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Experimental determination of the xenon isotopic fractionation during adsorption

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Key points

- Noble gas isotopic fractionation
- Origin of meteoritic noble gases
- Evolution of terrestrial and martian atmospheres

Abstract

Adsorption of noble gases into solids is often posited to account for their abundance patterns in meteorites, terrestrial rocks, and planetary atmospheres. Since these elements present isotope variations among geochemical reservoirs, we have experimentally tested the possibility that adsorption of neutral noble gases could result in isotopic fractionation. Our experiment consists of a cycle of adsorption/desorption processes in which xenon is progressively lost from a reservoir by equilibrium adsorption on kerogen and on montmorillonite. Any isotopic fractionation would then be amplified by the Rayleigh-like distillation experiment. The fractionation factors α are extrapolated to be -0.18 ± 0.08 ‰ per u and -0.22 ± 0.07 ‰ per u (both at the 2σ level) for kerogen and montmorillonite, respectively. Thus, adsorption of neutral noble gases alone cannot account for the specific isotopic composition of noble gases trapped in meteorites, nor for the isotopic composition of xenon in the terrestrial and martian atmospheres.

Index terms: 0325, 0343, 1028, 1060, 1065.

Keywords: xenon, adsorption, isotopic fractionation, Rayleigh distillation, atmosphere, phase Q.

1- Introduction

Among the physical processes that drive the noble gas behavior, adsorption is a retention mechanism by which the noble gases interact with solid surfaces via van der Waals attractive force arising from mutual electric dipole induction [Ozima and Podosek, 2002]. Such a process is dominant below a threshold energy corresponding to the energy at which a noble gas atom or ion starts to penetrate the first atomic layer (≈ 50 eV) [Smentkowski, 2000].

50 Adsorption tends to be more efficient for the heavy noble gases than for the light ones, due to
the higher polarizabilities of the former. As a result, adsorption is frequently posited as a
cause of noble gas captures in solids, in environments as different as the Earth, the Moon, and
the accretion disk that surrounded the early Sun 4.56 Ga ago [Ozima and Podosek, 2002]. It
has been proposed that adsorption could have led to the establishment of: (i) the noble gas
55 abundance observed in lunar breccias (especially the enrichment of heavy noble gases relative
to the light ones normalized to the solar composition) [Bernatowicz and Podosek, 1991; Leich
and Niemeyer, 1975; Lightner and Marti, 1974; Niederman and Eugster, 1992; Niemeyer and
Leich, 1976], (ii) the Earth's atmosphere composition (i.e., the depletion of atmospheric xenon
as the result of Xe preferential adsorption on sediments) [Bernatowicz et al., 1984; Podosek et
al., 1981], and (iii) the noble gas signature measured in insoluble organic meteoritic matter
60 (i.e., the so-called phase Q, also enriched in the heavy noble gases relative to light ones when
compared to the solar composition) [Fanale and Cannon, 1972; Marrocchi et al., 2005a;
Marrocchi et al., 2005b; Marrocchi et al., 2011; Wacker et al., 1985; Wacker, 1989; Yang
and Anders, 1982a; b; Yang et al., 1982; Zadnik et al., 1985]. However, variations of the
noble gas elemental patterns among solar system reservoirs and objects are often
65 accompanied by significant isotope differences relative to the inferred original compositions
(Fig. 1). For instance, meteoritic noble gases differ from the solar ones by enrichments in the
heavy isotopes of one percent or more per u (here u: atomic mass unit; Fig. 1). Likewise,
terrestrial xenon differs from both chondritic and solar compositions by 3-4 % per u
enrichments in the heavy Xe isotopes relative to light ones (Fig. 1). Trapping of ionized noble
70 gases in solids is known to result in significant isotopic fractionation [Bernatowicz and
Hagee, 1987; Frick et al., 1979; Hohenberg et al., 2002; Marrocchi et al., 2011; Ponganis et
al., 1997], and ionized xenon is more efficiently trapped than neutral xenon [Marrocchi et al.,
2011]. Such a mechanism induces significant noble gas isotopic fractionation but may be
limited to specific ionizing environments (e.g., accretion disk, planetary atmospheres...). In
75 contrast, Xe isotopic fractionation during adsorption of neutral Xe has not been detected so
far [Bernatowicz et al., 1984; Bernatowicz and Podosek, 1986; Marrocchi et al., 2011;
Podosek et al., 1981]. However, any limited isotopic fractionation could become a significant
effect in the residual gas reservoir if amplified by distillation. [Ozima et al., 1998] proposed
that some form of Rayleigh distillation could have generated the mass-dependent elemental
80 and isotopic fractionation observed in phase Q relative to Solar. To investigate this
possibility, we have developed a distillation experiment aimed at measuring at the sub permil
level Xe isotopic fractionation during adsorption of neutral xenon.

85 2- Experimental setup

Adsorption experiments were performed on terrestrial type III kerogen because it is
considered to be the best chemical analog of phase Q studied so far [Gardinier et al., 2000]
and on montmorillonite, an analog of oceanic sediments. Because these two samples are
90 characterized by contrasting surface chemistry and area (4 m²/g for kerogen and 80 m²/g for
montmorillonite, respectively)[Marrocchi et al., 2005b], the experiments were performed on
different amounts of material (3.6 g for kerogen and 1.3 g for montmorillonite, respectively).

The experimental device developed at CRPG consists of an electropolished stainless
steel volume of 10 liters (Vol. A; Fig. 2) that is connected to a quartz finger of 3 cm³ (Vol. B;
Fig. 2). Both volumes are isolated from each other by automatic valves and are connected to a
95 turbo-molecular pump in order to reach the high vacuum required for carrying out the
experiments (Fig. 2). The sample to be investigated was weighted and placed within the
quartz finger (Fig. 2). The whole system was baked at 373 K for 48 hours in order to reach a
residual pressure of 10⁻⁸ mbar. The system was then left to cool down to room temperature,

100 volumes A and B were isolated from each other by closing valve 2 (Fig. 2) and xenon was introduced at a pressure of ≈ 0.1 mbar in volume A from a manufactured xenon gas bottle (purity of 99.96%). Volume A was then pumped out down to a xenon pressure of around $5 \cdot 10^{-5}$ mbar, to provide the starting gas of the experiment. Given that this procedure might induce significant isotopic fractionation, we measured the xenon isotopic composition of this starting gas by taking an aliquot (0.1 cm^3 ; Fig. 2) of xenon at a pressure of $5 \cdot 10^{-5}$ mbar from volume
105 A. The aliquot was first expanded in a dilution line, purified using Ti-Zr getters to remove active gases (10 min at 800°C , 10 min at room temperature) and then analyzed by noble gas static mass spectrometry [Marrocchi *et al.*, 2005a]. The xenon isotopic composition of 3 aliquots separated from volume A shows a mass-dependent fractionated isotopic composition of 1.43% and 1.68% per u relative to air Xe for kerogen and montmorillonite experiments, respectively. The three aliquots present a good reproducibility that allows the composition of the starting gas to be well known (Tables 1 & 2).

The experiment consisted in performing adsorption cycles in order to mimic a distillation. Xenon from volume A was expanded in static mode in volume B and therefore put in contact with the sample located in the quartz finger. Two temperature conditions were
115 used. The kerogen sample was cooled down to 196 K using dry ice, whereas the montmorillonite sample was left at room temperature. The sample was equilibrated with the gas for 15 min, then the larger and smaller volumes were isolated by means of valve 2 (Fig. 2). Then, an aliquot was taken off from volume A and the xenon isotopic composition was measured following the same procedure as the starting gas. Before each new cycle, the sample
120 was heated to 200°C under pumping from volume B for 5 minutes (with valve 2 still closed and valve 1 open) in order to degas residual xenon from the absorbant.

The adsorption cycle was repeated several times in order to adsorb and then pump off most of the initial xenon. This process of repeated removal of xenon by adsorption is inferred to represent a Rayleigh distillation. Depending on the specific surface of the samples and the
125 experimental conditions, between 16 and 200 cycles of adsorption were required to adsorb more than 99% of xenon. The isotopic composition of volume A was measured regularly after several adsorption steps. If any isotopic fractionation was induced by adsorption, it should be seen in the evolution of the isotopic composition of xenon in volume A as a function of the number of cycles. It is important to note that the dead volume (i.e., the residual gas that is not adsorbed) located in the quartz tube corresponds to less than 0.03% of the amount adsorbed
130 and therefore has a negligible influence on the experiments.

3- Results

135 *Kerogen* - As the specific surface area of this sample is relatively low (i.e., $4 \text{ m}^2 \cdot \text{g}^{-1}$) [Marrocchi *et al.*, 2005b], adsorption experiments were performed at 196 K using dry ice. At this temperature, the amount of xenon adsorbed is rather important for the first cycles (e.g., 50% of xenon adsorbed after three cycles; Table 1). The evolution of the amount of adsorbed xenon as a function of the number of cycles follows a logarithmic relationship until $> 99\%$ of
140 xenon is adsorbed after 16 cycles (Fig. 3a). The isotopic composition of xenon measured after 3, 5, 10, 12, 14 and 16 cycles does not show any detectable isotopic variation (Fig. 3a; Table 1). The maximum isotopic fractionation factor can be calculated from this data. In the case of a Rayleigh distillation, the evolution of the isotopic ratios is linked to the remaining fraction of gas in the system as described by the following equation:

$$145 \quad \frac{R_f}{R_i} = f^{\alpha-1} \quad (1)$$

where R_i stands for the initial isotopic ratio, R_f is the final isotopic ratio (i.e., after 3, 5, 10, 12, 14 and 16 cycles), f is the fraction of xenon remaining in the system and α is the fractionation

150 factor. In order to calculate the maximum fractionation factor, we considered the $^{136}\text{Xe}/^{130}\text{Xe}$ isotopic ratio because it presents the larger mass difference with respect to the normalizing isotope (conventionally, ^{130}Xe at CRPG Nancy) among the other xenon isotopic ratios. Eqn. (1) can be rewritten as:

$$a - 1 = \frac{\ln\left(\frac{R_f}{R_i}\right)}{\ln(f)} \quad (2)$$

155 Thus in a diagram of $\ln(R_f/R_i)$ versus $\ln(f)$, the slope of the correlation (if any) permits the computation of $(\alpha-1)$ directly and therefore the fractionation factor α . For kerogen the maximum fractionation factor for the $^{136}\text{Xe}/^{130}\text{Xe}$ ratio was calculated to be $-1.08 \pm 0.56 \text{ ‰}$ (2σ) (Fig. 3b). Hence, considering a difference of one atomic mass unit, the maximum fractionation factor is determined to be: $\alpha_{\text{kerogen}} = -0.18 \pm 0.08 \text{ ‰ per u}$ (2σ).

160 *Montmorillonite* - In order to test the influence of the structural parameter of the sample on the isotopic fractionation, we performed an experiment on synthetic montmorillonite [Marrocchi et al., 2005b]. This sample presents a higher specific surface area ($80 \text{ m}^2/\text{g}^{-1}$) than kerogen and, more importantly, has an important concentration of microspores that may favor an isotopic fractionation of xenon. As the adsorption cycles were
165 performed at room temperature, 200 cycles were required to adsorb more than 99 % of the starting xenon. However, the results were the same as those observed with kerogen: (i) the evolution of the amount of xenon adsorbed follows a logarithmic relationship (Fig 4a; Table 2) and (ii) no isotopic fractionation was measured (Fig 4a; Table 2). Following the same approach than for kerogen, the maximum isotopic fractionation factor determined for
170 montmorillonite is $-1.32 \pm 0.48 \text{ ‰}$ (2σ) (Fig. 4b), which yields a $\alpha_{\text{montmorillonite}}$ value of $-0.22 \pm 0.07 \text{ ‰ per u}$. (2σ).

4- Discussion

175 The main carrier of meteoritic heavy noble gases, known as phase Q, is formed of carbonaceous material not fully characterized, obtained by acid attack of chondrites by HF/HCl [Busemann et al., 2000; Lewis et al., 1975]. Q-gases are characterized by several specific properties [Busemann et al., 2000], especially: (i) an elemental fractionation of noble gas relative to solar wind; light noble gases being depleted relative to heavy ones and (ii) a
180 mass-dependent isotopic fractionation relative to solar wind of 1.3 ‰ per u in favor of the heavy isotopes relative to the light ones. Over three decades, several adsorption experiments succeeded in reproducing the Q-like elemental abundance pattern [Fanale and Cannon, 1972; Marrocchi et al., 2005b; Wacker et al., 1985; Wacker, 1989; Yang and Anders, 1982a; b; Yang et al., 1982]. These results lead adsorption to be frequently invoked as a plausible
185 process at the origin of meteoritic noble gases [Marrocchi et al., 2005b; Wacker, 1989]. However, any model that derives Q-gases from solar nebula gases should reproduce, in addition to the elementary pattern, the isotopic noble gas fractionation observed in phase Q relative to Solar. Our results clearly do not support equilibrium adsorption as an isotopically fractionating process for noble gases, even when amplified by a Rayleigh distillation. Thus,
190 the isotopic difference of $+1.30 \pm 0.06 \text{ ‰ per u}$ observed between Xe-Q and Solar Xe [Busemann et al., 2000; Wieler and Baur, 1994] is unlikely to have been generated by adsorption of neutral xenon onto carbonaceous surfaces in the early solar system. To the contrary, our data confirm previous experiments that pointed out the dominant role of noble gas ions during trapping processes in generating Q-gas isotopic characteristics [Marrocchi et

195 *al.*, 2011]. Thus, the Q-gas properties imply a physical environment allowing efficient
ionizing of gaseous species, probably at the periphery of the solar system that underwent UV
light ionizing conditions from massive O/B stars or from the Sun itself at the surface of the
disk [Bally *et al.*, 2005].

200 Xenon in the terrestrial and martian atmospheres is under-abundant compared to other
noble gases and normalized to Chondritic, by a factor of about 20 relative to krypton. Because
xenon has the largest adsorption capability among noble gases [Ozima and Podosek, 2002],
its atmospheric depletion could be related to adsorption onto surface material with high
specific surface areas such as ice or sediments. This possibility, however, faces a mass
balance problem because there are not enough ices and sedimentary rocks at the Earth's
205 surface to adsorb the xenon presently missing in the atmosphere [Bernatowicz *et al.*, 1982;
Bernatowicz *et al.*, 1984; Podosek *et al.*, 1981]. The present data also dismiss this possibility:
atmospheric Xe is isotopically fractionated by 3-4 ‰ per u relative to Chondritic, or Solar,
which is two orders of magnitude larger than the maximum isotopic fractionation of -0.02 ‰
per u determined in this study. Assuming a Rayleigh distillation, for instance if surface
210 sediments having adsorbed xenon would be continuously recycled into the mantle, does not
solve the problem. In Eqn. 1, the fraction f corresponding to a 20-fold depletion is 0.05 and
the ratio R_f/R_i corresponding to a 3.5 ‰ per u is 1.035. Therefore the fractionation factor α
becomes 0.988, corresponding to a Xe isotope fractionation of -1.2 ‰ per u, still 2 orders of
magnitude higher than the limiting value determined in this work. We conclude that isotopic
215 fractionation during adsorption, if any, cannot account for the isotopic composition of
atmospheric xenon. Other processes, like Xe preferential ionization in the upper atmosphere
[Pujol *et al.*, 2011] are required to account for its specific isotopic composition.

220 5- Concluding remarks

We have estimated the maximum fractionation factor of xenon isotopes during
adsorption onto kerogen and montmorillonite to be -0.2 ± 0.1 ‰ per u. Hence, adsorption of
neutral noble gases cannot account for the specific isotopic composition of noble gases
trapped in meteorites, nor for the unique isotopic composition of xenon in the terrestrial and
225 martian atmospheres, which both differ from their presumed source compositions by one or
several percents. As a consequence, any adsorption model that requires a noble gas isotopic
fractionation relative to a starting gas should appeal to another mechanism, probably
ionization, in order to generate a mass-dependent isotopic fractionation.

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References

- Bally, J., *et al.* (2005), Evolution of UV-irradiated protoplanetary disks, In *Chondrites and the
protoplanetary disk*, ASP conference series. 341, 81-104.
Bernatowicz, T. J., *et al.* (1982), Adsorption and excess fission Xe: Adsorption of Xe on
vacuum crushed minerals., *J. Geophys. Res.*, 87, A465-A476.
Bernatowicz, T. J., *et al.* (1984), The atmospheric inventory of xenon and noble gases in
shales: the plastic bag experiment., *J. Geophys. Res.*, 84, 4597-4611.

Bernatowicz, T. J., and F. A. Podosek (1986), Adsorption and isotopic fractionation of Xe., *Geochim. Cosmochim. Acta*, 50(1503-1507).

Bernatowicz, T. J., and B. E. Hagee (1987), Isotopic fractionation of Kr and Xe implanted in solids at very low energies., *Geochim. Cosmochim. Acta*, 51, 1599-1611.

Bernatowicz, T. J., and F. A. Podosek (1991), Argon adsorption and the lunar atmosphere, *Proc. Lunar Planet. Sci. Conf.*, 21, 307-313.

Busemann, H., et al. (2000), Primordial noble gases in “phase Q” in carbonaceous and ordinary chondrites studied by closed system etching., *Meteorit Planet. Sci.*, 35, 949-973.

Fanale, F. P., and W. A. Cannon (1972), Origin of planetary primordial rare gas: The possible role of adsorption., *Geochim. Cosmochim. Acta*, 36, 319-328.

Frick, U., et al. (1979), Noble gas fractionation during synthesis of carbonaceous matter, paper presented at Lunar Planet. Sci. Conf. 10th.

Gardinier, A., et al. (2000), Solide state CP/MAS ¹³C NMR of the insoluble organic matter of the Orgueil and Murchison meteorites: Quantitative study., *Earth and Planetary Science Letters*, 184, 9-21.

Hohenberg, C. M., et al. (2002), Active capture and anomalous adsorption: New mechanisms for the incorporation of heavy noble gases., *Meteorit Planet. Sci.*, 37, 257-267.

Leich, D. A., and S. Niemeyer (1975), Traped xenon in lunar anorthitic breccia 60015, *Proc. Lunar Planet. Sci. Conf.*, 6, 1953-1965.

Lewis, R. S., et al. (1975), Host phase of a strange xenon component in Allende., *Science*, 190, 1251-1262.

Lightner, B. D., and K. Marti (1974), Lunar trapped xenon, *Proc. Lunar Planet. Sci. Conf.*, 2, 2023-2031.

Marrocchi, Y., et al. (2005a), Interlayer trapping of noble gases in insoluble organic matter of primitive meteorites., *Earth and Planetary Science Letters*, 236, 569-578.

Marrocchi, Y., et al. (2005b), Low-pressure adsorption of Ar, Kr, and Xe on carbonaceous materials (kerogen and carbon blacks), ferrihydrite, and montmorillonite: Implications for the trapping of noble gases onto meteoritic matter., *Geochim. Cosmochim. Acta*, 69, 2419-2430.

Marrocchi, Y., et al. (2011), Adsorption of xenon ions onto defects in organic surfaces: Implications for the origin and the nature of organics in primitive meteorites., *Geochim. Cosmochim. Acta*, 75, 6255-6266.

Niederman, S., and O. Eugster (1992), Noble gases in lunar anorthositic rocks 60018 and 65315: Acquisition of terrestrial krypton and xenon indicating an irreversible adsorption., *Geochim. Cosmochim. Acta*, 56, 493-509.

Niemeyer, S., and D. A. Leich (1976), Atmospheric rare gases in lunar rock 60015, *Proc. Lunar Planet. Sci. Conf.*, 7, 587-597.

Ozima, M., et al. (1998), Comparative studies of solar, Q-gases and terrestrial noble gases and implications on the evolution of the solar nebula., *Geochim. Cosmochim. Acta*, 62, 301-314.

Ozima, M., and F. A. Podosek (2002), *Noble gas geochemistry*, 286 pp., Cambridge University Press, Cambridge.

Podosek, F. A., et al. (1981), Adsorption of xenon and krypton on shales, *Geochim. Cosmochim. Acta*, 45, 2401-2415.

Ponganis, K. V., et al. (1997), Isotopic fractionation in low-energy ion implantation., *J. Geophys. Res.*, 102E, 19335-19343.

Pujol, M., et al. (2011), Chondritic-like xenon trapped in Archean rocks: A possible signature of the ancient atmosphere., *Earth and Planetary Science Letters*, 308, 298-306.

Smentkowski, V. S. (2000), Trends in sputtering., *Progress in Surface Science*, 64, 1-58.

Wacker, J. F., et al. (1985), Laboratory simulation of meteoritic noble gases. I. Soprtion of xenon on carbon: Trapping experiments., *Geochim. Cosmochim. Acta*, 49, 1035-1048.

- Wacker, J. F. (1989), Laboratory simulation of meteoritic noble gases. III. Sorption of neon, argon, krypton and xenon on carbon: Elemental fractionation., *Geochim. Cosmochim. Acta*, 53, 1421-1433.
- Wieler, R., and H. Baur (1994), Krypton and xenon from the solar wind and solar energetic particles in two lunar ilmenites of different antiquity., *Meteoritics*, 29, 570-580.
- Yang, J., and E. Anders (1982a), Sorption of noble gases by solids, with reference to meteorites. II. Chromite and carbon., *Geochim. Cosmochim. Acta*, 46, 861-875.
- Yang, J., and E. Anders (1982b), Sorption of noble gases by solids, with reference to meteorites. III. Sulfides, spinels and other substances; on the origin of planetary gases., *Geochim. Cosmochim. Acta*, 46, 877-892.
- Yang, J., et al. (1982), Sorption of noble gases by solids, with reference to meteorites. I. Magnetite and carbon., *Geochim. Cosmochim. Acta*, 46, 861-875.
- Zadnik, M. G., et al. (1985), Laboratory simulation of meteoritic noble gases. II. Sorption of xenon on carbon: Etching and heating experiments., *Geochim. Cosmochim. Acta*, 49 1049-1059.

# Cycles	^{130}Xe (moles)	% adsorbed	$^{124}\text{Xe}/^{130}\text{Xe}$	$^{126}\text{Xe}/^{130}\text{Xe}$	$^{128}\text{Xe}/^{130}\text{Xe}$	$^{129}\text{Xe}/^{130}\text{Xe}$	$^{131}\text{Xe}/^{130}\text{Xe}$	$^{132}\text{Xe}/^{130}\text{Xe}$	$^{134}\text{Xe}/^{130}\text{Xe}$	$^{136}\text{Xe}/^{130}\text{Xe}$
air			0.233 ± 0.0008	0.218 ± 0.0011	4.715 ± 0.007	64.96 ± 0.06	52.13 ± 0.06	66.07 ± 0.05	25.63 ± 0.04	21.76 ± 0.02
0	$1.12 \cdot 10^{-9}$	0	0.215 ± 0.002	0.208 ± 0.002	4.543 ± 0.006	63.54 ± 0.02	52.62 ± 0.03	67.79 ± 0.02	27.13 ± 0.04	23.84 ± 0.05
3	$5.49 \cdot 10^{-10}$	50.92	0.217 ± 0.004	0.209 ± 0.004	4.561 ± 0.008	63.52 ± 0.03	52.81 ± 0.04	67.56 ± 0.03	27.26 ± 0.05	23.86 ± 0.06
5	$3.22 \cdot 10^{-10}$	71.26	0.209 ± 0.004	0.211 ± 0.004	4.582 ± 0.008	63.61 ± 0.03	52.77 ± 0.03	67.81 ± 0.03	27.19 ± 0.06	23.82 ± 0.06
10	$1.32 \cdot 10^{-10}$	88.22	0.213 ± 0.004	0.208 ± 0.004	4.551 ± 0.008	63.73 ± 0.03	52.91 ± 0.03	67.78 ± 0.03	27.09 ± 0.06	23.88 ± 0.06
12	$7.71 \cdot 10^{-11}$	93.11	0.217 ± 0.004	0.213 ± 0.005	4.536 ± 0.009	63.42 ± 0.03	52.73 ± 0.03	67.70 ± 0.03	27.17 ± 0.06	23.81 ± 0.06
14	$1.73 \cdot 10^{-11}$	98.45	0.214 ± 0.005	0.209 ± 0.005	4.516 ± 0.009	63.59 ± 0.03	52.84 ± 0.04	67.65 ± 0.03	27.22 ± 0.06	23.86 ± 0.07
16	$1.04 \cdot 10^{-12}$	99.9	0.211 ± 0.005	0.212 ± 0.005	4.584 ± 0.009	63.74 ± 0.04	52.66 ± 0.04	67.59 ± 0.04	27.06 ± 0.06	23.86 ± 0.07

Table 1: Evolution of the amount of ^{130}Xe absorbed and the xenon isotopic ratio as a function of the number of adsorption cycle performed on kerogen. Air composition data are from [Ozima and Podosek, 2002]. * The value for the starting gas (corresponding to the 0 cycle line) represents the average of 3 measurements. Isotopic ratio $\times 10$.

# Cycles	^{130}Xe (moles)	% adsorbed	$^{124}\text{Xe}/^{130}\text{Xe}$	$^{126}\text{Xe}/^{130}\text{Xe}$	$^{128}\text{Xe}/^{130}\text{Xe}$	$^{129}\text{Xe}/^{130}\text{Xe}$	$^{131}\text{Xe}/^{130}\text{Xe}$	$^{132}\text{Xe}/^{130}\text{Xe}$	$^{134}\text{Xe}/^{130}\text{Xe}$	$^{136}\text{Xe}/^{130}\text{Xe}$
air			0.233 ± 0.0008	0.218 ± 0.0011	4.715 ± 0.007	64.96 ± 0.06	52.13 ± 0.06	66.07 ± 0.05	25.63 ± 0.04	21.76 ± 0.02
0	1.23 10 ⁻⁹	0	0.210 ± 0.002	0.201 ± 0.003	4.574 ± 0.006	63.54 ± 0.02	52.74 ± 0.03	67.69 ± 0.02	27.31 ± 0.04	23.90 ± 0.05
10	9.91 10 ⁻¹⁰	19.39	0.214 ± 0.004	0.209 ± 0.004	4.570 ± 0.008	63.52 ± 0.03	52.61 ± 0.04	67.81 ± 0.03	27.19 ± 0.05	23.86 ± 0.06
40	7.49 10 ⁻¹⁰	39.04	0.217 ± 0.004	0.205 ± 0.004	4.559 ± 0.008	63.61 ± 0.03	52.75 ± 0.03	67.59 ± 0.03	27.30 ± 0.05	23.90 ± 0.06
75	3.56 10 ⁻¹⁰	71.01	0.211 ± 0.004	0.223 ± 0.004	4.574 ± 0.008	63.73 ± 0.03	52.61 ± 0.03	67.66 ± 0.03	27.36 ± 0.05	23.90 ± 0.06
100	1.15 10 ⁻¹⁰	90.63	0.2215 ± 0.004	0.215 ± 0.004	4.556 ± 0.008	63.42 ± 0.03	52.90 ± 0.03	67.51 ± 0.03	27.37 ± 0.05	23.89 ± 0.06
120	6.58 10 ⁻¹¹	94.65	0.209 ± 0.004	0.207 ± 0.004	4.579 ± 0.008	63.59 ± 0.03	52.59 ± 0.03	67.64 ± 0.03	27.32 ± 0.05	23.89 ± 0.06
140	4.36 10 ⁻¹¹	96.45	0.211 ± 0.004	0.211 ± 0.004	4.553 ± 0.008	63.74 ± 0.03	52.76 ± 0.04	67.56 ± 0.03	27.36 ± 0.05	23.90 ± 0.06
160	2.89 10 ⁻¹¹	97.65	0.207 ± 0.005	0.226 ± 0.005	4.597 ± 0.009	63.74 ± 0.03	52.64 ± 0.04	67.71 ± 0.03	27.31 ± 0.06	23.84 ± 0.06
180	1.28 10 ⁻¹¹	98.96	0.202 ± 0.005	0.214 ± 0.005	4.579 ± 0.009	63.74 ± 0.04	52.81 ± 0.04	67.82 ± 0.04	27.40 ± 0.06	23.90 ± 0.07
200	4.42 10 ⁻¹²	99.64	0.215 ± 0.005	0.208 ± 0.005	4.582 ± 0.009	63.74 ± 0.04	52.70 ± 0.04	67.74 ± 0.04	27.30 ± 0.06	23.93 ± 0.07

Table 2: Evolution of the amount of ^{130}Xe adsorbed and the xenon isotopic ratio as a function of the number of adsorption cycle performed on montmorillonite. Same table caption as Table 1.

Figure captions

Fig.1: Xenon isotopic composition of phase Q [Busemann *et al.*, 2000] and the Earth's atmosphere [Ozima and Podosek, 2002] normalized to Solar Xe [Wieler and Baur, 1994]. Xe-Q is enriched in favor of the heavy isotopes by a factor of +1.3% per u relative to Solar while atmospheric xenon is even more fractionated relative to Solar (i.e., 3.5% per u).

Fig. 2: Schematic diagram of the Rayleigh-type distillation apparatus used in this work. It consists of an electropolished stainless steel volume of 10 liters (Vol. A) connected to a quartz finger of 3 cm³ (Vol. B). The experiment consists in performing adsorption cycles by allowing xenon equilibration between volume A and the sample located within the quartz finger. The isotopic composition of volume A was measured sequentially after several adsorption steps. If any isotopic fractionation is induced by adsorption, it should be visible in the evolution of the isotopic composition of xenon in the volume A as a function of the number of cycles.

Fig. 3: (a) Evolution of the amount of ¹³⁰Xe adsorbed on kerogen versus the ¹³⁶Xe/¹³⁰Xe isotopic ratio in volume A as a function of the number of cycles (isotopic ratio × 10). (b) Evolution of the ¹³⁶Xe/¹³⁰Xe isotopic ratio as a function of the remaining gas fraction (*f*) in the system during the experiment of xenon adsorption on kerogen. The slope permits the determination of the fractionation factor α (see text).

Fig. 4: (a) Evolution of the amount of ¹³⁰Xe adsorbed on montmorillonite versus the ¹³⁶Xe/¹³⁰Xe isotopic ratio in volume A as a function of the number of cycles (isotopic ratio × 10). (b) Evolution of the ¹³⁶Xe/¹³⁰Xe isotopic ratio as a function of the remaining gas fraction (*f*) in the system during the experiment of xenon adsorption on montmorillonite. The slope permits the determination of the fractionation factor α (see text).

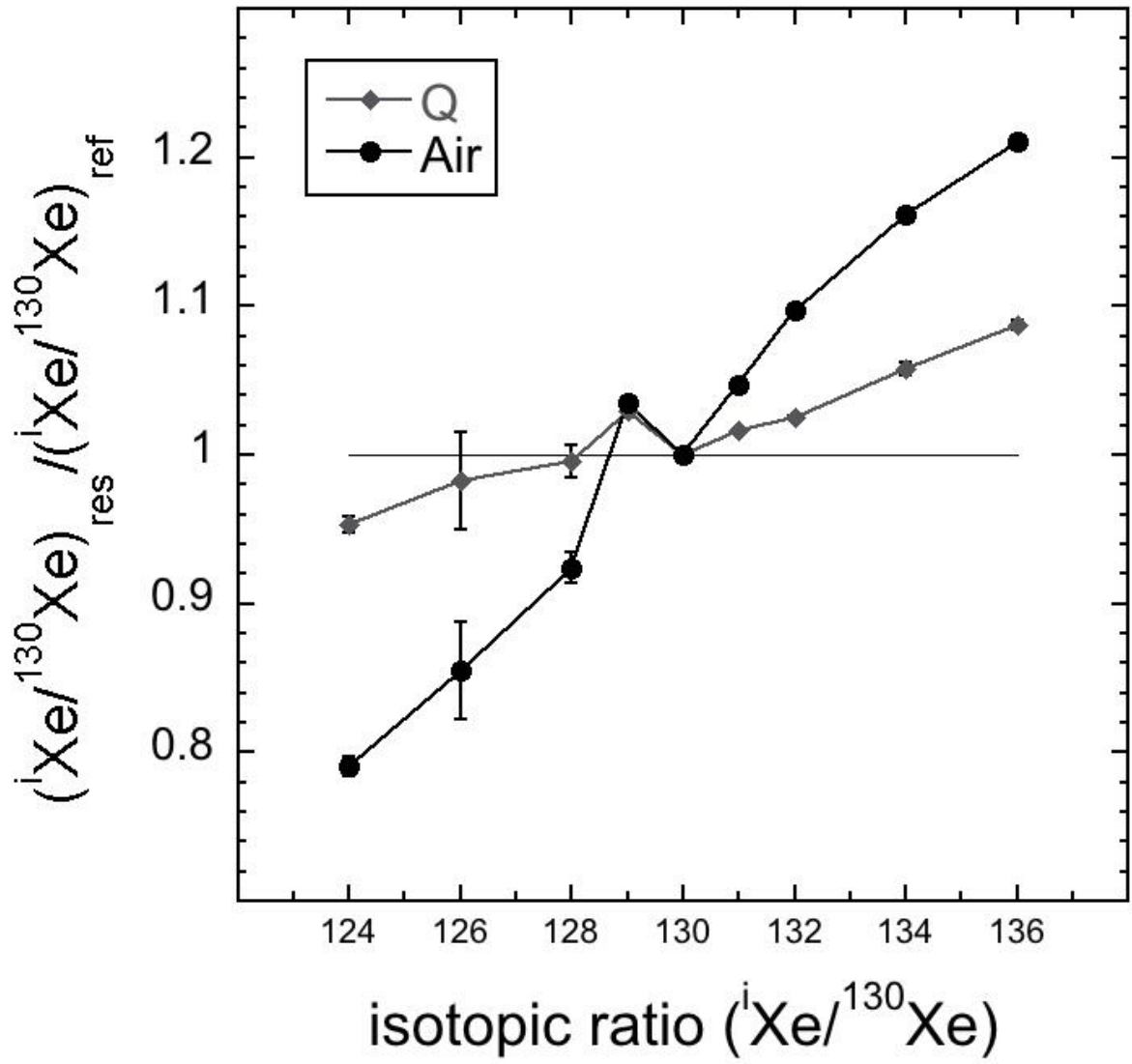


Fig. 1

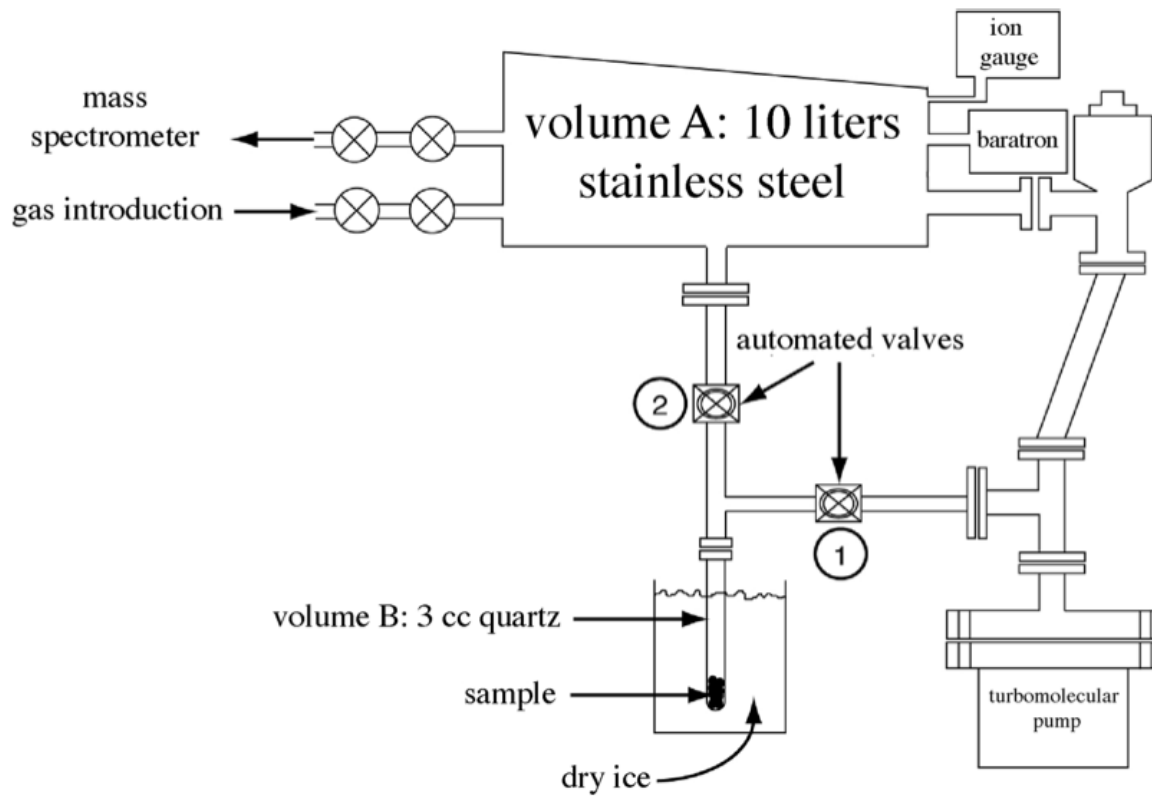


Fig. 2

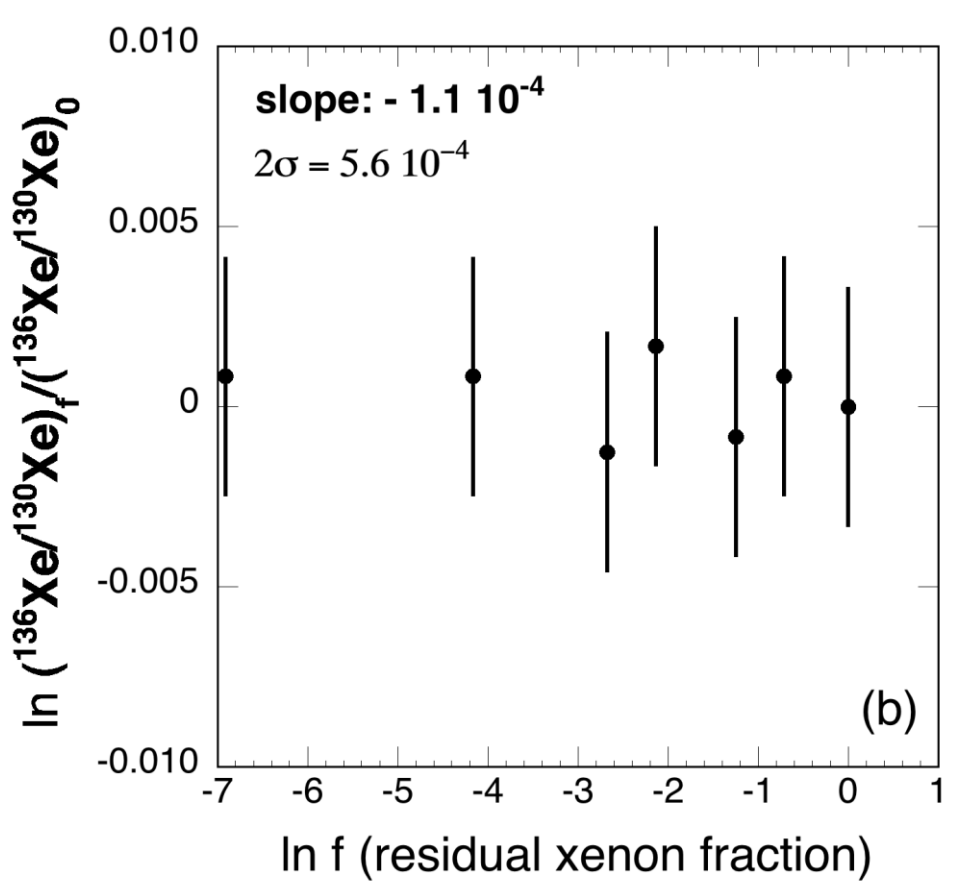
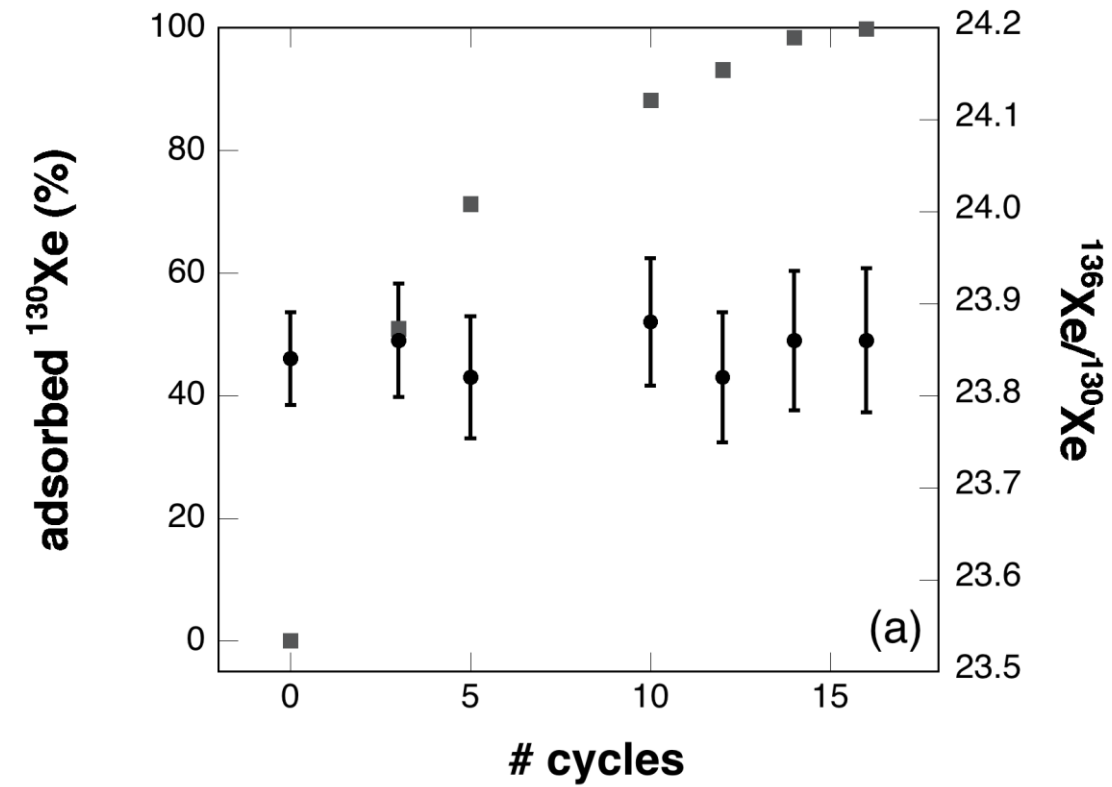


Fig. 3

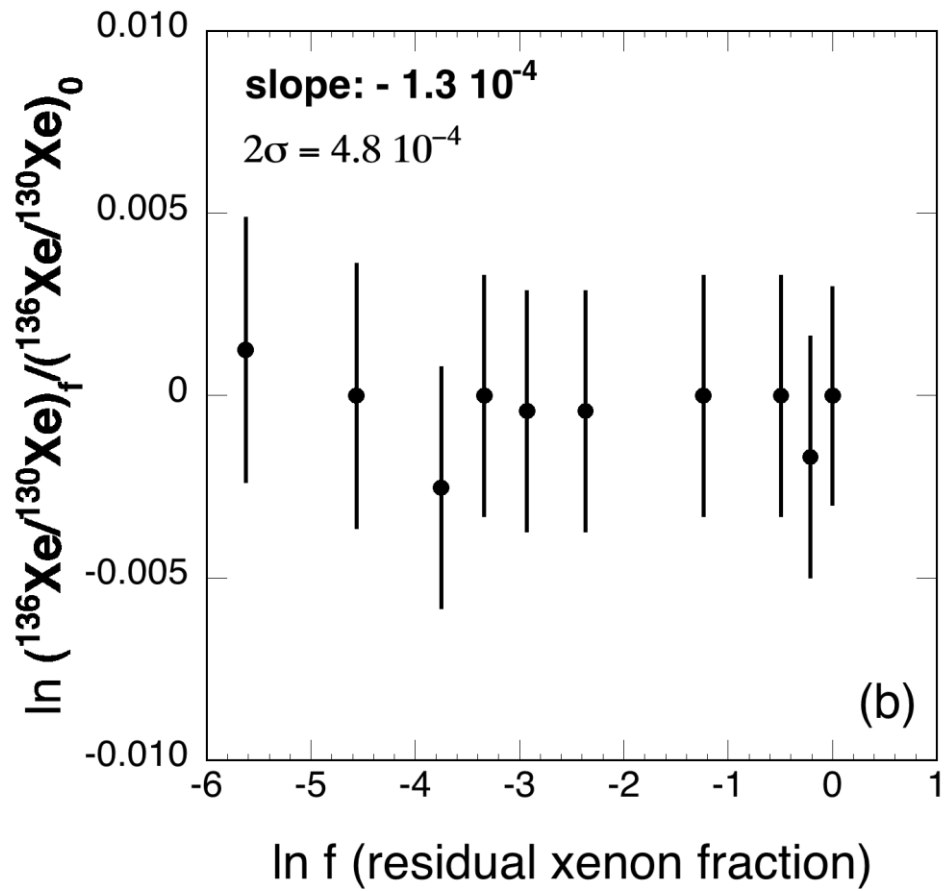
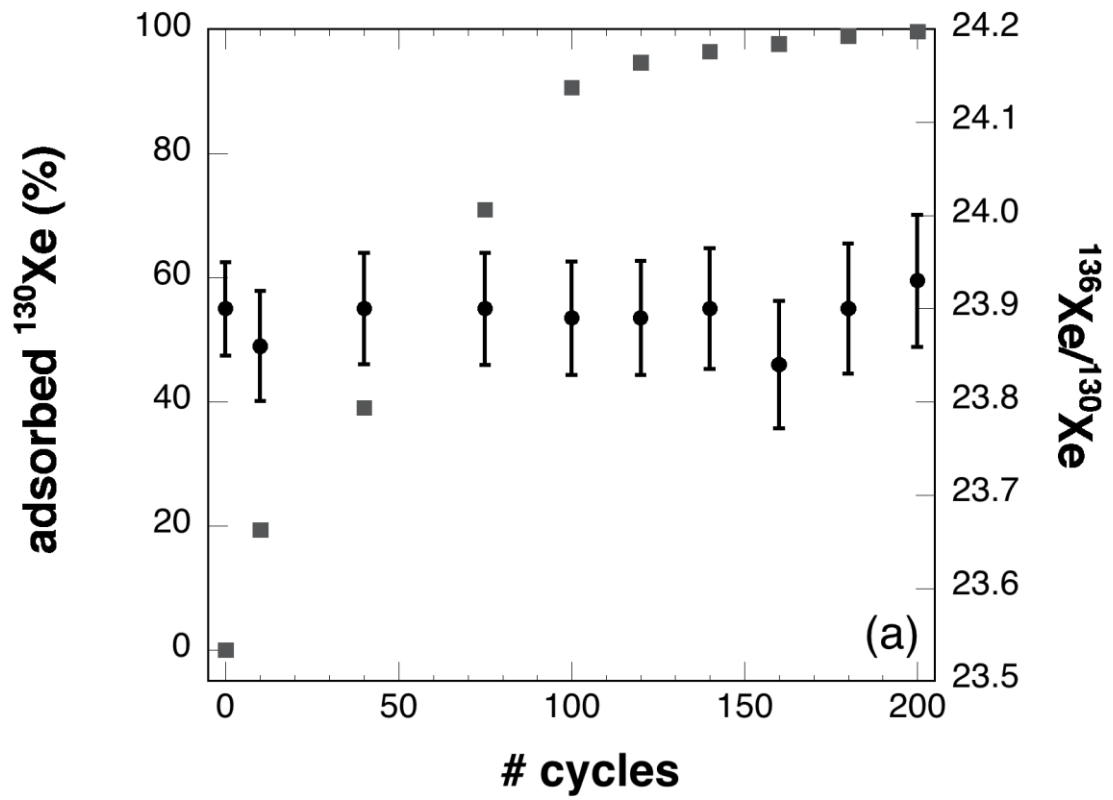


Fig. 4

