

diameter of the MSF (27 Å) is much smaller than the lamellar length of ordinary PE crystals (~100 Å) (16), the PE chains are likely prevented from folding within the mesopores. To lend support to the extrusion polymerization mechanism, we evaporated a reaction mixture of Cp<sub>2</sub>Ti-MSF with MAO in toluene to dryness and exposed the residue to ethylene. The SEM images of the polymerization mixture (Fig. 6) indicated the formation of PE only on the circular cross sections of the silica fibers where the pore exits are opened.

When a nonfibrous mesoporous silica such as MCM-41 (6) was used in place of MSF as the solid support of titanocene, a crystalline PE containing a fibrous fraction was obtained (17). However, it showed ordinary XRD and DSC patterns (a single endotherm at 142°C;  $\Delta H = 222 \text{ J g}^{-1}$ ). On the other hand, use of an amorphous silica-supported titanocene-MAO system (17) for the polymerization resulted in neither fibrous texture nor extraordinary XRD and DSC profiles of the product (a single endotherm at 140°C;  $\Delta H = 167 \text{ J g}^{-1}$ ).

It has been reported that a fibrous PE with a diameter of 0.2 to 0.5  $\mu\text{m}$ , containing a fraction of extended-chain crystals, can be obtained by crystallization of PE from a vigorously stirred xylene solution (18). In contrast, our approach is based on an essentially different conception, namely template-assisted extrusion polymerization. Regularly arranged nanoscopic pores on a honeycomb-like solid surface enable in situ formation of much thinner (30 to 50 nm) PE fibers of extended-chain crystals. The present method, using MSF as a nano-extruder, may be widely applicable to the production of fabricated crystalline polymers. Moreover, the use of mesoporous materials of different architectures as

templates for polymerization is expected to provide common polymers with some new bulk properties.

#### References and Notes

- O. W. Webster, *Science* **251**, 887 (1991); Y. Okamoto and T. Nakano, *Chem. Rev.* **94**, 349 (1994); S. Kobayashi, Ed., *Catalysis in Precision Polymerization* (Wiley, New York, 1997).
- P. Smith and P. J. Lemstra, *J. Mater. Sci.* **15**, 505 (1980); J. C. M. Torfs and A. J. Pennings, *J. Appl. Polym. Sci.* **26**, 303 (1981); J. H. Lee, R. M. Brown Jr., S. Kuga, S. Shoda, S. Kobayashi, *Proc. Natl. Acad. Sci. U.S.A.* **91**, 7425 (1994).
- E. Evans, H. Bowman, A. Leung, D. Needham, D. Tirrel, *Science* **273**, 933 (1996); S. B. Roscoe, J. M. Fréchet, J. F. Walzer, A. J. Dias, *ibid.* **280**, 271 (1998); K. Akagi et al., *ibid.* **282**, 1683 (1998).
- D. A. Tomalia, *Adv. Mater.* **6**, 529 (1994); D.-L. Jiang and T. Aida, *Nature* **388**, 454 (1997); M. Fisher and F. Vögtle, *Angew. Chem. Int. Ed.* **38**, 884 (1999).
- T. P. Nevell, Ed., *Cellulose Chemistry and Its Applications* (Halsted, New York, 1985), chap. 2.
- J. S. Beck et al., *J. Am. Chem. Soc.* **114**, 10834 (1992); A. Corma, *Chem. Rev.* **97**, 2373 (1997).
- G. D. Stucky et al., *Adv. Mater.* **9**, 974 (1997).
- For examples of polymerization with mesoporous materials, see C.-G. Wu and T. Bein, *Science* **266**, 1013 (1994); S. M. Ng, S. Ogino, T. Aida, K. A. Koyano, T. Tatsumi, *Macromol. Rapid Commun.* **18**, 991 (1997); K. Kageyama, S. Ogino, T. Aida, T. Tatsumi, *Macromolecules* **31**, 4069 (1998).
- For examples of olefin polymerization with mesoporous materials, see Y.-S. Ko, T.-K. Han, J.-W. Park, S.-I. Woo, *Macromol. Rapid Commun.* **17**, 749 (1996); J. Tudor and D. O'Hare, *Chem. Commun.* **1997**, 603 (1997); L. K. M. van Looveren et al., *Angew. Chem. Int. Ed.* **37**, 517 (1998).
- MSF (0.3 g) was treated with a dichloromethane solution of titanocene dichloride (Cp<sub>2</sub>TiCl<sub>2</sub>) at 20°C in the presence of triethylamine as a proton scavenger. After stirring for 18 hours, an insoluble material was isolated by filtration and washed repeatedly with dichloromethane. The amount of Cp<sub>2</sub>Ti mounted on the MSF surface was  $6 \times 10^{-5} \text{ mol Ti g}^{-1}$  (Si/Ti = 280), as determined by inductively coupled plasma mass spectrometry (ICP-MS). See T. Maschmeyer, F. Rey, G. Sankar, J. M. Thomas, *Nature* **378**, 159 (1995).
- Measured using a flotation method with methanol/dioxane at 30°C.
- G. B. Galland, R. F. de Souza, R. S. Mauler, F. F. Nunes, *Macromolecules* **32**, 1620 (1999).
- S. Krimm and A. V. Tobolsky, *J. Polym. Sci.* **7**, 57 (1951).
- B. G. Rånby, F. F. Morehead, N. M. Walter, *ibid.* **44**, 349 (1960); L. Mandelkern, A. S. Posner, A. F. Diorio, D. E. Roberts, *J. Appl. Phys.* **32**, 509 (1961).
- A. J. Pennings and A. Zwijnenburg, *J. Polym. Sci. Polym. Phys. Ed.* **17**, 1011 (1979).
- W. D. Niegisch and P. R. Swan, *J. Appl. Phys.* **31**, 1906 (1960).
- Prepared by a method similar to that for the preparation of Cp<sub>2</sub>Ti-MSF. The amounts of Cp<sub>2</sub>Ti mounted on MCM-41 and amorphous silica were both  $5 \times 10^{-5} \text{ mol Ti g}^{-1}$ . Polymerization conditions: supported catalyst, 50 mg ( $2.5 \times 10^6 \text{ mol}$ ) Ti; cocatalyst, MAO (Al/Ti = 500); ethylene pressure, 10 atm; 20°C, 13.5 hours. PE yields: 1.8 g Cp<sub>2</sub>Ti-MCM-41-MAO, 1.0 g Cp<sub>2</sub>Ti-amorphous silica-MAO.
- A. J. Pennings, C. J. H. Schouteten, A. M. Kiel, *J. Polym. Sci. C* **38**, 167 (1972).
- Partly supported by a grant-in-aid from the Ministry of Education, Science, Sports, and Culture, Japan, and by a grant from the New Energy and Industrial Technology Development Organization under the Ministry of International Trade and Industry, Japan. We thank S. Tanji, K. Ebara, and O. Mitsui for obtaining the viscometric molecular weight of PE and the SEM pictures of Cp<sub>2</sub>Ti-MSF, T. Sugawara for obtaining FE-SEM pictures of polyethylene fibers, and A. Takahara for discussion. K.K. thanks the Japan Society for the Promotion of Science for a Young Scientist Fellowship.

11 June 1999; accepted 30 July 1999

## Primordial Noble Gases from Earth's Mantle: Identification of a Primitive Volatile Component

M. W. Caffee,<sup>1</sup> G. B. Hudson,<sup>1</sup> C. Velsko,<sup>1</sup> G. R. Huss,<sup>2</sup>  
E. C. Alexander Jr.,<sup>3</sup> A. R. Chivas<sup>4</sup>

Carbon dioxide well gases in Colorado, New Mexico, and South Australia show excesses of <sup>124–128</sup>Xe correlated with <sup>129</sup>I-derived <sup>129</sup>Xe and <sup>20</sup>Ne/<sup>22</sup>Ne ratios that are higher than the atmospheric <sup>20</sup>Ne/<sup>22</sup>Ne ratio. The xenon isotopic data indicate the presence of a solarlike component deep within Earth. The presence of this component in crustal and upper mantle reservoirs may be explained by a steady-state transport of noble gases from the lower mantle, which still retains much of its juvenile volatile inventory. These measurements also indicate that the mantle source of these noble gases in the carbon dioxide well gases cannot be the source of Earth's present atmosphere. The variations observed in <sup>129</sup>Xe/<sup>130</sup>Xe between solar wind xenon, Earth's atmosphere, and mantle samples may be generated by variations of iodine/xenon in terrestrial reservoirs, as opposed to rapid early degassing.

The detailed nature of Earth's precursor material, the structure and volatile inventory of Earth's mantle, and the relation of the atmosphere to more primitive reservoirs within Earth are elusive problems that continue to be addressed with elemental and isotopic abundance studies (1, 2). The scarcity of the noble

gases in naturally occurring materials, their chemical inertness, and the presence of distinct identifiable isotopic and elemental compositions make noble gases ideal tracers for many of these investigations (3–5). Recognizing the difference between the noble gas signature in Earth's present atmosphere and

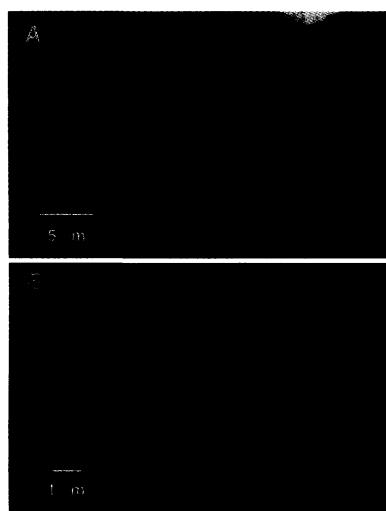


Fig. 6. (A and B) SEM images of a piece of Cp<sub>2</sub>Ti-MSF, treated with a toluene solution of MAO (Al/Ti = 1000), dried under reduced pressure, and then exposed to ethylene (10 atm), at two different magnifications.

that in the sun's, Brown (6) proposed that the present atmosphere is secondary and was derived from the degassing of Earth's mantle. The rate and extent of this outgassing are uncertain, but measurement of the noble gas isotopes,  $^{40}\text{Ar}$  from  $^{40}\text{K}$  [half-life  $T_{1/2} = 1250$  million years (My)] [for example, (7, 8)],  $^{129}\text{Xe}$  from  $^{129}\text{I}$  ( $T_{1/2} = 16$  My) [for example, (9, 10)], and  $^{131-136}\text{Xe}$  from  $^{244}\text{Pu}$

( $T_{1/2} = 82$  My) [for example, (11)] offers a means to investigate these issues. Excesses of  $^{129}\text{Xe}$  relative to atmospheric Xe have been detected in  $\text{CO}_2$  well gases from deposits in Harding County, New Mexico (12-16), and in other mantle-derived samples (17-25).

The short half-life of  $^{129}\text{I}$  potentially places temporal constraints on the timing of processes responsible for the provenance of the Xe isotopic signatures in terrestrial noble gas reservoirs. Specifically, if the difference between atmospheric Xe and Xe from mantle-derived samples in  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios is attributed to degassing, it must have occurred early in Earth's history, before much of the  $^{129}\text{I}$  decayed. Alternatively, these isotopic

differences could be attributed to intrinsic heterogeneities in the I/Xe ratio in terrestrial reservoirs.

For models assuming a uniform starting I/Xe ratio, the existence of  $^{129}\text{Xe}$  excesses predicts the presence of  $^{244}\text{Pu}$ -derived Xe daughters. However, in a reanalysis of the Harding County  $\text{CO}_2$  well gas, Phinney *et al.* (15) observed that the fission Xe excess relative to atmospheric Xe could be ascribed to U rather than Pu decay. This apparent lack of Pu-derived Xe is difficult to reconcile with the presence of  $^{129}\text{I}$ -derived Xe in presumed mantle reservoirs and the abundances of Pu, U, and I in other solar system materials (26). The progenitor of the fission Xe in other

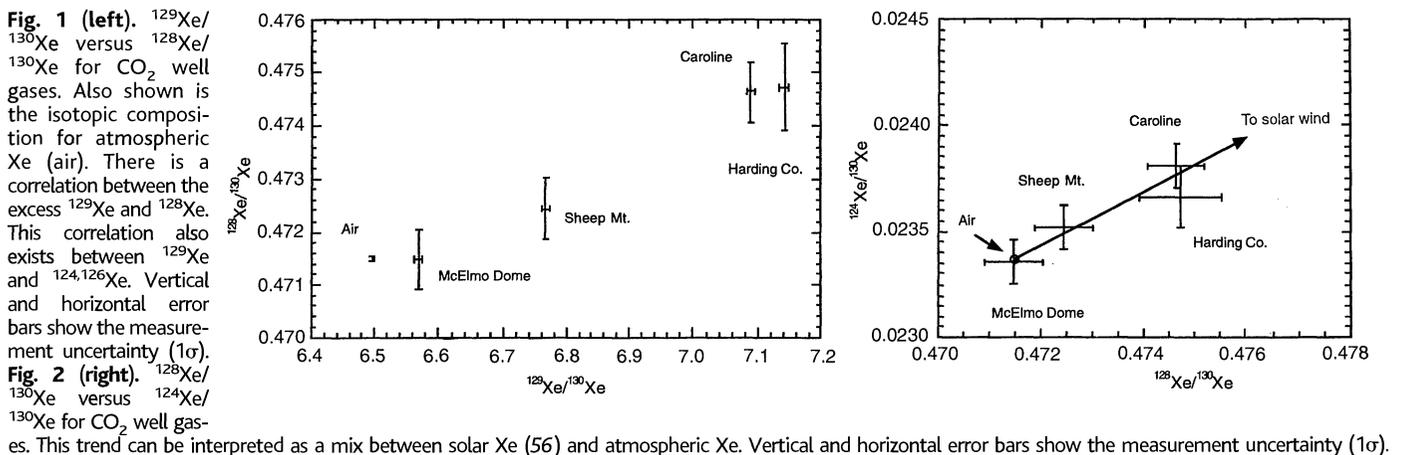
<sup>1</sup>Lawrence Livermore National Laboratory, Post Office Box 808, Livermore, CA 94550, USA. <sup>2</sup>Department of Geology, Arizona State University, Tempe, AZ 85287, USA. <sup>3</sup>Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, USA. <sup>4</sup>School of Geosciences, University of Wollongong, Wollongong, NSW 2522, Australia.

**Table 1.** Isotopic composition of Xe from  $\text{CO}_2$  well gases. Samples of  $\text{CO}_2$  were collected in double-ended stainless steel bottles (500 ml). The bottles were thoroughly purged and filled to the supply-line pressure of  $\sim 4.1 \times 10^6$  Pa, providing  $2 \times 10^4 \text{ cm}^3$  of gas at standard temperature and pressure (STP). Typical sample size for analysis was  $< 15 \text{ cm}^3$  STP, a small fraction of the total available gas. For Xe analysis, a small amount of  $\text{CO}_2$  was expanded into a known volume for pressure measurement. Carbon dioxide was removed by a Ti sublimation pump. Xenon was collected on activated charcoal at  $-80^\circ\text{C}$ , and nonsorbing gases were evacuated (except when Ne was analyzed). The Xe

was released from the charcoal and further purified by successive exposure to metal alloy getters. Sensitivity and mass bias were determined from multiple runs of air ( $0.005 \text{ cm}^3$  STP). The final measurements were performed on pulse-counting VG5400 noble gas mass spectrometers. Matched air and  $\text{CO}_2$  samples were repeatedly analyzed, and the average deviations of the  $\text{CO}_2$ -Xe isotopic ratios relative to air-Xe were determined. The uncertainties reflect measurement uncertainty but do not include uncertainties in the air-Xe composition. For the analysis of Ne, the air standard consisted of 50% air and 50% He to better match the He/Ne ratio of the  $\text{CO}_2$  samples.

Sample	$^{124}\text{Xe}/^{132}\text{Xe}$	$^{126}\text{Xe}/^{132}\text{Xe}$	$^{128}\text{Xe}/^{132}\text{Xe}$	$^{129}\text{Xe}/^{132}\text{Xe}$	$^{130}\text{Xe}/^{132}\text{Xe}$	$^{131}\text{Xe}/^{132}\text{Xe}$	$^{134}\text{Xe}/^{132}\text{Xe}$	$^{136}\text{Xe}/^{132}\text{Xe}$
Caroline, Australia	0.003557 $\pm 0.000015$	0.003307 $\pm 0.000015$	0.07090 $\pm 0.00007$	1.05920 $\pm 0.00053$	0.14940 $\pm 0.00010$	0.77945 $\pm 0.00039$	0.40564 $\pm 0.00020$	0.35278 $\pm 0.00018$
Sheep Mountain, CO	0.003490 $\pm 0.000015$	0.003247 $\pm 0.000014$	0.07010 $\pm 0.00007$	1.00410 $\pm 0.00050$	0.14838 $\pm 0.00010$	0.77601 $\pm 0.00039$	0.41140 $\pm 0.00021$	0.36073 $\pm 0.00018$
McElmo Dome, CO*	0.003476 $\pm 0.000015$	0.003231 $\pm 0.000014$	0.07017 $\pm 0.00007$	0.97745 $\pm 0.00049$	0.14883 $\pm 0.00010$	0.77892 $\pm 0.00039$	0.40514 $\pm 0.00020$	0.35276 $\pm 0.00018$
Harding County, NM	0.003511 $\pm 0.000021$	0.003303 $\pm 0.000020$	0.07044 $\pm 0.00010$	1.05980 $\pm 0.00052$	0.14838 $\pm 0.00014$	0.77549 $\pm 0.00041$	0.41359 $\pm 0.00027$	0.36279 $\pm 0.00025$
MORB†	0.003516 $\pm 0.000035$	0.003221 $\pm 0.000036$	0.06993 $\pm 0.00023$	1.07311 $\pm 0.00198$	0.14765 $\pm 0.00037$	0.77700 $\pm 0.00156$	0.40927 $\pm 0.00077$	0.35731 $\pm 0.00063$
Atmosphere (54, 55)	0.003537 $\pm 0.000011$	0.003300 $\pm 0.000017$	0.07136 $\pm 0.00009$	0.9832 $\pm 0.0012$	0.15136 $\pm 0.00012$	0.7890 $\pm 0.0011$	0.3879 $\pm 0.0006$	0.3294 $\pm 0.0004$
Solar (56)	0.00488 $\pm 0.00004$	0.00423 $\pm 0.00014$	0.08475 $\pm 0.00101$	1.0420 $\pm 0.0090$	0.16611 $\pm 0.00091$	0.8272 $\pm 0.0053$	0.36658 $\pm 0.00250$	0.29852 $\pm 0.00187$
$^{238}\text{U}$ (57)	$\sim 0$	0.15493 $\pm 0.00594$	1.45775 $\pm 0.03324$	1.76056 $\pm 0.03100$				
$^{244}\text{Pu}$ (58)	$\sim 0$	0.27772 $\pm 0.01728$	1.04132 $\pm 0.01597$	1.11982 $\pm 0.01630$				

\*This analysis was performed on a 1.5-liter gas sample using a VG5400 mass spectrometer with a Faraday cup for ion current measurement. †The MORB value was derived from a subset of the data presented by Kunz *et al.* (25). We used the weighted mean of 11 of 38 reported Xe compositions that are relatively radiogenic ( $^{136}\text{Xe}/^{130}\text{Xe} > 2.35$ ) and also contain enough Xe so that the precision of analysis was relatively high ( $^{130}\text{Xe} > 8 \times 10^{-14} \text{ cm}^3$  STP/g).



mantle-derived samples is more difficult to resolve; however, Kunz *et al.* (25) have identified Pu-derived Xe in selected mid-ocean ridge basalts (MORBs) and conclude that <sup>244</sup>Pu fission contributes 30 ± 10% of the total fission <sup>136</sup>Xe. Although this finding is important, it nevertheless underscores the apparent lack of <sup>244</sup>Pu-derived Xe in terrestrial reservoirs. A reservoir having a chondritic <sup>244</sup>Pu/<sup>238</sup>U signature produces ~30 times more <sup>244</sup>Pu-fission Xe than <sup>238</sup>U-fission Xe during 4.55 × 10<sup>9</sup> years.

To verify that the excess <sup>129</sup>Xe observed in the Harding County CO<sub>2</sub> well gas is more than a local phenomenon and to determine the Xe composition of the gas, we performed high-precision isotopic measurements on CO<sub>2</sub> from Harding County, Sheep Mountain, and McElmo Dome in Colorado and from Caroline in Australia (27). The samples selected for this work represent a variety of geophysical and geochemical conditions, possibly reflecting different origins for the CO<sub>2</sub> well gas. The Caroline, Harding County, and McElmo Dome samples are all principally associated with volcanic activity. The CO<sub>2</sub> from Sheep Mountain is derived from the decomposition of limestones, due to the intrusion of magma.

All of the CO<sub>2</sub> samples have excesses of <sup>129</sup>Xe (Table 1 and Fig. 1) relative to atmo-

spheric Xe, and all contained fission Xe. In addition to <sup>129</sup>Xe from <sup>129</sup>I and fission Xe, we observed variations in the light Xe isotopes (<sup>124–128</sup>Xe) that are correlated with the variation in <sup>129</sup>Xe (Figs. 1 and 2). Although nuclear processes can produce <sup>129</sup>Xe and <sup>131–136</sup>Xe, the variations in <sup>124–128</sup>Xe cannot be explained by this means. Processes involving mass-dependent fractionation could be responsible for excesses of <sup>124–128</sup>Xe relative to air Xe; however, they would not be expected to produce correlated excesses of <sup>124–128</sup>Xe and <sup>129</sup>Xe, the latter being a nuclear decay component.

A simple explanation of these data is that they indicate the presence of a primitive reservoir containing Xe that possesses the isotopic composition of solar Xe, which is enriched in the light Xe isotopes relative to Earth's atmosphere. This explanation is consistent with the trends observed in the Ne isotopic compositions. All of the CO<sub>2</sub> gases, except those from McElmo Dome, have <sup>20</sup>Ne/<sup>22</sup>Ne ratios higher than the atmospheric <sup>20</sup>Ne/<sup>22</sup>Ne ratio, which suggests a solar composition (Table 2 and Fig. 3). High <sup>20</sup>Ne/<sup>22</sup>Ne ratios have been observed in other mantle-derived samples (22, 24, 28–31). The Ne isotopic compositions from Caroline and

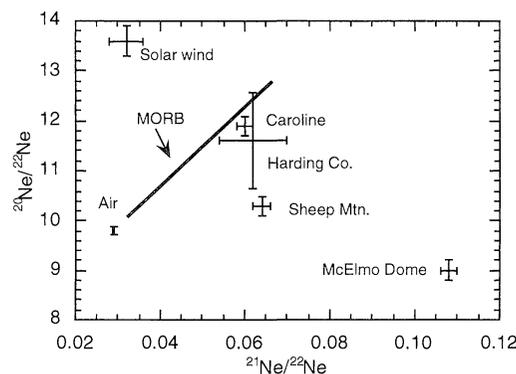
Harding County gas wells resemble MORB Ne isotopic compositions. The Harding County and the Caroline CO<sub>2</sub> well gases also have high <sup>3</sup>He/<sup>4</sup>He ratios, about three times the atmospheric ratio (15, 27). High <sup>3</sup>He/<sup>4</sup>He ratios are generally regarded as the manifestation of a primitive component that is still extant in Earth's mantle (32, 33).

Key issues in the evolution of Earth's noble gas inventory are the mechanism and timing of the processes responsible for the terrestrial noble gas signatures. Although the specific mechanism of the incorporation of solar noble gases in Earth is not known [compare (34) and (35)], the presence of unfractionated solarlike Xe and Ne in a mantle reservoir is direct evidence that solar noble gases were the dominant reservoir from which Earth acquired its noble gas signature. Earth may not be alone in this respect; measurements by Ott (36) indicate the presence of solarlike Xe in Chassigny, a basaltic meteorite ascribed to martian volcanic activity.

The Xe data from the CO<sub>2</sub> well gases address the timing of Xe fractionation. Atmospheric Xe appears to be related to a solarlike Xe composition (37) through mass fractionation. One group of scenarios proposes hydrodynamic escape-induced loss of volatiles

**Table 2.** Neon isotopic composition. The data for Harding County are from Phinney *et al.* (15).

Location	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>21</sup> Ne/ <sup>22</sup> Ne
Caroline, Australia	11.9 ± 0.2	0.060 ± 0.002
Sheep Mountain, CO	10.4 ± 0.2	0.064 ± 0.002
McElmo Dome, CO	9.0 ± 0.2	0.108 ± 0.002
Harding County, NM	11.6 ± 1.1	0.062 ± 0.008



**Fig. 3.** <sup>21</sup>Ne/<sup>22</sup>Ne versus <sup>20</sup>Ne/<sup>22</sup>Ne for CO<sub>2</sub> well gases. Also shown are the Ne isotopic compositions of atmospheric Ne and solar wind Ne. The Harding County data are from Phinney *et al.* (15). Isotopic compositions with <sup>20</sup>Ne/<sup>22</sup>Ne values higher than the atmospheric ratio (air) may indicate the presence of a "solar-type" reservoir of Ne in the mantle. Values displaced to the right of the solar-air mixing line generally reflect nucleogenic production of <sup>21</sup>Ne. The MORB trend line is from Sarda *et al.* (59). The <sup>21</sup>Ne/<sup>22</sup>Ne ratio in all samples indicates <sup>21</sup>Ne excesses due to <sup>18</sup>O(α,n)<sup>21</sup>Ne reactions (57).

**Table 3.** Decomposition of Xe from CO<sub>2</sub> well gases into underlying components. The component decomposition was calculated by minimizing the sum of the squared weighted deviations of the measured value with respect to a mixture of the assumed four underlying components. We used seven isotope ratios: <sup>124</sup>Xe, <sup>126</sup>Xe, <sup>128</sup>Xe, <sup>130</sup>Xe, <sup>131</sup>Xe, <sup>134</sup>Xe, and <sup>136</sup>Xe relative to <sup>132</sup>Xe. The deviations were inversely weighted by the calculated variance in the deviation. The uncertainties reported for the decomposition results were deter-

mined with a Monte Carlo simulation. The quoted uncertainties are strongly correlated. The error correlation coefficients, *c<sub>xy</sub>*, are similar for all of the decompositions and are as follows: air – SW = –0.95, U – Pu = –0.94, air – U = 0.80, SW – U = –0.77, and SW – Pu = 0.82, where *c<sub>xy</sub>* = σ<sub>xy</sub>/(σ<sub>x</sub><sup>2</sup>σ<sub>y</sub><sup>2</sup>)<sup>1/2</sup>. The subscripts refer to the different components: air, solar wind (SW), <sup>238</sup>U fission (U), and <sup>244</sup>Pu fission (Pu); σ<sub>x</sub><sup>2</sup> is the variance in x, σ<sub>y</sub><sup>2</sup> is the variance in y, and σ<sub>xy</sub> is the covariance of x and y.

Sample	Fraction from air ( <sup>132</sup> Xe)	Fraction from solar wind ( <sup>132</sup> Xe)	Fraction from <sup>238</sup> U ( <sup>132</sup> Xe)	Fraction from <sup>244</sup> Pu ( <sup>132</sup> Xe)	<sup>244</sup> Pu/( <sup>244</sup> Pu + <sup>238</sup> U) ( <sup>136</sup> Xe)
Caroline, Australia	0.9102 ± 0.0140	0.0700 ± 0.0127	0.0154 ± 0.0015	0.0044 ± 0.0029	0.15
Harding County, NM	0.9076 ± 0.0092	0.0665 ± 0.0084	0.0237 ± 0.0012	0.0022 ± 0.0023	0.06
Sheep Mountain, CO	0.9556 ± 0.0083	0.0225 ± 0.0074	0.0218 ± 0.0011	0.0001 ± 0.0021	0.00
McElmo Dome, CO	0.9835 ± 0.0040	0.0000 ± 0.0036	0.0158 ± 0.0007	0.0007 ± 0.0013	0.03
MORB (25)	0.9384 ± 0.0249	0.0353 ± 0.0224	0.0125 ± 0.0032	0.0138 ± 0.0061	0.41

from Earth. Mechanisms proposed for triggering hydrodynamic escape are intense ultraviolet radiation bombardment by the primordial sun (37–43) or giant impacts (44). Alternatively, Ozima and Igarashi (45) argued that Xe mass fractionation, driven by gravitational loss, occurred on the accreting planetesimals before their incorporation into Earth's mantle. The presence of a primitive reservoir of Xe in Earth's mantle favors scenarios in which the fractionation of atmospheric Xe occurred after Earth's accretion.

From the decomposition of the well gas Xe into four possible components (atmosphere, solar, Pu, and Xe), we determined that the fraction of fission Xe attributable to Pu is <20% in the CO<sub>2</sub> well gases (Table 3). For the data of Kunz *et al.* (25), we calculated that ~40% of the <sup>136</sup>Xe-fission Xe is due to <sup>244</sup>Pu. This value is higher than that given by Kunz *et al.* (25) and reflects the addition of solar Xe into the calculation. Although the uncertainties preclude a definitive conclusion, the MORB samples appear to have a greater fraction of fission Xe from <sup>244</sup>Pu relative to the CO<sub>2</sub> well gases. It is possible that the CO<sub>2</sub> well gas samples have contributions of fission Xe from crustal <sup>238</sup>U. The presence of a crustal U-derived component is supported by the presence of nucleogenic <sup>21</sup>Ne in all of the samples (Fig. 2).

The characteristic Pu/I ratio derived from the Xe in the CO<sub>2</sub> well gases indicates that the Xe in Earth's present atmosphere was not extracted from the same source as the Xe in the CO<sub>2</sub> well gases. Ozima *et al.* (46) and Marty (21) argued, on the basis of the derived Pu/I ratio from the Harding County CO<sub>2</sub>, that atmospheric Xe was not derived from the same reservoir as the Xe from the CO<sub>2</sub> well gas, and our data strengthen their conclusions. Given accretionary time scales of tens of millions of years for Earth's mantle (47), a considerable amount of time exists for the decay of <sup>129</sup>I to <sup>129</sup>Xe in objects before accretion. Longer accretionary time scales would allow for less incorporation of live <sup>129</sup>I into Earth. Accordingly, much of the <sup>129</sup>Xe we observed may have been produced before accretion.

A long-standing enigma in the study of terrestrial xenology is the apparent lack of Pu-derived Xe, given the presence of I-derived Xe. The association of the Xe in the CO<sub>2</sub> well gases with a primitive reservoir suggests a possible resolution. The identification of most radiogenic noble gas components is made possible because of the degassing of volatiles before the decay of the radionuclides. If a primitive mantle reservoir has retained most of its volatiles, as has been suggested for <sup>3</sup>He, or if most of the primordial noble gases were not outgassed until after decay of the radiogenic species, then the fission components are effectively masked by the primordial noble gases. Accordingly, it seems plausible that Earth inherited its full

complement of Pu, and much of the Xe derived from Pu decay still resides in the lower mantle, its Xe daughters only barely detectable.

Our preferred interpretation indicates that the source region of the CO<sub>2</sub> well gases is characterized by materials that are slightly richer in I relative to primordial Xe when compared to the reservoir from which the atmosphere was derived. It is important that there are meteorite classes characterized by high I/Xe ratios, specifically the enstatite chondrites (35, 48). Among meteorites, the enstatite chondrites have O isotopic abundances that most closely match those of Earth (49). It has been suggested that much of the Earth accreted from a reduced component, such as the enstatite chondrites (50, 51). Because the enstatite chondrites are rich in Xe and I, only a small amount of such material would be required to produce the differences in I/Xe that we propose.

The existence of primordial noble gas, including He, Ne, and Xe, in mantle emanations can be explained as a flux, albeit low, of juvenile volatiles out of a primitive volatile-rich reservoir. Our measurements are consistent with the recent models that propose the steady-state transport of noble gases, including Xe, from the lower mantle into the upper mantle (52, 53). For this lower mantle isotopic signature to remain intact, there must be limited mixing of the juvenile noble gases with atmospheric noble gases over the history of Earth. The variations observed in <sup>129</sup>Xe/<sup>130</sup>Xe between solar wind Xe, Earth's atmosphere, and mantle samples may be generated by variations of I/Xe in Earth's reservoirs rather than by rapid early degassing.

References and Notes

1. C. J. Allegre and E. Lewin, *Earth Planet. Sci. Lett.* **136**, 629 (1995).
2. D. L. Turcotte and L. H. Kellogg, *Rev. Geophys.* **24**, 311 (1986).
3. T. J. Bernatowicz and F. A. Podosek, Eds., *Nuclear Components in the Atmosphere* (Japan Scientific Society Press, Tokyo, 1978).
4. C. J. Allegre, T. Staudacher, P. Sarda, M. Kurz, *Nature* **303**, 765 (1983).
5. M. Ozima, *Rev. Geophys.* **32**, 405 (1994).
6. H. Brown, in *The Atmospheres of the Earth and Planets*, G. P. Kuiper, Ed. (Univ. of Chicago Press, Chicago, 1952), pp. 258–266.
7. H. A. Shillibeer and R. D. Russell, *Geochim. Cosmochim. Acta* **8**, 16 (1955).
8. K. K. Turekian, *ibid.* **17**, 37 (1959).
9. J. H. Reynolds and G. Turner, *J. Geophys. Res.* **69**, 3263 (1964).
10. C. M. Hohenberg, F. A. Podosek, J. H. Reynolds, *Science* **156**, 233 (1967).
11. R. J. Drozd *et al.*, *Astrophys. J.* **212**, 567 (1977).
12. W. A. Butler, P. M. Jeffrey, J. H. Reynolds, G. J. Wasserburg, *J. Geophys. Res.* **68**, 3283 (1963).
13. M. S. Boulos and O. K. Manuel, *Science* **174**, 1334 (1971).
14. E. W. Hennecke and O. K. Manuel, *Earth Planet. Sci. Lett.* **27**, 346 (1975).
15. D. Phinney, J. Tennyson, U. Frick, *J. Geophys. Res.* **83**, 2313 (1978).
16. S. P. Smith and J. H. Reynolds, *Earth Planet. Sci. Lett.* **54**, 236 (1981).
17. I. Kaneoka and N. Takaoka, *ibid.* **39**, 382 (1978).
18. T. Staudacher and C. J. Allegre, *ibid.* **60**, 605 (1982).

19. M. Ozima and S. Zashu, *ibid.* **62**, 24 (1983).
20. ———, *Geochim. Cosmochim. Acta* **52**, 19 (1988).
21. B. Marty, *Earth Planet. Sci. Lett.* **94**, 45 (1989).
22. H. Hiyagon, M. Ozima, B. Marty, S. Zashu, H. Sakai, *Geochim. Cosmochim. Acta* **56**, 1301 (1992).
23. R. Poreda and K. A. Farley, *Earth Planet. Sci. Lett.* **113**, 129 (1992).
24. M. Ozima and S. Zashu, *ibid.* **105**, 13 (1991).
25. J. Kunz, T. Staudacher, C. J. Allegre, *Science* **280**, 877 (1998).
26. I. Y. Azbel and I. N. Tolstikhin, *Meteoritics* **28**, 609 (1993).
27. A. R. Chivas, I. Barnes, W. C. Evans, J. W. Lupton, J. O. Stone, *Nature* **326**, 587 (1987).
28. M. Honda, I. McDougall, D. B. Patterson, A. Douglis, D. A. Clague, *ibid.* **349**, 149 (1991).
29. ———, *Geochim. Cosmochim. Acta* **57**, 859 (1993).
30. K. A. Farley and R. J. Poreda, *Earth Planet. Sci. Lett.* **114**, 325 (1993).
31. P. Sarda and T. Staudacher, *Nature* **352**, 388 (1991).
32. H. Craig, W. B. Clarke, M. A. Beg, *Earth Planet. Sci. Lett.* **26**, 125 (1975).
33. H. Craig and J. E. Lupton, *ibid.* **31**, 369 (1976).
34. D. S. Woolum, P. Cassen, D. Porcelli, G. J. Wasserburg, *Lunar Planet. Sci.* **XXX** (1999) [CD-ROM].
35. J. Crabb and E. Anders, *Geochim. Cosmochim. Acta* **45**, 2443 (1981).
36. U. Ott, *Meteoritics* **52**, 1937 (1988).
37. R. O. Pepin, *Icarus* **92**, 2 (1991).
38. D. M. Hunten, R. O. Pepin, J. C. G. Walker, *ibid.* **69**, 532 (1987).
39. D. M. Hunten, R. O. Pepin, T. C. Owen, in *Meteorites and the Early Solar System*, J. F. Kerridge and M. S. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1988), pp. 565–591.
40. R. O. Pepin, *Annu. Rev. Earth Planet. Sci.* **20**, 389 (1992).
41. K. J. Zahnle and J. C. G. Walker, *Rev. Geophys. Space Phys.* **20**, 280 (1982).
42. K. J. Zahnle, J. F. Kasting, J. B. Pollack, *Icarus* **84**, 502 (1990).
43. K. J. Zahnle, J. B. Pollack, J. F. Kasting, *Geochim. Cosmochim. Acta* **54**, 2577 (1990).
44. R. O. Pepin, *Icarus* **126**, 148 (1997).
45. M. Ozima and G. Igarashi, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. K. Atreya, J. B. Pollack, M. Matthews, Eds. (Univ. of Arizona Press, Tucson, AZ, 1989), pp. 306–327.
46. M. Ozima, F. A. Podosek, G. Igarashi, *Nature* **315**, 471 (1985).
47. S. J. Weidenschilling, *Icarus* **44**, 172 (1980).
48. B. M. Kennedy, B. Hudson, C. M. Hohenberg, F. A. Podosek, *Geochim. Cosmochim. Acta* **52**, 101 (1988).
49. R. N. Clayton and T. K. Mayeda, *J. Geophys. Res.* **89**, 245 (1984).
50. E. Anders and T. Owen, *Science* **198**, 453 (1977).
51. K. K. Turekian and S. P. Clark, *Earth Planet. Sci. Lett.* **6**, 346 (1969).
52. D. Porcelli and G. J. Wasserburg, *Geochim. Cosmochim. Acta* **59**, 1991 (1995).
53. ———, *ibid.*, p. 4921.
54. J. R. Basford, J. C. Dragon, R. O. Pepin, M. R. Cosico, V. R. Murthy, *Proc. Lunar Sci. Conf.* **4th**, 1915 (1973).
55. A. O. Nier, *Phys. Rev.* **77**, 789 (1950).
56. R. Wieler and H. Baur, *Meteoritics* **29**, 570 (1994).
57. G. W. Wetherill, *Phys. Rev.* **96**, 679 (1954).
58. G. B. Hudson, B. M. Kennedy, F. A. Podosek, C. M. Hohenberg, *Proc. Lunar Planet. Sci. Conf.* **19th**, 547 (1989).
59. P. Sarda, T. Staudacher, C. J. Allegre, *Earth Planet. Sci. Lett.* **91**, 73 (1988).
60. This work benefited from the efforts of many colleagues. B. Ruiz and W. Culham provided technical assistance throughout the experiment, and we profited from discussions with D. Phinney, M. Ozima, and R. Pepin. We acknowledge the anonymous reviewers, whose efforts have improved this manuscript. M.C. acknowledges support from the Lawrence Livermore National Laboratory (LLNL) Institute of Geophysics and Planetary Physics. This work was performed at LLNL, operating under the auspices of U.S. Department of Energy contract ENG-7405.

12 November 1998; accepted 17 August 1999

## LINKED CITATIONS

- Page 1 of 1 -



You have printed the following article:

### **Primordial Noble Gases from Earth's Mantle: Identification of a Primitive Volatile Component**

M. W. Caffee; G. B. Hudson; C. Velsko; G. R. Huss; E. C. Alexander Jr.; A. R. Chivas  
*Science*, New Series, Vol. 285, No. 5436. (Sep. 24, 1999), pp. 2115-2118.

Stable URL:

<http://links.jstor.org/sici?sici=0036-8075%2819990924%293%3A285%3A5436%3C2115%3APNGFEM%3E2.0.CO%3B2-5>

---

This article references the following linked citations:

## References and Notes

### <sup>10</sup> **Xenon-Iodine Dating: Sharp Isochronism in Chondrites**

C. M. Hohenberg; F. A. Podosek; John H. Reynolds  
*Science*, New Series, Vol. 156, No. 3772. (Apr. 14, 1967), pp. 233-236.

Stable URL:

<http://links.jstor.org/sici?sici=0036-8075%2819670414%293%3A156%3A3772%3C233%3AXDSIIC%3E2.0.CO%3B2-P>

### <sup>13</sup> **The Xenon Record of Extinct Radioactivities in the Earth**

Mervet S. Boulos; Oliver K. Manuel  
*Science*, New Series, Vol. 174, No. 4016. (Dec. 24, 1971), pp. 1334-1336.

Stable URL:

<http://links.jstor.org/sici?sici=0036-8075%2819711224%293%3A174%3A4016%3C1334%3ATXROER%3E2.0.CO%3B2-O>

### <sup>25</sup> **Plutonium-Fission Xenon Found in Earth's Mantle**

Joachim Kunz; Thomas Staudacher; Claude J. Allègre  
*Science*, New Series, Vol. 280, No. 5365. (May 8, 1998), pp. 877-880.

Stable URL:

<http://links.jstor.org/sici?sici=0036-8075%2819980508%293%3A280%3A5365%3C877%3APXFIEM%3E2.0.CO%3B2-2>

### <sup>50</sup> **Mars and Earth: Origin and Abundance of Volatiles**

Edward Anders; Tobias Owen  
*Science*, New Series, Vol. 198, No. 4316. (Nov. 4, 1977), pp. 453-465.

Stable URL:

<http://links.jstor.org/sici?sici=0036-8075%2819771104%293%3A198%3A4316%3C453%3AMAE0AA%3E2.0.CO%3B2-N>

**NOTE:** The reference numbering from the original has been maintained in this citation list.