Reports

Plutonium-Fission Xenon Found in Earth's Mantle

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Data from mid-ocean ridge basalt glasses indicate that the short-lived radionuclide plutonium-244 that was present during an early stage of the development of the solar system is responsible for roughly 30 percent of the fissiogenic xenon excesses in the interior of Earth today. The rest of the fissiogenic xenon can be ascribed to the spontaneous fission of still live uranium-238. This result, in combination with the refined determination of xenon-129 excesses from extinct iodine-129, implies that the accretion of Earth was finished roughly 50 million to 70 million years after solar system formation and that the atmosphere was formed by mantle degassing.

Xenon isotopes can be used as powerful tracers for early processes in the solar system, because the extinct radionuclides ¹²⁹I (half-life = 16×10^6 years) and ²⁴⁴Pu (half-life = 80×10^6 years) decay to produce measurable contributions of isotopically distinct Xe (1). Large anomalies have been found for meteorites, and the I-Xe system is an established tool that can be used to study age differences during the first few million years of solar system formation (2). The 129 Xe anomalies found in midocean ridge basalt (MORB) glasses established a time scale of $\sim 150 \times 10^6$ years for accretion, MORB differentiation, and degassing of Earth (3-5).

Because ¹²⁹I was able to contribute to the present-day mantle Xe budget, this possibility should also be the case for ²⁴⁴Pu in view of its longer half-life. However, the anomalies found in terrestrial mantle rocks are rather small, and therefore this question has remained unanswered. A complication is that spontaneous fission of ²³⁸U (halflife = 4.47×10^9 years), which is still present in the mantle, yields the same Xe isotopes as ²⁴⁴Pu with somewhat different ratios. We describe here results that allow these two different fission sources in the mantle to be distinguished and discuss implications for Earth's early history.

Analyses on CO_2 well gases from different sites show considerable excesses of fissiogenic Xe isotopes that are in some cases accompanied by 129 Xe excesses. However, plutoniogenic $^{131-136}$ Xe is missing (6). These results led to the hypothesis that ¹²⁹Xe excesses are the product not of live ¹²⁹I after the accretion of Earth but of chemical fractionation of ²³⁸U (spontaneous) and ²³⁵U (neutron-induced) disintegration products (7). This interpretation implies that the ¹²⁹Xe excesses observed in mantle-related samples are meaningless for understanding the degassing history of Earth. On the other hand, Xe isotopic compositions found in diamonds seem to indicate that all the fission excesses can be attributed to ²⁴⁴Pu (8). Mantle-derived diamonds (that are assumed to have a considerable crystallization age) and present-day MORBs apparently show the same correla-tion of 129 Xe with fissiogenic 136 Xe excesses: this correlation should have changed with time if ²³⁸U contributed considerably. This result critically depends on assumptions about crystallization and Xe closure

Fig. 1. The correlation of ¹²⁹Xe with ¹³⁶Xe excesses in MORB glasses (13) can be explained in terms of the mixing of two components, one being the atmosphere and the other being the uppermantle reservoir. Data labels are as follows: MORB (old) refers to earlier data from our laboratory (3, 10, 27). Well gas data (open triangles) from Harding County, New Mexico, are from various sources in (6): upward-pointing triangles from Boulos and Manuel; downward-pointing triangles from Hennecke and Manuel: leftward-pointing triangles from Phinney et al.; ages of the diamonds because the analytical precision was too low to permit the fission Xe components to be identified directly. However, it supports earlier estimates (4) that the initial ²⁴⁴Pu/²³⁸U ratio of Earth had the chondritic value, 0.0068 (9). For this ratio ¹³⁶Xe_{Pu} should be up to 27 times the amount of ¹³⁶Xe_U in a mantle reservoir that has retained most of its fission Xe since 4.5×10^9 years ago.

We have improved our analytical precision sufficiently to detect even small isotopic deviations from predictions for pure uranogenic or plutoniogenic contributions by the installation of a single ioncounting facility in one of our noble gas mass spectrometers. We reanalyzed previously measured MORB glasses, with a special focus on the so-called "popping rock" $2\Pi D43$ (10), which appears to bear the most pristine sampling of upper-mantle volatiles (11, 12). Our data (Table 1 and Fig. 1) show a close correlation between the excesses in ¹²⁹Xe and fission product 136 Xe (slope: 3.125 \pm 0.084) that is consistent with earlier results (slope: 3.01 \pm 0.10) (13). However, the well gas (slope: 2.37 ± 0.10) and the diamond data sets (slope: 2.34 \pm 0.11) deviate from the MORB trend. Most likely, they represent Xe samples from the upper mantle that are contaminated by some additional fissiogenic contribution from ²³⁸U. This conclusion, contrary to earlier ideas (14), is further supported by data on Ne isotopes.

The new MORB data set shows the contributions of 238 U and 244 Pu to the fissiogenic isotopes $^{131-136}$ Xe (Fig. 2, A through C). The isotopic ratios scatter between the evolution lines for pure plu-





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toniogenic and pure uranogenic fission Xe and show a linear correlation. They resemble mixing between the atmosphere and a MORB pole, which itself is a mixture of ²³⁸U and ²⁴⁴Pu fission products. We cannot deduce the absolute position of the MORB pole from Xe systematics, but Ne-Xe correlations (12) and Fig. 1 restrict $2.5 < (1^{36}Xe/1^{30}Xe)_{MORB} < 2.8$. However, the geometry of the plot implies that the relative contributions of ²³⁸U and ²⁴⁴Pu in excess to atmospheric composition are given by the slopes of the mixing lines (Fig. 2D). Our data set indicates that $32 \pm$ 10% (error, 2σ) of the fissiogenic ¹³⁶Xe excesses to air are produced by ²⁴⁴Pu.

The measurements of the fission-shielded, nonradiogenic isotopes ^{124,126,128}Xe have considerable uncertainties because amounts are small and we reserved most of the time of the measurements for the radiogenic and fissiogenic isotopes. The available data imply that the isotopic ratios 124,126,128 Xe/ 130 Xe in the mantle are atmospheric (Fig. 3), because they do not correlate with 136 Xe excesses. Atmospheric and mantle Xe reservoirs are likely to have a common origin, which is another constraint in favor of models that explain atmosphere formation by mantle degassing (3, 4).

With our data we can couple the geochronometers ¹²⁹I-¹²⁹Xe, ²⁴⁴Pu-¹³⁶Xe, and ²³⁸U-¹³⁶Xe. In this approach we use elemental and isotopic ratios rather than absolute amounts, which appear to be less reliable. A minimum ¹²⁹I/²⁴⁴Pu ratio of 5.1×10^{-4} is required to explain presentday ¹²⁹Xe and plutoniogenic ¹³⁶Xe excesses in the mantle (*15*). The difference between this value and a reasonable initial ¹²⁹I/²⁴⁴Pu ratio for bulk Earth of 7.5×10^{-3} is caused by radioactive decay of I and Pu with a time constant of $(\lambda_{129} - \lambda_{244})^{-1} = 28.9 \times 10^6$ years for the coupled system. This short time constant implies for a simple model approach of total degassing before the accretion time Δt and total accumulation after Δt that the mantle started to accumulate radiogenic and fissiogenic Xe not later than $\Delta t \sim 78 \times 10^6$ years after the solar system had formed 4.556 $\times 10^9$ years ago (5).

However, a similar calculation for Earth's ²⁴⁴Pu/²³⁸U ratio gives a time interval of $\Delta t \sim 400 \times 10^6$ years. This difference is a result of our oversimplified model. After accretion, Earth most likely suffered partial degassing over some time, producing the atmosphere (16), and partial accumulation of radiogenic and fissiogenic Xe isotopes in the mantle must have started even earlier than

Table 1. Xenon data on MORB. Column 2 gives temperature (For step heating) or cumulative number of hits (for step crushing experiments). ¹³⁰Xe amounts (column 3) are in cubic centimeters (at standard temperature and pressure) per gram. Numbers in parentheses designate 1 σ errors in the last

digits. Precision for absolute amounts is about 10%. Earlier analyses of the samples may be found in (*10, 17, 26*); see there for sample description details. Parts of the data for 2IID43 no. 6 have already been published in (*12*).

Sample weight	Step heat./ crush.	¹³⁰ Xe [10 ⁻¹⁴]	¹²⁴ Xe	¹²⁶ Xe	¹²⁸ Xe	¹²⁹ Xe	¹³¹ Xe	¹³² Xe	¹³⁴ Xe	¹³⁶ Xe
			Normalized to $^{130}Xe = 100$							
All 96-18	650°C	35.3	2.35 (5)	2.11 (5)	46.6 (3)	647 (3)	520 (3)	655 (4)	256 (1)	216 (1)
3.2683 g	1600°C	8.4	2.47 (5)	2.12 (7)	47.9 (7)	733 (4)	529 (3)	683 (3)	283 (2)	246 (2)
211D26	800°C	6.6	2.71 (15)	1.96 (14)	47.3 (7)	692 (12)	525 (8)	666 (10)	266 (5)	233 (4)
2.4326 g	1100°C	2.5	2.79 (20)	1.87 (21)	47.5 (1.0)	695 (10)	526 (9)	675 (11)	271 (5)	231 (5)
	1400°C	1.7	2.44 (19)	1.79 (26)	47.3 (9)	726 (12)	541 (10)	695 (10)	273 (5)	239 (5)
211D43, #1	600°C	0.5	3.08 (94)	1.24 (89)	48.3 (8.4)	699 (86)	557 (78)	700 (79)	266 (31)	235 (33)
1.9035 g	1600°C	1.8	2.22 (14)	1.74 (25)	47.8 (7)	695 (6)	526 (6)	682 (8)	271 (3)	238 (7)
211D43, #2	600°C	145.4	2.41 (2)	2.16 (2)	47.0 (3)	673 (3)	521 (2)	661 (3)	263 (1)	225 (1)
3.0164 g	1000°C	92.2	2.36 (4)	2.28 (4)	47.4 (3)	702 (3)	525 (3)	671 (2)	272 (1)	234 (2)
	1600°C	13.6	2.18 (11)	2.12 (8)	47.6 (7)	721 (6)	524 (5)	675 (6)	277 (3)	241 (2)
211D43, #3	4x	249.4	2.35 (2)	2.18 (3)	47.0 (2)	673 (2)	521 (2)	664 (2)	267 (1)	230 (1)
2.0874 g	8x	47.9	2.36 (8)	2.15 (7)	47.1 (5)	738 (3)	523 (4)	675 (6)	280 (1)	246 (1)
	16x	17.7	2.47 (10)	2.33 (12)	47.4 (6)	734 (3)	528 (2)	675 (6)	276 (1)	241 (1)
	100x	10.2	2.59 (14)	2.27 (18)	46.7 (9)	731 (7)	533 (6)	681 (8)	276 (4)	244 (1)
211D43, #4	660°C	204.5	2.38 (3)	2.20 (3)	47.2 (2)	693 (2)	523 (1)	671 (2)	269 (1)	232 (1)
3.0312 g	1000°C	39.1	2.40 (5)	2.18 (7)	47.5 (4)	723 (5)	523 (3)	677 (5)	277 (2)	241 (2)
	1600°C	8.4	2.24 (17)	2.14 (15)	46.9 (6)	709 (6)	526 (5)	674 (6)	273 (2)	238 (2)
211D43, #5	600°C	443.1	2.32 (8)	2.15 (5)	46.7 (3)	656 (3)	523 (2)	663 (3)	259 (1)	220 (1)
1.637 g	1000°C	83.9	2.45 (10)	2.22 (8)	47.5 (4)	695 (4)	520 (4)	667 (4)	268 (2)	229 (2)
	1200°C	4.0	2.21 (26)	1.84 (24)	46.4 (1.2)	723 (13)	523 (10)	673 (14)	271 (6)	240 (7)
	1400°C	24.5	2.50 (18)	2.44 (12)	47.8 (9)	673 (9)	523 (7)	670 (8)	264 (3)	221 (4)
211D43, #6	Зx	1040.1	2.29 (5)	2.11 (3)	46.6 (3)	655 (3)	519 (2)	663 (3)	259 (1)	222 (1)
1.4052 g	6x	47.0	2.30 (7)	2.23 (5)	47.1 (3)	713 (4)	523 (3)	672 (4)	273 (2)	238 (1)
	10x	50.2	2.32 (7)	2.19 (6)	47.3 (4)	712 (4)	526 (4)	676 (4)	274 (2)	239 (2)
	15x	12.3	2.26 (12)	2.18 (10)	48.0 (7)	706 (6)	525 (5)	671 (6)	269 (3)	235 (3)
	25x	11.3	2.38 (13)	2.14 (11)	48.3 (6)	750 (6)	530 (5)	686 (7)	285 (3)	251 (3)
	50x	17.9	2.42 (10)	2.40 (10)	47.4 (6)	691 (6)	519 (5)	664 (6)	267 (3)	231 (3)
	100x	4.5	2.34 (28)	1.96 (25)	46.2 (1.1)	724 (10)	515 (10)	664 (14)	272 (5)	238 (5)
	400x	1.1	2.60 (39)	2.02 (49)	48.3 (2.0)	711 (22)	528 (18)	676 (22)	273 (11)	240 (9)
211D47	800°C	5.3	2.38 (12)	2.25 (16)	49.4 (6)	688 (7)	534 (6)	673 (7)	270 (3)	230 (3)
2.463 g	1100°C	1.3	2.42 (25)	1.85 (29)	46.5 (1.4)	693 (13)	529 (9)	675 (10)	262 (7)	229 (6)
	1400°C	1.3	2.04 (28)	1.76 (37)	45.7 (1.3)	692 (11)	532 (9)	674 (14)	263 (6)	228 (6)
211D48	800°C	25.9	2.26 (9)	2.06 (7)	46.4 (5)	663 (3)	520 (3)	661 (3)	260 (2)	222 (2)
3.3547 g	1100°C	3.5	2.45 (19)	2.29 (16)	48.1 (8)	666 (8)	522 (7)	672 (8)	263 (4)	223 (4)
	1400°C	2.9	2.23 (22)	2.34 (40)	48.0 (1.3)	650 (9)	520 (8)	647 (10)	257 (4)	219 (4)
Searise I, DR04	800°C	0.1			44.1 (6.2)	765 (70)	569 (51)	764 (66)	255 (26)	273 (23)
3.3011 g	1100°C	2.6	2.33 (38)	1.78 (40)	48.7 (1.7)	671 (15)	533 (11)	676 (16)	264 (7)	228 (7)
	1400°C	1.4	2.08 (41)	1.88 (41)	47.5 (1.9)	702 (13)	537 (12)	686 (10)	268 (7)	233 (7)
Air contemporary			2.337 (7)	2.18 (1)	47.15 (5)	649.6 (6)	521.3 (6)	660.7 (6)	256.3 (4)	217.6 (2)
nonradiogenic			2.337 (7)	2.18 (1)	47.15 (5)	605.3 (2.9)	518.7 (7)	651.8 (1.3)	247.0 (1.3)	207.5 (1.3)

 $\Delta t \sim 78 \times 10^6$ years after solar system formation to compensate. We thus applied a two-stage exponential degassing model that was developed to describe the evolution of radiogenic 40 Ar and 129 Xe in the atmosphere and the mantle (17). The degassing time scales best suited to the Xe data (18) are similar to time scales given previously (Fig. 4). Our model calculations also indicate that the mantle started to retain (partially) radiogenic and fissiogenic Xe isotopes not later than $\Delta t \sim 50 \times 10^6$ to 70×10^6 years after solar system formation, which is just after the extraction of the moon from the young Earth



Fig. 2. The correlations of fissiogenic ¹³¹Xe (A), ¹³²Xe (B), and ¹³⁴Xe (C) excesses with fissiogenic 136Xe indicate a mixing between air and the upper-mantle reservoir. The latter reveals a mixture of plutoniogenic and uranogenic contributions. For reasons of clarity we show only MORB data with ${}^{132}Xe/{}^{130}Xe > 6.7$, ${}^{136}Xe/{}^{130}Xe > 2.3$, and relative error in 136 Xe/ 130 Xe < 1.5%. However, because the correlation lines were error-weighted best fits to the data (13), the results remain nearly the same when all data points are included. For each figure part we find quite similar ratios of $^{136}\!Xe_{Pu}\!/^{136}\!Xe_{Pu+U}$ in excess to air: (A) 42% (+29%, -18%); (B) 25% ± 8%; (C) 29% ± 18% determined by the slopes of the correlation lines as shown in (D). Thus, $32\% \pm 10\%$ (2 σ error) of fissiogenic ¹³⁶Xe excesses to air are plutoniogenic. Data labels are as in Fig. 1; line labels are as in (A). Panel (C) includes the evolution line for neutron-induced fission of ²³⁵U.

by a giant impact $\sim 4.51 \times 10^9$ years ago (19).

At that time, mantle degassing, the remains of which were from now on accumulating in the atmosphere, was massive but decreased rapidly. About 80% of the rare gas budget at $\Delta t \sim 50 \times 10^6$ to $70 \times$ 10⁶ years after solar system formation were lost from the mantle to the atmosphere within the following 20×10^6 to 30×10^6 years. Then the degassing became more constant at a low level, and the presentday degassing state of \sim 99% for the upper mantle (4, 20, our model calculation) was achieved during the following $\sim 4.4 \times 10^9$ years. A possible interpretation of this early change in degassing flux is the initiation of a two-layer convection of the mantle such that the upper mantle has begun to degas efficiently while the lower mantle



Fig. 3. Fission-shielded, nonradiogenic Xe isotopes (i) in MORB glasses in comparison to air, solar, planetary, and U-Xe (23). MORB points were calculated from linear fits in 124,126,128Xe/ ¹³⁰Xe versus ¹³⁶Xe/¹³⁰Xe diagrams extrapolated to 136 Xe/ 130 Xe = 2.5.



Fig. 4. The ¹³⁰Xe degassing flux in units of the initial mantle concentration at accumulation time = 0 (which is $\sim 50 \times 10^6$ to 70×10^6 years after solar system formation) per million years. At this point in time, Earth's atmosphere starts to accumulate the degassing flux from the mantle. The degassing flux steeply decreased with a time constant of $\sim 3 \times 10^6$ years during the first $\sim 20 \times$ 10^6 to 30×10^6 years. As in an earlier Ar + Xe approach (17), we find a bend in the curve indicating a change in the degassing dynamics with a new time constant of $\sim 0.2 \times 10^9$ years.

has remained more or less closed since then and may still contain ~ 15 to 20% of its primordial volatile budgets. Although it is not clear whether the present-day mantle is still divided into two independently convecting layers, this interpretation explains why lower-mantle rare gases, which are most pristinely sampled in glasses and xenoliths from Loihi seamount (Hawaii), appear to be slightly radiogenic and nucleogenic in comparison to primordial isotopic ratios and much less radiogenic and nucleogenic than the uppermantle reservoir (21).

REFERENCES AND NOTES

- 1. J. H. Reynolds, Phys. Rev. Lett. 4, 351 (1960); P. K. Kuroda, Nature 187, 36 (1960).
- J. H. Reynolds, J. Geophys Res. 65, 3843 (1960); 2. C. M. Hohenberg, M. N. Munk, J. H. Reynolds, ibid. 72, 3139 (1967)
- T. Staudacher and C. J. Allègre, *Earth Planet. Sci.* Lett. 60, 389 (1982); C. J. Allègre, T. Staudacher, P. Sarda, M. Kurz, Nature 303, 762 (1983).
- 4. C. J. Allègre, T. Staudacher, P. Sarda, Earth Planet. Sci. Lett. 81, 127 (1986/87)
- C. J. Allègre, G. Manhès, C. Göpel, Geochim. Cos-5. mochim. Acta 59, 1445 (1995).
- CO₂ well gas from Bueyeros Field, Harding County, NM [M. S. Boulos and O. K. Manuel, *Science* 174, 1334 (1971); E. W. Hennecke and O. K. Manuel, Earth Planet. Sci. Lett. 27, 346 (1975); D. Phinney, J. Tennyson, U. Frick, J. Geophys. Res. 83, 2313 (1978); S. P. Smith and J. H. Reynolds, Earth Planet. Sci. Lett. 54, 236 (1981)]. CO2 well gas from Navajo C-1, Wildcat Field, NM [W. B. Clarke and H. G. Thode, in *Isotopic and Cosmic Chemistry*, H. Craig, S. L. Miller, G. J. Wasserburg, Eds. (North-Holland, Amsterdam, 1964), pp. 471-487; W. J. Lin and O. K. Manuel, Geochem. J. 21, 197 (1987)]. All groups working on the same CO₂ well used
- X. Brouge Works of the same aliquot.
 A. Meshik, E. K. Jessberger, O. V. Pravdivtseva, Y. A. Shukolyukov, *J. Conf. Abstr.* 1, 400 (1996).
 M. Ozima and S. Zashu, *Earth Planet. Sci. Lett.* 105,
- 13 (1991)
- G. B. Hudson, B. M. Kennedy, F. A. Podosek, C. M. 9 Hohenberg, Proc. Lunar Planet. Sci. Conf. 19, 547 (1989).
- 10. T. Staudacher et al., Earth Planet. Sci. Lett. 96, 119 (1989).
- M. Javoy and F. Pineau, ibid. 107, 596 (1991); F. Pineau and M. Javoy, ibid. 123, 179 (1994).
- 12. M. Moreira, J. Kunz, C. Allègre, Science 279, 1178 (1998)
- 13. All line fittings were performed according to the procedure of D. York [Earth Planet. Sci. Lett. 5. 320 (1969)] without error correlations. We could use 125 data points for the fitting of our earlier MORB data set, which explains the comparably small uncertainty in the slope
- T. Staudacher [Nature 325, 605 (1987)] suggested that 14. Harding County well gas (6) originates directly from the upper mantle because of isotopic similarities with MORB glasses for Ne. Ar. Xe. and C. whereas Ozima and Zashu (8) suggested that diamonds reveal an even more pristine noble gas signature than MORB glasses. Since this time, new analyses have refined the rare gas systematics for Earth's mantle (12 and references therein) and Ne isotopic ratios have become the most sensitive tool with which to detect the presence of different components. The Ne in Harding County well gas is more nucleogenic than the MORB trend. The ²⁰Ne/²²Ne ratio in diamonds is rather constant, with a mean value of 11.8 \pm 0.4, which is, contrary to earlier hypotheses (8), well below the established minimum values for mantle reservoirs [12.5 for upper mantle, 13.2 for lower mantle: see (12) and references therein]
- 15. Our model can be summarized as follows: p_1 $(^{129}I/^{127}I)_0 = 1 \times 10^{-4}$ [C. M. Hohenberg, F. A.

Podosek, J. H. Reynolds, Science 156, 202 (1967)]; $p_2 = \binom{244}{P} \frac{1}{2^{238}} \frac{1}{0} = 6.8 \times 10^{-3} \text{ (9); } p_3 = \binom{127}{2} \frac{1}{2^{238}} \frac{1}{9} \frac{1}{100} = 100 \text{ [E. Anders and N. }$ Grevesse, Geochim. Cosmochim. Acta 53, 197 (1989); $p_{3,0} = (1^{27})^{238}$ U)_{solar,0} = $p_3/2.03 = 49$ (corrected for ²³⁸U decay); $p_4 = (I/U)_{be} = (11 \text{ ppb/20 ppb}) \times 238/127 = 1.0$ (ppb, parts per billion) [see (5); C. J. Allègre, J.-P. Poirier, E. Hummler, A. W. Hofmann, Earth Planet. Sci. Lett. 134, 515 (1995)]; p₅ = mann, *Larth Planet. Sci. Lett.* **134**, 515 (1995)]; $p_5 = (1^{29}Xe/1^{30}Xe)_{0,m} = 6.053; <math>p_6 = (1^{36}Xe/1^{30}Xe)_{0,m} = 2.075 \text{ [nonradiogenic air (23)]; } p_7 = (1^{29}Xe/1^{30}Xe)_{m} = 7.5; <math>p_8 = (1^{36}Xe_{P_0}/1^{30}Xe)_m = 2.28 \text{ (present mantle corrected for } 2^{38}U \text{ fission}); p_9 = \text{yield}(2^{44}Pu \rightarrow 1^{36}Xe) = 7 \times 10^{-5} (24); (1^{29}/2^{244}Pu)_{0,0} = p_1 \times p_{3,0} \times p_4/(p_2 \times p_3) = 7.5 \times 10^{-3}; (1^{29}/2^{244}Pu)_{min} = p_9 \times 10^{-5} = 5.1 \times 10^{-4} \text{ Schematric 1}$ $(p_7 - p_5)/(p_8 - p_6) = 5.1 \times 10^{-4}$. Subscript 0, initial value at time of solar system formation 4.556×10^9 years ago (5); "be," bulk Earth; "m," Earth's mantle; "solar," solar value; "min," minimum value to explain mantle excesses. This model implies a homogeneous accretion of Earth, at least for the isotopes of I, U, Pu, and Xe. Conservative error estimates may indicate that the ratio $(1291/244Pu)_{o}/(1291/244Pu)_{min} = 0.068$ is rather uncertain within a factor of 2 (0.034 to 0.136). However, even this large error assumption translates in just $\sim 20 \times 10^6$ years time uncertainty if we use $(^{129}/^{244}Pu)_{min} = (^{129}/^{244}Pu)_0 \times e^{-\Lambda \times \Delta t}$; with $\Lambda = (\lambda_{129} - \lambda_{244}) = (28.9 \times 10^6 \text{ years})^{-1}$. 16. A review of mantle degassing and atmosphere evo-

- A review of mantle degassing and atmosphere evolution models can be found in (24). More recent approaches can be found in (3, 4, 20, 22, 23).
- P. Sarda, T. Staudacher, C. J. Allègre, *Earth Planet.* Sci. Lett. **72**, 357 (1985).

18. We adjusted the degassing parameters to the follow-We adjusted the degassing parameters to the following constraints: $r_1 = [(^{129}Xe)^{130}Xe)_m - (^{129}Xe)^{130}Xe)_m - (^{139}Xe)^{130}Xe)_m - (^$ parameters as described in (17), the mathematical expressions for r_1 and r_4 also contain the accretion time Δt (15), which is treated as an additional free parameter in the model. Subscripts and isotopic ratios are as in (15). Subscript "a" designates atmosphere. Further parameters are chosen as follows: $p_{10} = \text{yield}(^{238}\text{U} \rightarrow ^{136}\text{Xe}) = 3.5 \times 10^{-8}$ (24); one may prefer a more recent determination of this fission yield (4.4×10^{-8}) determined by R. A. Ragettli, E. H. Hebeda, P. Signer, and R. Wieler [Earth Planet. Sci. Lett. 128, 653 (1994)]. However, this parameter has only little influence on the time scale for the second stage of degassing, and changes in the results are stage of begassing, and charges in the estatis are minor. $p_{11} = ({}^{136}\text{Ke}){}^{130}\text{Xe})_m = 2.30$ (present mantle corrected for ${}^{244}\text{Pu}$ fission); $p_{12} = ({}^{129}\text{Xe}){}^{130}\text{Xe})_a = 6.496$; $p_{13} = ({}^{136}\text{Xe}){}^{430}\text{Xe})_a = 2.176$ [present atmosphere (24)]; $p_{14} = ({}^{129}\text{Xe}){}^{430}\text{Xe})_{a,0} = 6.14$; $p_{15} = ({}^{136}\text{Xe}){}^{430}\text{Xe})_{a,0} = 2.16$ (initial isotony of atmosphere (24)]; $p_{14} = ({}^{129}\text{Xe}){}^{430}\text{Xe})_{a,0} = 6.14$; $p_{15} = 2.16$ $(^{136}\text{Xe}/^{130}\text{Xe})_{a,0} = 2.16$ (initial isotopy of atmosphere = surface-correlated solar Xe (25), fractionated with ~3.1% per atomic mass unit. One may argue that "nonradiogenic air" as in (15) would be a more consistent choice for the initial isotopy of atmosphere. However, the two-stage model reveals no solution in this case. Instead of making the model more complicated (for example, three stages), we preferred to change the atmospheric initials in a manner that meets models that suggest a late veneer volatile component mixing with mantle degassing to explain Earth's atmosphere (22).

 D.-C. Lee, A. N. Halliday, G. A. Snyder, L. A. Taylor, Science 278, 1098 (1997).

- 22. B. Marty, *Earth Planet. Sci. Lett.* **94**, 45 (1989). 23. R. O. Pepin, *Icarus* **92**, 2 (1991).
- 24. M. Ozima and F. A. Podosek, Noble Gas Geochem-
- J. S. Kim and K. Marty, *Proc. Lunar Planet Sci. Conf.* 22, 145 (1992).

Sci. Lett. 91, 73 (1988). Shem- 27. J. Kunz, T. Staudacher, C. J. Allègre, unpublished

, 1982). data. t Sci, Conf.

2 February 1998; accepted 11 March 1998

26. P. Sarda, T. Staudacher, C. J. Allègre, Earth Planet.

Reaction Sequence of Iron Sulfide Minerals in Bacteria and Their Use as Biomarkers

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Some bacteria form intracellular nanometer-scale crystals of greigite (Fe_3S_4) that cause the bacteria to be oriented in magnetic fields. Transmission electron microscope observations showed that ferrimagnetic greigite in these bacteria forms from nonmagnetic mackinawite (tetragonal FeS) and possibly from cubic FeS. These precursors apparently transform into greigite by rearrangement of iron atoms over a period of days to weeks. Neither pyrrhotite nor pyrite was found. These results have implications for the interpretation of the presence of pyrrhotite and greigite in the martian meteorite ALH84001.

Intracellular Fe sulfide crystals are produced by two morphological types of magnetotactic bacteria, one of which is referred to as a magnetotactic many-celled prokaryote (MMP) (1); the other constitutes a morphologically similar group of rod-shaped bacteria (2). Magnetosomes (membranebounded magnetic crystals) in the rodshaped bacteria were originally reported to contain greigite (Fe₃S₄) (3), whereas greigite and pyrite (FeS_2) (4) and, tentatively, pyrrhotite ($Fe_{1-x}S$) (5) were identified in magnetosomes in the MMP. Neither pyrrhotite nor pyrite were identified in subsequent studies, however, and the role of pyrite in magnetotactic bacteria is unknown (6). Here, we report observations that elucidate the mechanisms of formation of Fe sulfide minerals in bacteria, and we discuss whether structural features exist to distinguish Fe sulfide minerals formed in bacteria from those formed inorganically.

Attempts to culture magnetotactic bacteria that produce Fe sulfides have been unsuccessful. Thus, we collected cells from natural sites where they are abundant, including the water column of Salt Pond, Woods Hole, Massachusetts, and the water and sediments of shallow salt-marsh pools in the Parker River Wildlife Refuge, Rowley, Massachusetts, and Sweet Springs Nature Preserve, Morro Bay, California. Cells were deposited onto carbon-coated and Formvar-coated Ni grids for transmission electron microscopy (TEM) (7). Both rodshaped magnetotactic bacteria and the MMP containing Fe sulfide crystals were present in the sediments and water samples collected from these sites (Fig. 1).

We obtained interpretable selected-area electron diffraction (SAED) patterns from between 95 and 100 crystals from several tens of bacteria; the studied crystals were chosen either randomly from the chains of magnetosomes or on the basis of their distinctive morphologies. Consistent with the results of earlier studies (3), most of these crystals were greigite in both types of bacteria. However, we identified several grains of mackinawite. Like greigite, mackinawite was present in both the rod-shaped bacteria and the MMP. A third phase, cubic FeS with the sphalerite structure, also may have been present in these magnetotactic bacteria. We found no pyrite or pyrrhotite.

We only observed mackinawite crystals in relatively fresh (less than a few weeks old) specimens; the mackinawite crystals converted to greigite over time. The two SAED patterns in Fig. 2, A and B, were obtained 10 days apart from the same crystal in a rod-shaped bacterium. The angular relationships and d spacings show that the original mackinawite transformed into greigite. We did not observe any changes in the crystal (either as mackinawite or as greigite) while it was exposed to the electron beam; the transformation occurred during the time the sample was stored between the two studies. These results indicate that mackinawite can be a precursor to

^{20.} Y. Zhang and A. Zindler, *J. Geophys. Res.* **94**, 13719 (1989).

Constraints on lower mantle: I. Kaneoka and N. Takaoka, *Earth Planet. Sci. Lett.* **39**, 382 (1978); *Science* **208**, 1366 (1980); M. D. Kurz, W. J. Jenkins, S. R. Hart, *Nature* **297**, 43 (1982); M. Honda, I. M. Dougall, D. B. Patterson, A. Doulgeris, D. A. Clague, *ibid.* **349**, 149 (1991); P. J. Valbracht, T. Staudacher, A. Malahoff, C. J. Allègre, *Earth Planet. Sci. Lett.* **150**, 399 (1997). Constraints on upper mantle: (*10*, *12*, *17*, *26*); M. D. Kurz, W. J. Jenkins, J.-G. Schilling, S. R. Hart, *Earth Planet. Sci. Lett.* **58**, 1 (1982).

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