A description of the nine smokes analyzed in this study is given in Table 1. The samples consist of silicate smokes exposed to either a mixture of noble gases (NG) (#14), a mixture of CH<sub>4</sub> + NH<sub>3</sub> + H<sub>2</sub>O (MAW) and NG (#10 and #13) or a deposition of NG followed by MAW (#12); organic (carbonaceous) ice residues produced with mixtures of MAW and NG (#2 and #6); and an inorganic silane residue (Fe(CO)<sub>5</sub>:SiH<sub>4</sub>:H<sub>2</sub>O) mixed with NG (#1). Control samples were prepared without the addition of noble gases (#15) and without noble gases and the MAW varnish (#9); these were exposed only to atmospheric gases, but not to enhanced noble gas concentrations at low temperatures. All of the silicate smokes were exposed to the atmosphere after silicate condensation and prior to MAW, NG and irradiation processing. However, the absence of detectable noble gases in control sample #9 demonstrates that noble gases are not significantly trapped in pure silicates during exposure to the atmosphere. The ices were condensed on the Al substrates at ~10 K and at pressures lower than 10<sup>-6</sup> torr, maintained by continuous pumping. The noble gases (Ne:Ar:Kr:Xe = 49:49:1:1) and the ice mixtures were sprayed through a capillary tube at supersonic velocities on the Al substrates which, except for samples #1, #2 and #6, had previously been coated by condensed amorphous silicate grains. In samples #1, #2 and #6 the noble gases were trapped in the ices alone on the Al substrate in the absence of any silicates. Viscous flow within the capillary inhibits isotopic fractionation of the gas jet itself.

To simulate the energetic particle environment expected in molecular clouds, the smokes (still at ~10 K) were irradiated with 1 MeV protons with a fluence of  $1.5 \times 10^{15}$  p/cm<sup>2</sup> (except for sample #1 which received  $5 \times 10^{14}$  p/cm<sup>2</sup>). As the samples were slowly warmed from 10 K to room temperature, mass spectra of the evolved gases were measured qualitatively using a residual gas analyzer; the original quantity of noble gases originally deposited at 10 K is unknown. Heavy noble gases, Kr and Xe, were not detected during this warming until the temperature exceeded ~200 K, but large quantities of the lighter noble gases desorbed from the samples. The samples were prepared at Goddard Space Flight Center and subsequently mailed to Washington University for noble gas analysis. Prior to mass spectrometry of the processed material, now at room temperature, samples were weighed using a Cahn-31 microbalance, wrapped in Pt foil, loaded into the ultra-high vacuum sample system and baked at 150 °C for 24 hours to lower system blanks. The gases were released using conventional step-wise heating, purified on three freshly deposited Ti films and separated on activated charcoal fingers (Kr and Xe via a CO<sub>2</sub>/acetone slurry at -78 °C and Ar via liquid N<sub>2</sub> at -196 °C) prior to ion-counting noble gas mass spectrometry (Hohenberg, 1980).

## RESULTS AND DISCUSSION

Earlier work on silicate smokes focused on the noble gases trapped during silicate grain condensation at higher tempera-

ture, but in the absence of organic varnishes and energetic particle irradiation (Nuth *et al.*, 1988). These initial smokes, prepared in various ambient atmospheres of noble gases, did not carry significant amounts of the lighter noble gases with the possible exception of Ar and were far lower in heavy noble gas concentration than the present samples. In the present study of proton-irradiated silicate smokes any trapped Ne and Ar was still below our spectrometer blank levels, but Xe and Kr were clearly retained much more efficiently than in any previous work.

## Noble Gas Concentrations

Table 2 shows the total concentrations of Kr and Xe present in the smokes and the average isotopic ratios. Xenon-132 concentrations ranged up to  $6.6 \times 10^{-5}$  ccSTP/g, and <sup>84</sup>Kr concentrations up to  $3.6 \times 10^{-6}$  ccSTP/g. Argon and Ne were below detection limits (between 10<sup>-8</sup> and 10<sup>-9</sup> ccSTP/g, depending upon sample mass). The source gas mixture had the proportions <sup>132</sup>Xe:<sup>84</sup>Kr:<sup>40</sup>Ar:<sup>20</sup>Ne of 1:2:182:164, respectively. By comparison, the retained trapped noble gas ratios were (1:0.05:0:0), demonstrating the great preference for Xe retention. One control smoke (#15), prepared in a noble gas free environment, released surprisingly large amounts of <sup>132</sup>Xe ( $6.7 \times 10^{-6}$  ccSTP/g). This smoke was, however, prepared and irradiated in the presence of a molecular ice coating unlike the other control smoke (#9), which had no coating, and whose concentrations of Kr and Xe were at or below the procedural blank levels. Smoke #15 apparently incorporated atmospheric Kr and Xe in high energy sites after condensation, presumably while the smoke was exposed to the ambient atmosphere at room temperature during handling and prior to the deposition of the organic coating or irradiation. Smoke #9 either did not incorporate noble gases while exposed to the atmosphere or did not retain any of the adsorbed noble gases. Xenon incorporation in smoke #15 is probably due to the sealing of the silicate grain by the organic mantle (varnish), preventing the atmospheric noble gas contamination from being replaced by more chemically active atmospheric species or from being lost during bakeout. This effect, enhanced here by irradiation in the presence of the organic mantle, is similar to the "anomalous" adsorption of Xe first

TABLE 2A. Noble gas results: Kr compositions.§

Sample	Mass (mg)	<sup>84</sup> Kr (10 <sup>-8</sup> ccSTP/g)	<sup>78</sup> Kr	<sup>80</sup> Kr	<sup>82</sup> Kr ( <sup>84</sup> Kr ≡ 100)	<sup>83</sup> Kr	<sup>86</sup> Kr	Peak release temp.† (fraction of total Kr)
15	0.445	76.3	0.614 0.016	3.899 0.018	19.986 0.075	19.935 0.068	30.673 0.098	700 °C (9.8%) 900 °C (67.9%)
14	0.401	359.8	0.580 0.009	3.875 0.015	19.904 0.038	20.042 0.035	30.910 0.053	700 °C (52.7%)
12	1.050	76.3	0.512 0.053	3.899 0.044	19.992 0.153	20.099 0.115	31.135 0.153	600 °C (71.6%)
10	0.160	3.4	1.178 0.472	5.291 0.373	20.448 0.846	20.055 0.784	31.903 0.743	600 °C (85.4%)
13	0.164	43.9	0.628 0.054	3.926 0.059	20.179 0.165	19.897 0.154	31.373 0.199	700 °C (26.1%) 1000 °C (33.1%)
2	0.031	28.1	0.730 0.123	3.622 0.160	19.552 0.571	20.000 0.482	30.581 0.624	1000 °C (71.0%)
6	0.091	12.2	0.776 0.118	3.999 0.160	19.739 0.362	19.850 0.490	31.069 0.556	1200 °C (65.6%)

§ Each sample subjected to stepped heating from 600 °C to 2000 °C, typically in 100 °C intervals; W coil temperatures given here are ~100–200 °C higher than actual sample temperature; the total amounts and average ratios of all temperature fractions are reported here. Complete results available upon request. Blanks were subtracted from each step (~4 × 10<sup>-14</sup> ccSTP <sup>84</sup>Kr).

† Multiple Kr peak releases (relative to other temperature fractions) occurred for samples 15 and 13.

reported by Garrison *et al.* (1987; 1988) in which Xe atoms remain tightly bound to unoccupied high energy sites until desorption or displacement by more active chemical species (*cf.* below). The inorganic silicate mixture (#1), prepared without the MAW varnish, also contained Kr and Xe, but only slightly above blank levels. The two organic samples (containing only noble gases and MAW varnish without any silicates) had Kr and Xe concentrations somewhat intermediate, but well above blank level. The sample with the largest concentration was smoke #14, which was prepared in the absence of the MAW varnish. The <sup>84</sup>Kr and <sup>132</sup>Xe concentrations in this smoke, 3.6 × 10<sup>-6</sup> and 6.6 × 10<sup>-5</sup> ccSTP/g, respectively, were at least a factor of two greater than concentrations observed in the other smokes. In sample #14, the chemically bound heavy noble gases dominate any potentially preemptive chemically active species com-

peting for these sites, as evidenced by their large relative concentrations. The second highest Xe concentration was observed in sample #12, where the noble gas layer was deposited before the MAW resulting in an advantage for the noble gases. In samples #10 and #13 the noble gases were co-deposited with the MAW rendering the NG less effective in the competition for the irradiation-produced retention sites.

Figure 1 shows the relationship between noble gas composition and smoke composition and indicates that the incorporation of noble gases in these smokes is not solely contingent on the presence of the MAW varnish. The incorporation may occur (i) by trapping noble gases in the Si<sub>2</sub>O<sub>3</sub>, *e.g.*, #9 vs. #15 or (ii) by partial trapping noble gases in the varnish, *e.g.*, #2 and #6. The Kr and Xe concentrations in these irradiated smokes exceed those observed in the unirradiated smokes previously

TABLE 2B. Noble gas results: Xe compositions.§

Sample	Mass (mg)	<sup>132</sup> Xe (10 <sup>-8</sup> ccSTP/g)	<sup>124</sup> Xe	<sup>126</sup> Xe	<sup>128</sup> Xe	<sup>129</sup> Xe ( <sup>132</sup> Xe ≡ 1)	<sup>130</sup> Xe	<sup>131</sup> Xe	<sup>134</sup> Xe	<sup>136</sup> Xe	Peak release temp.† (fraction of total Xe)
15	0.445	668.6	0.349 0.001	0.329 0.001	7.070 0.004	98.01 0.02	15.078 0.005	78.849 0.014	38.841 0.011	33.028 0.010	1300 °C (32.3%)
14	0.401	6568.8	0.341 0.001	0.322 0.001	6.997 0.003	97.17 0.02	14.995 0.003	78.619 0.010	39.039 0.009	33.351 0.008	700 °C (31.7%)
12	1.050	2537.1	0.347 0.001	0.325 0.001	7.048 0.005	97.74 0.03	15.053 0.008	78.768 0.019	38.895 0.025	33.095 0.019	600 °C (39.1%)
10	0.160	2032.3	0.335 0.003	0.319 0.004	6.956 0.025	97.15 0.43	14.926 0.049	78.432 0.402	38.796 0.099	33.238 0.071	600 °C (51.2%)
13	0.164	142.7	0.348 0.001	0.327 0.001	7.056 0.004	97.75 0.03	15.066 0.011	78.770 0.032	38.878 0.026	33.099 0.013	700 °C (52.9%)
2	0.031	270.2	0.354 0.004	0.330 0.002	7.103 0.012	98.09 0.06	15.122 0.017	78.848 0.053	38.775 0.036	33.011 0.028	1200 °C (54.9%)
6	0.091	162.3	0.352 0.002	0.330 0.002	7.074 0.007	97.95 0.04	15.096 0.011	78.820 0.033	38.823 0.022	33.016 0.019	1500 °C (70.0%)
1	0.150	0.7	0.287 0.035	0.270 0.025	6.790 0.125	96.13 0.62	15.022 0.169	78.156 0.474	39.641 0.293	33.713 0.306	800 °C (79.5%)

§ Blanks were subtracted from each step (~4 × 10<sup>-14</sup> ccSTP <sup>132</sup>Xe).



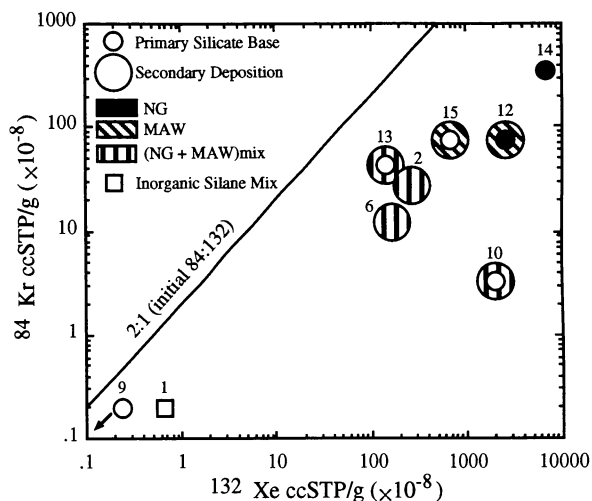


FIG. 1. Relationship between the specific chemistry of the smokes and the heavy noble gas concentrations. Qualitatively, an inverse correlation exists between the presence of the methane, ammonia and water (MAW) mantle and noble gas concentrations, suggesting that the MAW mixture competes with the noble gases (NG) for active binding sites in the samples. Xenon is preferentially retained over Kr in all of the samples, excluding control sample #9 which was not exposed to noble gases. The other control sample, #15, apparently acquired the heavier noble gases upon exposure to atmosphere.

reported (Nuth *et al.*, 1988). Even though the details of sample preparation in the two works are not identical, the enhanced noble gas concentrations observed here suggest that the trapping of the heavy noble gases is greatly enhanced by the effects of energetic particle irradiation. In addition, the various coatings probably protect the trapped heavy noble gases from displacement by more active species in the atmosphere. Since the source  $^{84}\text{Kr}:^{132}\text{Xe}$  ratio was the same for all samples, relative trapping efficiencies for Xe to Kr can be compared directly. Table 1 shows that all samples retain more Xe than Kr.

To emphasize the magnitude of these concentrations, we note that the Xe concentrations in the present smokes exceed those of trapped Xe found in typical HF/HCL meteoritic residues, which are dominated by phase Q, the carrier of 90–95% of the heavy planetary gases. For example, the Xe concentration in an HF/HCL residue from Allende ( $\sim 2\text{--}4 \times 10^{-7}$  ccSTP  $^{132}\text{Xe}/\text{g}$ ; Ott *et al.*, 1981) is 200 times less than the Xe concentration in smoke #14. Although the present experiment focuses on artificially-prepared silicates and not on meteoritic carbonaceous phases, the enhanced trapping mechanisms observed here could have played a key role during the incorporation of the heavy noble gases in phase Q. However, any further inference from this work on the trapping properties of phase Q would only be speculative primarily because the exact nature of phase Q is still unknown; it may be a discrete phase, a grain-surface coating or a heavily radiation-damaged grain-surface region where trapping is enhanced (Huss and Alexander, 1987). Nevertheless, the primary conclusion of this work is simply that enhanced trapping of the heavy noble gases (but not the light noble gases) in silicate phases can be caused by conditions of cold condensation and energetic particle irradiation.

Variation in the gas retention properties of these smokes appears to be caused by competition between the noble gases and the MAW for incorporation into the irradiation-produced de-

fects, *e.g.*, #12 and #14. The concentration of Xe eventually trapped in such sites is comparable to that found in the most efficient planetary heavy noble gas carrier, phase Q. Although the specific processes involved in the trapping and retention of the heavy noble gases are uncertain, the large concentrations of the heavy noble gases suggest that the incorporation is governed by surface phenomena rather than solubility in the bulk. The quantity of Xe incorporated further suggests that physical (Van der Waals) adsorption cannot be the dominant process. Samples processed in similar ways (*e.g.*, samples #10 and #13) can differ greatly in Xe content (in this case by a factor of 14), indicating that subtle differences in processing can make enormous differences in Xe retention, a property in common with “anomalous” Xe adsorption in other material (Garrison *et al.*, 1988). Variations in peak Kr and Xe release temperatures (Table 2) also imply that large variations in Xe retention do exist.

### Anomalous Adsorption

“Anomalous” trapping of Xe has long been observed in vacuum deposited materials and on freshly broken surfaces in high vacuum systems. This effect has been attributed to chemical adsorption of Xe at high energy sites, *i.e.*, the bonding of Xe at sites normally occupied by the more chemically reactive gases (Garrison *et al.*, 1987, 1988). This trapping mechanism is to be distinguished from physical adsorption, where bonding is due to Van der Waals forces, the only forces normally available for noble gases since more reactive species usually occupy all of the chemically active sites. Deposition of solids in an ultra-high vacuum system sometimes results in “anomalous” Xe trapping, an effect that can best be explained by chemical bonding of the Xe at high energy sites. Exposure to atmospheric gases terminates the effect, presumably because Xe cannot compete with oxygen, nitrogen and water, and the higher energy sites once again become dominated by species with greater bonding energy. The same mechanism has also been proposed to explain the incorporation of terrestrial Xe in crushed lunar samples, where fresh surfaces (and fresh high energy adsorption sites) become available to incorporate ambient terrestrial Xe (Niemeyer and Leich, 1976; Niedermann and Eugster, 1992).

### Isotopic Fractionation

Both Kr and Xe are heavily fractionated in all of these samples. The average Kr and Xe isotopic fractionations are linear, to first order, in favor of the heavy isotopes (Table 1). Smoke #14 exhibits the largest and best-defined linear isotopic fractionation, where Kr is fractionated by  $\sim 6$  permil/amu and Xe by  $\sim 4$  permil/amu. Varying degrees of fractionation were observed for the other samples, with Xe showing less scatter about the best fit fractionation lines than Kr. The differences in the degree to which samples are fractionated probably reflect changes in the composition of the residual surface reservoir with varying degrees of gas loss or retention. However, the lack of a clear correlation between the quantity of gas retained and the magnitude of the observed fractionation suggests a variation in binding energy among the different samples. Even more extreme fractionations ( $> 10$  permil/amu) were observed and were usually in temperature fractions above the peak release fractions cited in Table 2. Because these fractions were depleted in gas relative to the peak releases by several orders of magnitude, the extreme fractionations are probably due to the effects of a largely

depleted residual reservoir. The overall fractionations are consistent with partial gas loss from the surface layers (at some time prior to noble gas analysis) or with mass-dependent trapping (after irradiation and during the initial warming to room temperature). These effects clearly did not occur during the initial physical adsorption process because adsorption of all isotopes of Xe and Kr is effectively complete at 10 K. Thus, fractionation caused by gas phase partitioning, as described by Bernatowicz and Podosek (1986), is not directly relevant to this work.

### Planetary Noble Gases In Silicates?

The results of this study show that proton irradiation provides a mechanism for incorporating large quantities of heavy noble gases into silicates as well as carbonaceous materials, a mechanism that may well have been operable in the giant molecular cloud from which the nebula formed. The proton irradiation, with and without the molecular organic mantle, produces active sites by radiation damage, broken bonds and free radicals, which are located in intimate association with Xe and Kr adsorbed on the surface at 10 K. Bonds significantly stronger than those of simple physical adsorption (Van der Waals) can form with Xe, binding this noble gas firmly in place. The specific role of the organic mantle is probably quite complex, but the final refractory organic surface coating could in some cases protect the chemically bonded Xe from being displaced by more active species. Prior to polymerization during warming, the molecular MAW may actually compete with the Xe for active sites.

To put this in a cosmochemical framework, let us refer to the interstellar dust models (*cf.* Huss and Alexander, 1987), whereby noble gases are envisioned as being adsorbed onto the icy mantles of interstellar grains. Most of the heavy planetary noble gases are carried by carbonaceous material and not by pristine silicates, although silicates can be expected to be present in the oxygen-rich molecular cloud from which our sun formed. This work shows that irradiated amorphous silicate condensates can trap large quantities of noble gases, with and without carbonaceous mantles. The affinity that some carbonaceous matter has for the planetary noble gases is, perhaps, augmented, or even due to, the effects of energetic particle irradiation. Some of the carbonaceous matter most effective in trapping planetary heavy noble gases may, in fact, be in the form of surface coatings like these produced here.

### CONCLUSIONS

This work demonstrates that silicate condensates irradiated by protons can trap and retain extremely large quantities of heavy noble gases, particularly Xe. The light noble gases are not retained, and Xe is preferentially retained over Kr. The Xe concentrations in these smokes are much larger than those observed for most meteoritic planetary gas carriers. Varying degrees of fractionation are observed, with the most fractionated sample on the order of 5–10 permil/amu. Radiation-produced sites, such as free radicals or defects, may be an important part of the trapping process. Competition between the noble gases

and the various organic molecules for radiation-produced defect sites can account for the general trends observed among the samples that retained the largest quantities of the heavy noble gases.

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