



Active capture and anomalous adsorption: New mechanisms for the incorporation of heavy noble gases

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Abstract—Active capture is a new process for the incorporation of large quantities of heavy noble gases into growing surfaces. Adsorption in the conventional sense involves surface bonding by polarization (Van der Waals forces). What is referred to as "anomalous adsorption" of heavy noble gases involves chemical bonds and can occur when other (more chemically active) species are not available to preempt sites with unfilled bonds. Anomalous adsorption has been observed under conditions of fracture, vacuum deposition and ionizing radiation. Active capture depends upon anomalous adsorption to retain noble gases on a surface long enough to be captured in a growing surface film as it is deposited. The fundamental principle may be the impingement onto the growing film with sufficient energy to liberate surface electrons (work function energy of a few electronvolts) so that they are retained by anomalous adsorption long enough to be entrapped in the growing surface. Trapping efficiencies of ~1% have been observed for Kr and Xe in laboratory experiments, implying a fundamentally new mechanism for the incorporation of heavy noble gases onto surfaces. It may play a role in explaining the large concentrations of planetary noble gases contained in phase-Q.

INTRODUCTION

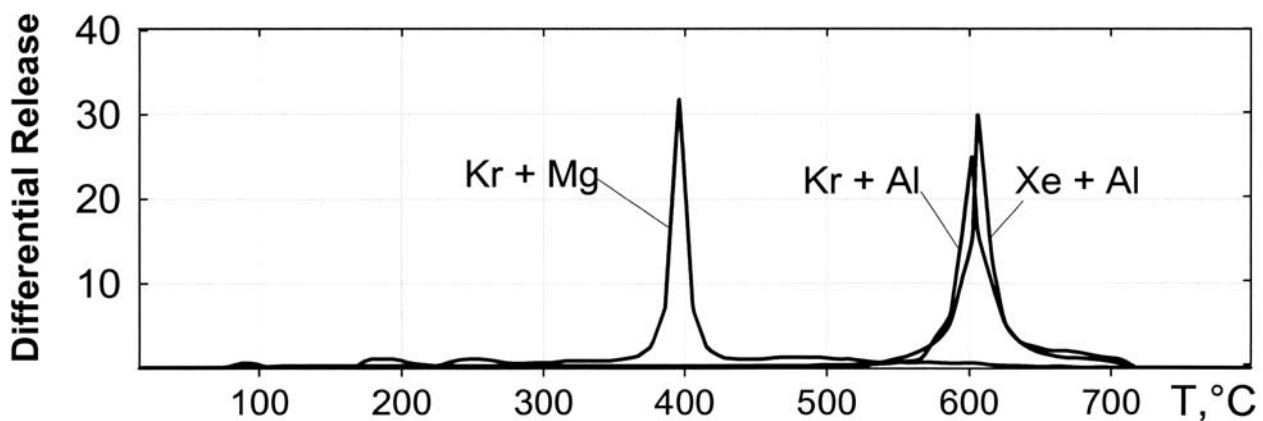
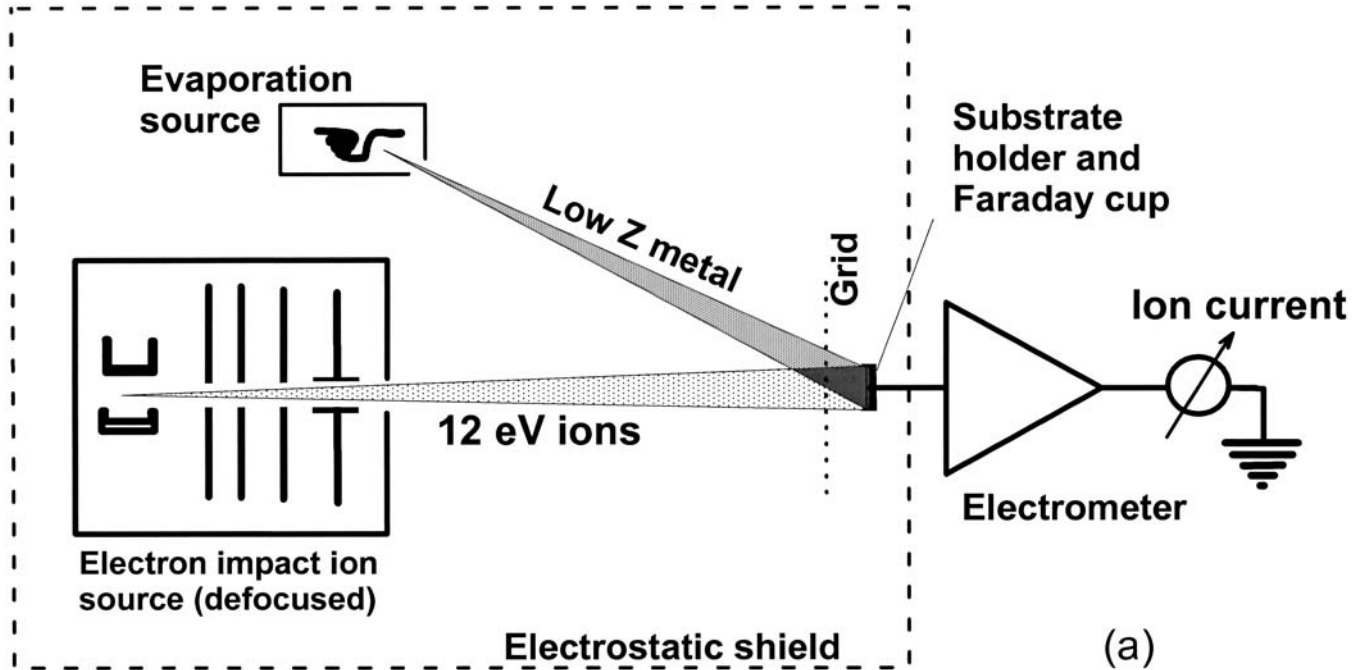
The Sun contains more than 99.5% of the mass of the solar system, representing the most important reservoir of unfractionated material. Consequently, the Sun provides a vital baseline of information about the elemental and isotopic abundances of the primitive solar system. However, the elemental and isotopic compositions of noble gases found in meteorites are clearly different from those found in the Sun. In fact, there appears to be not one but two major reservoirs of heavy noble gases in the solar system: "solar", corresponding to noble gases contained in the Sun and exhaled in solar outflows, and those historically called "planetary", which dominate all except the "gas-rich" meteorites (which contain solar gases). Solar noble gases were acquired in the nebula, or on parent body regoliths, from solar corpuscular radiation. Planetary heavy noble gases are contained in "phase-Q", a tiny and elusive reservoir, comprising only 0.02–0.04% of the bulk meteorite, yet they dominate the Kr and Xe inventory of most meteorites (Lewis *et al.*, 1975). Phase-Q is thought to be a two-dimensional structure, probably carbonaceous in nature, containing enormous concentrations of heavy noble gases (cf., Wieler *et al.*, 1991; Busemann *et al.*, 2000). Unless these two different reservoirs had independent origin, there must be a way by which planetary

heavy noble gases were derived from solar, but no known mechanism seems capable of achieving the required concentrations and compositions. However, it was not this observation, but an effort to collect cometary volatiles (Hohenberg *et al.*, 1997) that led to discovery of a new process for the incorporation of large quantities of heavy noble gases into surface material.

Collecting a sample of cometary volatiles requires use of special techniques since the energy relative to the spacecraft is so low (0.15 eV/amu for a 6 km/s encounter). The trapping probability by direct implantation at these energies is $<10^{-6}$ for Xe and it decreases by decades for each of the lighter species (Kornelson, 1964), rendering this method of capture inoperative. Nor are cometary volatiles likely to be captured and successfully preserved by passive methods such as active surfaces, aerogels or materials with enhanced surface areas. Enhanced surface areas (such as provided by activated charcoal or zeolites) do not work because, at the pressures of encounter, comet gases are in molecular, not viscous, flow so it is the cross-sectional area, not the total surface area, which determines the capture probability. But, because the terrestrial atmospheric environment is viscous, active or enhanced surfaces suffer massive terrestrial contamination problems. To put this into proper perspective, the total amount of water (the most abundant cometary volatile) encountered during coma passage is less than

that intercepted by passage through *one millimeter* of the terrestrial atmosphere at typical humidity levels. The only successful method for returning cometary volatiles will be one that captures and binds them in such a way that they are protected from terrestrial or spacecraft contamination.

The active capture of heavy noble gases, which was investigated with the apparatus shown schematically in Fig. 1a, was confirmed during the development of the Stardust Active Volatile Collector (Hohenberg *et al.*, 1997, 1998). Active capture represents a new mechanism for the



(b)

FIG. 1. (a) Schematic diagram of the active capture experimental setup. A conventional thermal evaporation source was used for the metal film deposition; the ion source design was taken from a quadrupole mass spectrometer, modified to produce a broader beam. The beam energy was measured by varying the voltage on the grid and the flux measured using a Keithley electrometer. (b) Step-wise heating of aluminum and magnesium matrices. Actively captured Kr and Xe in co-deposited Al and Mg films are tightly bound, released only when the melting (or sublimation) point of the matrix is reached. Magnesium sublimates in vacuum, releasing captured heavy noble gases at ~ 400 °C.

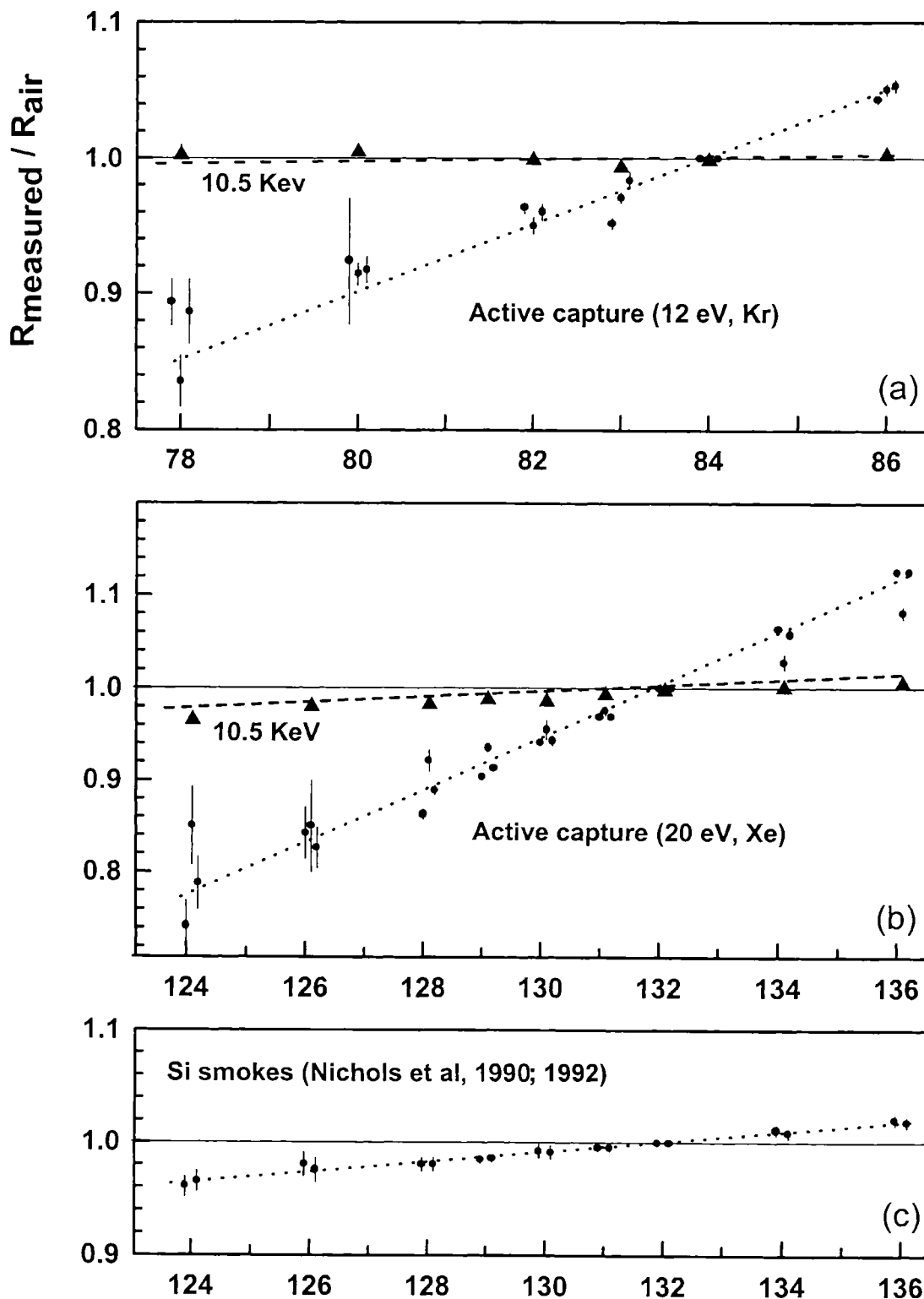


FIG. 2. Active capture of Kr (a) and Xe (b) in Al and Mg films have efficiencies of $\sim 1\%$ and result in concentrations exceeding 10^{-4} ccSTP/g. Kr and Xe mass fractionation ($\sim 3\%/amu$) are produced in active capture. Shown for reference are the isotopic ratios measured for ions implanted at 10 500 eV using the same apparatus, showing a capture efficiency of 100% and very little mass fractionation. (c) Capture by anomalous adsorption of Xe in silicate smokes condensed at ~ 10 K and irradiated with 1 MeV protons (Nichols *et al.*, 1990, 1992). Large Xe concentrations ($\sim 2 \times 10^{-4}$ ccSTP) were produced with less mass fractionation than in the active capture experiment ($\sim 0.4\%/amu$) but, unlike the active capture experiment with metal films, this process captured Xe with a much greater efficiency than Kr. With an ambient Kr/Xe ratio of 1:1, silicate smokes trapped $\sim 20\times$ more Xe than Kr.

incorporation of heavy noble gases into growing surface films. It may play a role in the acquisition of heavy planetary gases, and possibly, in the derivation of planetary heavy noble gases from solar. Active capture preferentially incorporates the heavy noble gases, and it does so with surprising efficiency, providing a mechanism for the formation of surface films with enormous capacities for heavy noble gases. If planetary Xe were derived from solar Xe by some surface trapping process, it would require mass fractionation of $\sim 1.5\%$ /amu favoring the heavy masses. Using conditions simulating Stardust comet coma passage (~ 6 km/s or 0.15 eV/amu), active capture results in $\sim 3\%$ /amu mass fractionation favoring the heavy masses (Fig. 2a,b), although the degree of mass fractionation changes with capture conditions and efficiency (Fig. 2c). Kr and Ar present special problems since the isotopic differences between planetary and solar are much less than for Xe, although the capture probabilities are likely to be less (certainly for Ar). If active capture or anomalous adsorption plays a role for deriving planetary Xe from solar, it is unclear if this mechanism is dominant for the other noble gases.

ACTIVE CAPTURE: A NEW PROCESS FOR HEAVY NOBLE GAS INCORPORATION

Excluding *in situ* production by nuclear processes, noble gases seem to be incorporated into solid material by three fundamental processes: They can reside in solution in the original melt; they can be incorporated onto grain surfaces by adsorption and they can be implanted as particles with sufficient energy to penetrate the lattice (~ 100 eV). None of these processes, by themselves, can account for the concentrations of heavy noble gases observed in phase-Q, typically $\sim 10^{-4}$ ccSTP $^{132}\text{Xe/g}$ (Lewis *et al.*, 1975; Busemann *et al.*, 2000). The solubility of noble gases in silicate melts, quantitatively described by Henry's Law, is far too small to be important for the host phase of planetary heavy noble gases (cf., Lancet and Anders, 1973). Nor can either implantation or surface adsorption provide noble gases in the concentration, component purity, and presumed two-dimensional distribution that seem to be required for Q-gases. While common surface adsorption is a well-understood process in the terrestrial atmosphere, with an abundance of water vapor and active gases, it is not necessarily a simple process when bonds are newly broken at the surface under hard vacuum conditions. What is observed under most circumstances, and commonly called "adsorption", is surface bonding due to local polarization, governed by Van der Waals forces and also described by Henry's Law (cf., Bernatowicz and Podosek, 1986). This type of adsorption cannot account for the concentrations required of phase-Q, nor can it account for the large surface concentrations of parentless radiogenic Xe from extinct radionuclides observed on lunar highland breccias and troctolite 76535 (Behrman *et al.*, 1973; Hohenberg *et al.*, 1980; Bernatowicz *et al.*, 1982). However, under special conditions, not observable when 3×10^{19}

chemically active molecules are available per cubic centimeter, chemical forces can also become involved in the surface adhesion of heavy noble gases.

Surfaces are, by definition, two-dimensional structures. To form surfaces in an isotropic medium requires a rearrangement of the bonds. In a liquid, when the asymmetry can be satisfied by a local geometrical rearrangement, this manifests itself as surface tension. However, if a fresh surface is created in a solid, for instance by fracture, new high-energy sites are created by broken bonds, resulting in strong local chemical affinities at the surface. Exposure to ionizing radiation can also produce dangling bonds at the surface and, correspondingly, new active adsorption sites. We normally observe adsorption under saturated conditions, where any high-energy surface sites created are quickly filled by the multitude of chemically active species readily available in the atmosphere (O_2 , N_2 , H_2O , *etc.*). Under these conditions, surface attraction, and hence adsorption, is primarily due to polarization effects (Van der Waals forces). Enhanced or "anomalous" adsorption effects are sometimes observed in the laboratory when new surface sites are created in vacuum allowing occupation by heavy noble gases before they can be preempted by more active species. In these cases the bonding is due more to chemical, than Van der Waals forces, so Kr and Xe temporarily lose their labels as "inert" gases. He, Ne and Ar do not seem to participate in anomalous adsorption.

Anomalous adsorption effects have been observed when fresh surfaces are created in vacuum by fracture or deposition and when existing bonds are broken by ionizing radiation. Although generally a nuisance in the laboratory, and seldom a factor in the terrestrial environment, in other regimes anomalous adsorption provides the driving mechanism for significant physical effects. Enhanced surface capture effects of heavy noble gases have been observed in lunar regolith breccias 14301 and 14303, and troctolite 76535, where concentrations of Xe from decay of extinct ^{129}I and ^{244}Pu on grain surfaces far exceed that expected from conventional adsorption (Drozd *et al.*, 1972; Behrman *et al.*, 1973; Bernatowicz *et al.*, 1978; Hohenberg *et al.*, 1980). The "anomalous adsorption" of Xe onto newly deposited silicate surfaces in ultra-high vacuum has been reported by Garrison *et al.* (1987). The crushing or grinding of lunar and meteoritic material, even at atmospheric pressure, can replace indigenous Kr and Xe with that of atmospheric composition (Niemeyer and Leich, 1976; Phinney, 1972; Bernatowicz *et al.*, 1982; Niedermann and Eugster, 1992). Exposure to ionizing radiation can result in the same effect, shown by the enhanced capture of heavy noble gases in proton-irradiated silicate smokes (Nuth *et al.*, 1987; Nichols *et al.*, 1992), where free radicals, or dangling bonds, are created on local surfaces.

While anomalous adsorption may be a poorly explored and under-appreciated mechanism for chemical bonding of heavy noble gases to surfaces, its capacity is limited. The active sites available for capture are unfilled bonds in the surface monolayer of material, so the total amount of heavy noble gases that can be chemically adsorbed at these sites is therefore limited.

Moreover, retention of the heavy noble gases by these sites is poor since they will likely be replaced by more active species as soon as they come along. If, however, new surfaces are constantly being created in the presence of heavy noble gases by film deposition, and new high-energy sites are being created on these new surfaces, the anomalously enhanced trapping rate can continue unabated. Coverage by the growing film converts the tenuous chemical surface traps into stable traps within the lattice. Surface distributions can therefore be transformed into volume concentrations by the growth of these surface films in much the same way that ion pumps transform surface-implanted layers of noble gas into volume-distributions by the sputter-deposition of titanium. In fact, the ion pump analogy provided the inspiration for the development of an instrument to actively capture cometary volatiles for the Stardust mission (Hohenberg *et al.*, 1997, 1998). Although time constraints did not allow this instrument to be flown with the mission, the active capture of volatiles experiment demonstrated a new mechanism for the incorporation of heavy noble gases into solid material. This mechanism combines anomalous adsorption and deposition to build a three-dimensional matrix capable of enormous concentrations of heavy noble gases. Figure 1b shows that these gases are tightly held, being released in step-wise heating only when the melting (or sublimation) point of the metal lattice is exceeded.

The active capture of volatiles experiment (Fig. 1a) involved the simultaneous deposition of the capture film, a low-Z metal (to reduce backscatter), and the species to be captured, as shown in Fig. 1a. In that experiment, the capture film was evaporated from a conventional evaporation source onto the capture surface, initially a bare sapphire substrate. Low-energy ions (0.15 eV/amu, characteristic of a 6 km/s comet coma fly-through) were simultaneously directed onto the growing metal film by a specially modified quadrupole ion source and the ion current continuously monitored using an electrometer. The beam energy was confirmed by varying the potential on a grid positioned between the source and the collector. Electrostatic effects are difficult to prevent for ions of this low energy, even with careful shielding. Although the beam intensity profile was measured by scanning several apertures across the collector, the inferred capture efficiencies are relatively uncertain, principally due to large spatial variations in the ion current density, leading to considerable uncertainty in actual beam flux at any given point. What is not at all uncertain, however, is that low-energy ion capture works with surprising efficiency. Active capture depends upon "anomalous" adsorption to bind heavy noble gases long enough for capture in the growing metal matrix. In order for active capture to work the surface dwell time must be comparable with, or longer than, the time required for the deposition of a monolayer of matrix, resulting in a three-dimensional distribution within the freshly deposited surface material.

During the course of that work, capture efficiencies were measured for 6 eV Ar, 12 eV Kr and 20 eV Xe in codeposited Al, Mg and Zn films (Table 1). It was found that Al and Mg films had about the same capture efficiency (~1%), with Zn

somewhat lower (not shown), in accordance with the predicted dependence on Z . Variability (of up to a factor of 2) in apparent capture efficiencies are almost certainly due to electrostatic effects, which produce variations in the ion current density as a function of position. The specific profiles were difficult to replicate from run-to-run, making it even more difficult to correlate the ion fluence with position on the sample.

As expected, when collecting volatiles at less than unity efficiency, there is significant mass discrimination favoring the heavy isotopes. Figure 2a,b show the mass discrimination of actively captured 12 eV Kr and 20 eV Xe compared with Kr and Xe derived from the same ion source but post-accelerated to 10.5 KeV. The flat pattern observed for high-energy implantation shows that the mass discrimination effects in active capture are entirely due to the low-energy active capture process itself and not the ion source or inlet system. Mass discriminations of about this magnitude are, in fact, expected for processes that retain only ~1% of the impinging ions. However, capture of noble gases, even at the 1% level, cannot be explained by conventional adsorption during the deposition process. When deposition occurs with no implantation, but in an atmosphere of pure Kr or Xe, no capture occurs, demonstrating that thermal energies (~1/40 eV) are insufficient for active capture (Table 1). Actually, this fact was already known, since Ti flash getters (freshly deposited Ti films) are typically operated in the presence of noble gases with no measurable Kr or Xe capture (*e.g.*, Hohenberg, 1980). Note also that the capture efficiency for Ar is much less than for the heavier noble gases, consistent with the absence of anomalous adsorption for Ar.

The large variation of observed capture efficiency for Kr and Xe are most likely due to the electrostatic effects mentioned above. However, the low efficiencies measured for the replicate runs 093 and 094 may be due to the low deposition rate of 5 Å/s, when the average "sticking time" for the few electronvolts noble gas atoms could be too short for a significant fraction to be permanently trapped by the slowly growing film. Also, at low deposition rates, the relatively high base pressure of $\sim 2 \times 10^{-7}$ Torr may allow more active species to preempt heavy noble gases and preferentially occupy the newly created sites, defeating anomalous adsorption. Exploration of active capture and anomalous adsorption effects are currently being carried out and more detailed account of work in progress will be presented elsewhere. It is, however, clear even from these preliminary results, that active capture is a new process for the incorporation of large amounts of Kr and Xe into growing surface films. Deposition of metal films in Kr and Xe atmospheres result in no capture at all, demonstrating that thermal energies (~1/40 eV) are insufficient for active capture to occur, and it seems to be ineffective for capture of the lighter noble gases. The following discussion outlines our understanding of active capture and the operative physical principles.

The active capture of volatiles experiment demonstrated enhanced surface capture (anomalous adsorption) and the

TABLE 1. Active capture of low-energy (0.15 eV/amu) noble gases by co-deposition of metal films.*

Gas + Film (Energy)	Sample #	Deposition rate (Å/s)	Fluence (10 ⁹ ions/mm ²)	Recovered (10 ⁶ atoms/mm ²)	Efficiency‡ (%)	
³⁶ Ar + Al (5.4 eV)	059-1	40	3.6	2.40	0.07	0.06
	059-2			1.98	0.06	
Kr + Al (12.6 eV)	049-1	40	2.2	30.3	1.36	1.1
	050-1			22.8	1.02	
	050-2			21.2	0.95	
Xe + Al (19.8 eV)	054-1	40	1.9	9.49	0.49	0.32
	054-2			4.87	0.25	
	054-3			3.81	0.20	
	055-1			8.69	0.45	
	055-2			5.15	0.27	
Kr + Mg (12.6 eV)	072-1	50	4.2	47.5	1.13	1.1
	085-1			38.4	0.97	
	092-1†			62.1	1.48	
	092-2†			32.6	0.80	
	092-3†			42.1	1.01	
	083			104	1.54	
084	40	6.8	123	1.82	1.7	
Xe + Mg (19.8 eV)	065-1	120	2.6	34.4	1.31	1.3
	066-1			34.7	1.32	
	093-1	5	4.2	3.43	0.08	0.08
	094-1			3.31	0.08	
Xe + Al	030-1‡	120	§	0.057	6.7 × 10 ⁻⁹	6 × 10 ⁻⁹
	030-2‡			0.044	5.2 × 10 ⁻⁹	

*All samples preheated in vacuum for ~24 h at 150 °C.

†Samples were stored at atmospheric pressure and room temperature for 6 months.

‡Last column is the mean capture efficiency.

§Deposition was made in a Xe atmosphere at a pressure of $\sim 1.4 \times 10^{-5}$ Torr and 300 K. This temperature and pressure corresponds to a fluence of $\sim 8 \times 10^{14}$ neutral Xe/mm² and a mean thermal energy ~ 0.0025 eV. Although the other implantations were done in similar atmospheres of the implanted gas, this measurement proves there will be negligible contributions from this low-energy component.

transformation of the two-dimensional surface distribution into a volume distribution by the continued deposition of an overlying metal film. Like also occurring in an ion pump, any noble gas atom that remains long enough on the surface will be captured in a growing matrix of freshly deposited metal. However, unlike an ion pump, which implants ions at several kiloelectronvolts, the active capture experiment demonstrated capture of ions with energies of only a few electronvolts, insufficient to penetrate the lattice. What was not known at the time of the early experiments was whether the surface dwell times for such a low-energy irradiation (~ 0.15 eV/amu) would be long enough to allow capture by the codeposited metal film. Ions of this low energy cannot penetrate the lattice of the target material. It is, therefore, the bonding energy at the surface that establishes

their surface residence times. Extrapolating from the work of Wilmoth and Fisher (1978) for the temperature dependence of surface stay-times for Kr and Xe atoms on Ni and Cu at temperatures below 120 K, we calculate Kr and Xe surface stay-times at 300 K to be less than the $\sim 10^{-13}$ s typical atomic vibration period. This is many orders of magnitude less than the 10^{-1} to 10^{-2} s required for the deposition of a monolayer of evaporated metal in these experiments (Hohenberg *et al.*, 1997, 1998).

As shown in Table 1, $\sim 1\%$ of all 12 eV Kr and 20 eV Xe incident on a growing surface are securely bound within the metal matrix, retained during long-term heating and only released when the metal is heated beyond melting (or sublimation), as shown in Fig. 1b. Although impacting ions of 12 eV lack sufficient energy to penetrate the lattice, and remain

on the surface by Van der Waals forces for too short a time to be covered, they are captured with surprising efficiency. The fact that active capture works at all provides confirmation that anomalous surface adsorption itself is not only a real process, but dominates the surface force when new bonds are freshly created. Anomalous adsorption effects cannot be ignored in ultra-high vacuum depositions or under conditions where dangling bonds exist. The short surface dwell times provided by Van der Waals forces are not sufficient for capture but, when new high-energy surface sites are locally created, Van der Waals forces are replaced by chemical bonds, providing much stronger forces and sufficiently long surface residence times to be covered with the codeposited metal. For instance, in order to capture with the observed 1% efficiency, a sticking time of $\sim 10^{-4}$ s would be required and one would have to conclude that, without anomalous adsorption, active capture should never be observed at all.

Anomalous adsorption effects have been observed on fresh surfaces created by crushing, by ultra-high vacuum deposition and fracture, and by ionizing radiation, presumably due to the creation of free radicals or dangling bonds at the surface. Anomalous adsorption also occurs in silicate smokes, condensing in a Xe atmosphere and irradiated with 1 MeV protons (Nuth *et al.*, 1987; Nichols *et al.*, 1992). Extremely large concentrations of Xe are trapped in these smokes, accompanied by less mass fractionation than is observed in the current active capture experiments (Fig. 2c). This illustrates that anomalous adsorption, the efficiency of active capture and fractionation are clearly condition dependent.

What distinguishes low-energy active capture (~ 10 eV) from ion impingement with only room temperature energies (~ 0.025 eV) during deposition, where no capture is observed, must be attributed to a longer surface dwell time for the higher energy particles. The longer surface dwell time is most likely due to the presence of anomalous adsorption effects for the higher energies, with conventional adsorption the only operative surface bonding process for the lower energy particles. The higher energy particles must therefore be able to create broken or dangling bonds on the metal surface. Since the work function of metals is typically a few electronvolts, this may well define the critical energy: 10 eV is enough energy to liberate electrons from the surface and generate dangling bonds, 0.0025 eV is not. Anomalous adsorption, and hence active capture, could happen only when the incident particle has enough energy to liberate a surface electron and generate a local trap where chemical bonding can occur. The relatively long surface dwell times required for active capture is supplied by chemical bonding at these new sites. In the transformation of surface populations into volume populations within the codeposited film, active capture also provides a mechanism to trap enormous quantities of heavy noble gases into a growing surface. Active capture may, therefore, provide a mechanism that can explain the large concentrations of planetary heavy noble gases that characterize phase-Q. Figure 1b shows that these

gases are tightly held within the matrix, being released in step-wise heating only when the melting (or sublimation) point of the metal lattice is reached, suggesting that actively captured noble gases should be stable during thermal processing and metamorphic evolution in the early solar system.

PHASE-Q: HOST OF HEAVY PLANETARY NOBLE GASES

Phase-Q, the carrier of planetary heavy noble gases, was first identified and characterized during meteorite demineralization studies of the carbonaceous chondrite Allende (Alèrts *et al.*, 1979a,b; Lewis *et al.*, 1975; Lewis and Anders, 1981; Wieler *et al.*, 1991). Removal of 99.5% of the Allende starting material, by dissolution with HF/HCl, leaves most of the planetary noble gas intact. Further reaction with highly oxidizing acids, such as concentrated HNO₃, removes very little material, only $\sim 5\%$ of the residue mass but it liberates essentially all of the planetary heavy noble gases. The carrier for heavy planetary noble gases was subsequently denoted "phase-Q", for *Quintessence*, by Alèrts *et al.* (1979a,b), who also concluded that Q is most likely carbonaceous in nature since it is removed by strongly oxidizing acids.

Phase-Q contains most of the planetary heavy noble gases ($(1-2) \times 10^{-8}$ ccSTP ¹³²Xe/g for Orgueil, Murray and Mighei (Pepin and Signer, 1965), yet it corresponds to a tiny fraction of the mass, typically ~ 0.00025 g/g for carbonaceous chondrites (Lewis *et al.*, 1975; Busemann *et al.*, 2000). Implied is a ¹³²Xe concentration of $\sim 10^{-4}$ ccSTP ¹³²Xe/g for phase-Q, the largest observed for any natural material, 4 orders of magnitude larger than solar wind Xe in the finest, most gas-rich, illmenite fraction of mature lunar soils (Eberhardt *et al.*, 1972). This inferred concentration is actually a lower limit since it assumes that all material removed by the oxidizing acid is Q, that nothing but Q is removed, and that all Q carries Xe uniformly. Phase-Q, so low in abundance yet dominating meteoritic heavy noble gases, has efficiency as a planetary gas carrier that is impressive. Even though the mechanism for incorporation is not known, it must not only have been quite effective, but also mass selective since phase-Q primarily carries heavy, not light, planetary noble gases. The large concentration of heavy planetary noble gases observed for phase-Q suggests that Q may not be a distinct mineral in the usual sense but perhaps a two-dimensional surface with unique properties and an anomalously high capacity for heavy noble gases.

Carbonaceous chondrites contain large concentrations of both planetary gases (and its carrier, phase Q) and an abundance of 10–100 Å nanodiamonds, typically 0.005 g/g. This raises the possibility that Q may somehow be related to nanodiamonds, perhaps as a surface layer of amorphous carbon. If uniformly distributed, the amorphous layer, distinguished from crystalline diamond by desolution in oxidizing acids such as HNO₃, would be between 1/10 and 1/100 Å thick, much less than a single monolayer. This would seem to suggest a non-uniform distribution, if nanodiamonds are indeed the site of Q, so that

not all nanodiamond surfaces need to carry this material. Several other observations can also be made that bear upon this association. First, planetary Xe is the dominant Xe component of carbonaceous meteorites, yet it is separable from, and seems not to be correlated with, Xe-HL, the dominant Xe component of the nanodiamond. To achieve this, Q-Xe would have to be removed by the oxidizing acid treatment without releasing measurable quantities of Xe-HL, and it seems that little Q-Xe can remain within the nanodiamonds. However, as reported by Huss and Lewis (1994), another component, Xe-P1, does seem to be associated with nanodiamonds with a planetary isotopic composition, similar to Q-Xe, and released at lower extraction temperatures than Xe-HL. In fact, Huss and Lewis (1994) propose that Xe-P1 may be trapped at surface defects on diamond so, in principle, Xe-P1 could be residual Q-Xe not removed by acid dissolution of the amorphous carbon. Although the origins of these two components differ, Xe-HL is an exotic (pre-solar) component, whereas conventional wisdom tells us that planetary Xe must be of solar system origin, they may be associated with a similar carrier. For this observation to be satisfied, all of the Q-Xe (Xe-P1) would have to be added by some process within the solar nebula after the pre-solar substrate material arrived. Finally, if Q is associated with the surfaces of nano-diamonds, the Xe cannot be adsorbed in a conventional sense, by Van der Waals forces, nor implanted in the surface at energies sufficient for significant lattice penetration. Conventional adsorption cannot retain the planetary gases long enough, nor obtain the high concentrations observed (Kornelson, 1964; Wilmoth and Fisher, 1978), and high-energy implantation would render inseparable the planetary and Xe-HL in the underlying diamond lattice. Nevertheless, circumstantial evidence in the high abundance of both Q-Xe and nanodiamond in carbonaceous chondrites, and the large surface area presented by the nano-diamonds is interesting. However, if phase-Q is somehow associated with the nanodiamonds, another process must be involved in the capture and retention of the heavy planetary noble gases. Perhaps active capture has occurred on the surfaces of some of the nanodiamond.

Feigleson *et al.* (unpubl. data) report new observations of magnetic flaring in young stars and conclude that the pre-main sequence Sun exhibited a 10^5 fold enhancement in energetic protons compared with contemporary conditions. This confirms the source of excess spallation ^{21}Ne measured in meteoritic grains (Caffee *et al.*, 1987, 1988; Woolum and Hohenberg, 1993). As pointed out by the authors, it also provides a potential source for some short-lived radionuclides in the early solar system. More pertinent to phase-Q, these flares provide in abundance a source of ionizing radiation that can create free radicals on the surfaces of nanodiamonds that are capable of anomalous adsorption of Kr and Xe. Moreover, these radiation damaged, perhaps amorphous, surfaces can be preferentially attacked by oxidizing acids, the defining characteristic of phase-Q.

ISOTOPIC AND ELEMENTAL CONSIDERATIONS

Planetary noble gases were first identified as those present in the most heavy noble gas rich objects, the carbonaceous chondrites. Figure 3a shows the composition of planetary Xe relative to solar. "Planetary" Xe was first identified and denoted AVCC, for average value carbonaceous chondrite Xe by Pepin and Signer (1965), and later OC-Xe, for ordinary chondritic Xe (Lavielle and Marti, 1992). These objects, however, are not only rich in planetary noble gases, but also nanodiamonds, which contain significant quantities of Xe-HL, so AVCC and OC-Xe, the early synonyms for planetary Xe, also contain small amounts of exotic Xe-HL. This was, in fact, recognized by differences in the heavy isotopes of AVCC and denoted CCF-Xe (carbonaceous chondrite fission; Pepin, 1964). As previously mentioned Q-Xe, released in the oxidation step of meteorite chemical processing, contributes all of the "planetary" (AVCC) Xe. This is demonstrated in Fig. 3b where we remove a sufficient quantity of Xe-HL from either OC-Xe or AVCC required to match the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio of Q-Xe. Figure 3b shows that the isotopic composition of "planetary" Xe is identical to Q-Xe once the Xe-HL contribution contained in the pre-solar diamond has been removed.

Let us consider the possibility that Q-gases might be produced by mass fractionation of solar noble gases. How large are the required isotopic and elemental fractionations? Do they have a simple mass dependency that is consistent with kinetic theory? Figure 3c shows the relative elemental compositions of solar and planetary noble gases. The light planetary noble gases (Q-gases) are fractionated from the heavy by more than 7 orders of magnitude (Busemann *et al.*, 2000). The isotopic fractionation of planetary Xe, shown in Fig. 3b, while in the same direction as the elemental fractionation, is far less, $\sim 1.5\%$ /amu. Moreover, there are substantial differences in mass fractionation between the light and heavy noble gases. The elemental mass fractionation between Kr and Xe is $\sim 30\%$ /amu and between Kr and Ar it is $\sim 50\%$ /amu. However, between Ar and Ne it is more than 6000% /amu, decreasing to $\sim 60\%$ /amu between Ne and He (Busemann *et al.*, 2000). The substantial discontinuity in fractionation (2 orders of magnitude) between the light and heavy gases shown in Fig. 3c suggests that simple kinetic processes cannot generate these effects. Any operative process that can generate planetary noble gases from solar must effectively discriminate against the light noble gases but capture the heavy noble gases with sufficient efficiency to dominate the meteoritic inventory. If solar gases represent the starting reservoir, it should result in a Xe isotopic fractionation of $\sim 1.5\%$ /amu and it should be generated by a process that is much less efficient in the capture of light noble gases.

While the observed mass fractionation for Kr in active capture seems to be about the same as that for Xe, planetary Kr seems to be much less fractionated from solar than Xe. Given kinetic theory, one would expect Kr to be captured with less efficiency than Xe and, given the uncertainties in measuring

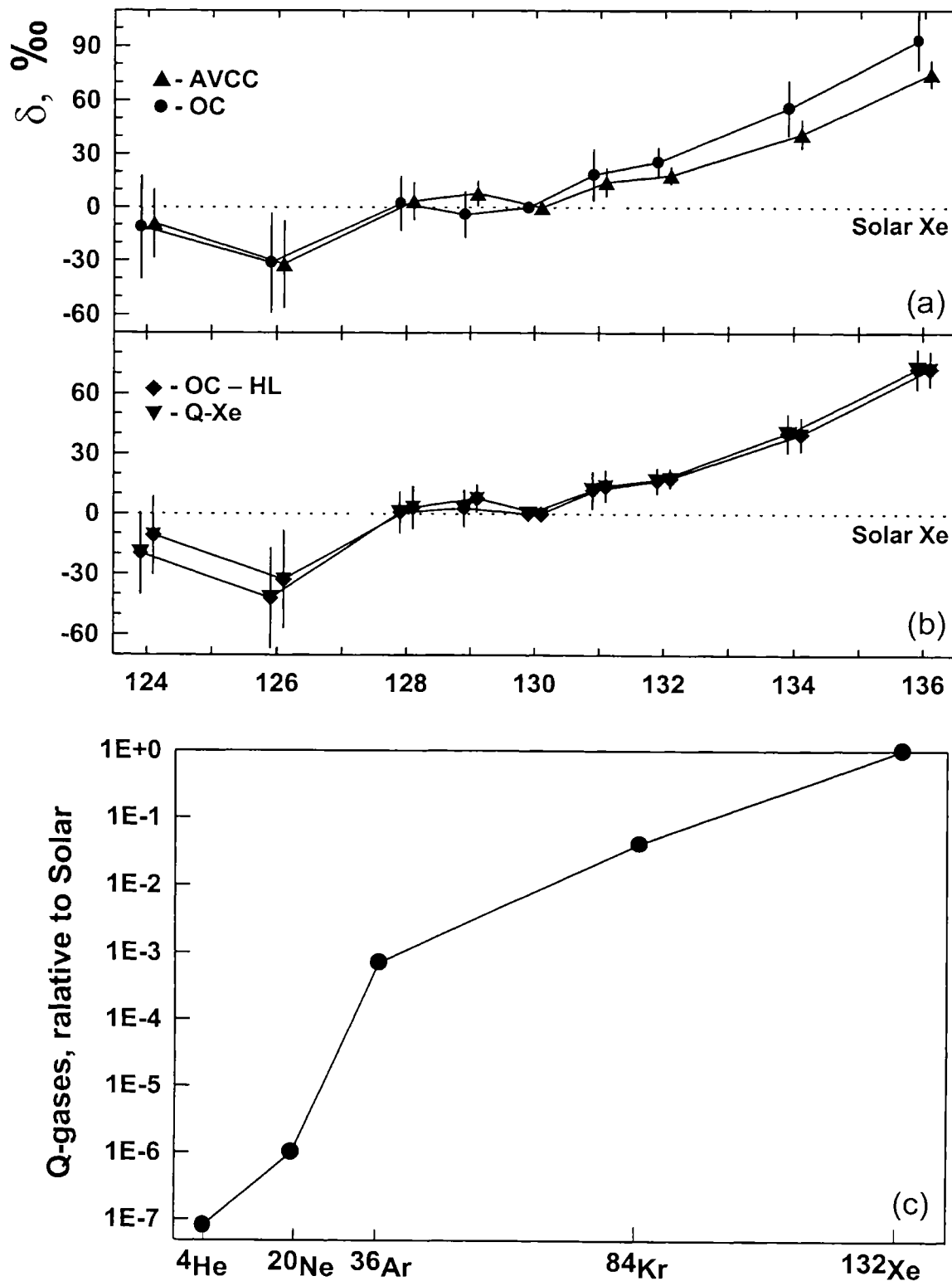


FIG. 3. (a) Isotopic composition of planetary Xe relative to solar Xe (normalized to ^{130}Xe), as first identified in carbonaceous chondrites (AVCC; Pepin and Signer, 1965), and later as ordinary chondritic Xe (OC; Lavielle and Marti, 1992). (b) Removal of Xe-HL from OC-Xe (or AVCC), as required, to match the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio of Xe-Q. Note that planetary Xe, without the contribution from Xe-HL, closely matches the composition of Xe-Q. (c) Noble gas elemental fractionation, relative to solar Xe, for planetary (Q-type) gases (cf., Pepin and Signer, 1965; Ozima and Podosek, 1983; Busemann *et al.*, 2000).

capture efficiency, we cannot exclude this possibility. However, that would tend to produce even greater mass fractionation for Kr, not less. It is clear that experiments in exploring active capture are just beginning and much careful work remains to be done.

CONCLUSIONS

Anomalous adsorption of Xe has been observed in the laboratory when fresh silicate surfaces (but not metal films) are deposited under ultra-high vacuum conditions, when insulating material is subjected to ionizing radiation and when fresh surfaces are created by fracture or crushing. In this process Vander der Waals forces, responsible for common adsorption, are replaced by much stronger chemical forces when high-energy sites are created by ionization or bond rupture. Under conditions where these sites are not preempted by more active species, these sites provide heavy noble gases with surface dwell times up to 10 orders of magnitude longer than conventional adsorption. If heavy noble gases impinge upon a surface with sufficient energy to create an active site (kinetic energy exceeding the work function), they can be chemically bound (anomalous adsorption) long enough to be covered over by an evaporated metal film, designated here as active capture. Active capture has now been demonstrated as a new mechanism capable of incorporating enormous quantities of heavy noble gases into a growing surface. This process may have been important in the early solar nebula for the incorporation of planetary heavy noble gases into phase-Q.

It has been suggested that one mechanism important for heavy noble gases may have been low-energy ion implantation. This process has been modeled using cathodeless glow discharge at ~100 eV (Bernatowicz and Hagee, 1987) and a modified Bayard-Alpert ion gauge (Bernatowicz and Fahey, 1986; Ponganis *et al.*, 1997). Low-energy implantation alone is probably not a viable mechanism for the incorporation of the planetary gases into phase-Q because it occurs in a single exposed monolayer, limiting the concentration that can be achieved, and because there is no fundamental discrimination against similar incorporation of the light noble gases.

Light noble gases associated with phase-Q are present in a much lower abundance than the heavy noble gases (Busemann *et al.*, 2000). Phase-Q must have an enormous capacity for heavy noble gases, >10⁻⁴ ccSTP ¹³²Xe/g. If derived from solar, Q-Xe seems to be fractionated, favoring heavy masses, by ~1.5%/amu (Fig. 3b). Active capture on the surface of a growing low-Z matrix seems to be able to reproduce both of these features (Hohenberg *et al.*, 1997, 1998). Low-energy capture simultaneous with a growing surface (carbon, perhaps produced by solar hydrogen reduction of CO, is low-Z, hence an effective film for active capture) can result in large Xe capacities and little affinity for the light noble gases. Could this be phase-Q? While there are indeed quantitative (achievable concentrations) and qualitative (mass fractionation favoring the heavy masses) similarities between actively

captured solar Xe and planetary Xe, the study of active capture in growing low-Z films is only now beginning. Clearly more work needs to be done in a well-shielded, ultra-high vacuum environment and a wide database will have to be obtained before this mechanism is fully understood. Perhaps then, the relationship (if any) between active capture and phase-Q can be convincingly demonstrated. For the present active capture is an interesting new process with a suggestive link to phase-Q.

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