lowing sources: E. Wada, M. Terazaki, Y. Kabaya, T. Nemoto, *Deep-Sea Res.* **34**, 829 (1987) (Southern Ocean); P. Schafer and V. Ittekkot, *Naturwissenschaften* **80**, 511 (1993) (Arabian Sea); S. M. Libes and W. G. Deuser, *Deep-Sea Res.* **35**, 517 (1988) (Peru margin suspended particles); B. Fry *et al.*, *Deep-Sea Res.* **38**, S1003 (1991) (Peru margin, Black Sea, and Cariaco Trench suspended particles); D. J. Velinsky and M. L. Fogel, *Mar. Chem.* **67**, 161 (Framvaren Fjord).

30. Microbial nitrate reduction (denitrification) in the absence of oxygen is associated with a large kinetic isotope effect that causes isotopic enrichment of the remaining nitrate pool [F. A. Richards and B. B. Benson, *Deep-Sea Res.* **7**, 254 (1961); J. D. Cline and I. R. Kaplan, *Mar. Chem.* **3**, 271 (1975)], a signal transferrable to phytoplankton and sediments [T. Saino and A. Hattori, *Deep-Sea Res.* **34**, 807 (1987); M. A. Altabet, R. Francois, D. W. Murray, W. L. Prell, *Nature* **373**, 506 (1995); R. S. Ganeshram, T. F. Pedersen, S. E. Calvert, J. W. Murray, *Nature* **376**, 755 (1995)]. However, denitrification will lead to an increase in δ^{15}N only if the rate of nitrate replenishment is greater than the rate of denitrification. If the rate of denitrification exceeds the rate of nitrate supply, the likely case during eastern Mediterranean sapropel events when deep-water ventilation was reduced (*32*) and thermohaline circulation was similar or slowed (*32*) [R. Zahn, M. Sarnthein, M. Erlenkeuser, *Paleoceanography* **2**, 543 (1987)]) compared with today, no net isotopic fractionation is expressed. In addition, if eastern basin nitrate was isotopically enriched through denitrification during sapropel events, it should be expressed in both chlorophyll and sediments. Instead, we observe that chlorophyll δ^{15}N remains constant whereas sediment δ^{15}N decreases in sapropels compared with contemporary and non-sapropel values.
31. A. Mangini and J. Dominik, *Sediment. Geol.* **23**, 113 (1979); H. F. Passier *et al.*, *Nature* **397**, 146 (1999).
32. P. G. Myers, K. Haines, E. J. Rohling, *Paleoceanography* **13**, 586 (1998).
33. The incursion of nutrient-rich intermediate waters into the euphotic zone would not lead to excess supply of nutrients and ensuing nitrogen isotopic fractionation (*5*). When the pycnocline lies within the euphotic zone of a stratified basin, a deep algal community develops and autotrophic nutrient uptake causes the retreat of the nutricline below the euphotic depth (*6*). Implicit in this retreat is expansion of the algal population to meet the increased supply of nutrients. Thus, a nutrient excess within the euphotic zone would not occur, and kinetic fractionation would not be expressed (*14*).
34. M. Rossignol-Strick, W. Nesteroff, P. Olive, C. Vergnaud-Grazzini, *Nature* **295**, 105 (1982); H. F. Shaw and G. Evans, *Mar. Geol.* **61**, 1 (1984); M. Rossignol-Strick, *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **49**, 237 (1985); *Paleoceanography* **2**, 333 (1987).
35. A. I. M. Aly, M. A. Mohamed, E. Hallaba, in *Stable Isotopes*, H.-L. Schmidt, H. Förstel, K. Heinzinger, Eds. (Elsevier, Amsterdam, 1982), pp. 475–481.
36. T. D. Jickells, *Science* **281**, 217 (1998).
37. Estimates of the water flux from a flooding Nile are about 2.5 times the modern (pre–Aswan Dam) flow (*34*), or 100 to 200 km^3 year^{-1} [W. F. Wadie, *Acta Adriatica* **25**, 29 (1984)]. Nitrogen concentrations in desert rivers are very low, with total dissolved nitrogen being 3 μM in a representative unpolluted river (*38*). A conservative assumption is that Nile River dissolved nitrogen concentrations increased during its flood, possibly to the high values associated with tropical rivers, which are between 2 to 20 μM nitrate (*38*). Assuming the high value of 20 μM [compared with total dissolved nitrogen concentrations of 8.3 μM in average world river water (*38*)], and twice the high estimate of predam discharge rates, nitrogen input from the Nile during flood is estimated at 0.06×10^{12} g N year^{-1}. Estimates of new production from nutrient and oxygen budgets in the contemporary eastern Mediterranean Sea range from 6 to 12 g C m^{-2} year^{-1} (*1*). Assuming a molar C/N ratio of 6.6 gives nitrogen new production fluxes of 1.1 to 2.3 g N m^{-2} year^{-1}, similar to a previous estimate of 1.5 g N m^{-2} year^{-1} (*2*) derived from measured primary production. Given an area of 1.66×10^{12} m^2, today's integrated new nitrogen production for the entire eastern basin is 1.9 to 3.8×10^{12} g N year^{-1}. Finally, comparing our conservative estimate of dissolved inorganic nitrogen discharge from a flooding Nile (0.06×10^{12} g N year^{-1}) to total eastern Mediterranean new nitrogen production today (1.9 to 3.8×10^{12} g N year^{-1}) demonstrates that nutrient delivery from the Nile was unlikely to have increased new nitrogen production by more than 1.6 to 3.2% over contemporary rates. Increasing the Nile discharge rate beyond 2.5 times the modern value, and adding a contribution from Eurasian rivers such that riverine runoff was four times that of the predam Nile discharge would only increase new nitrogen production by 5 to 10%.
38. M. Meybeck, *Am. J. Sci.* **282**, 401 (1982).
39. D. M. Sigman *et al.*, *Mar. Chem.* **57**, 227 (1997).
40. We thank B. Fry and D. Sigman for isotopic analyses. P. Rimbault, H. Claustre, and the crew of R/V *Le Suroit* provided ship time and assistance with sampling. The Ocean Drilling Program provided sediment samples. Funding came from NSF Chemical Oceanography (D.J.R.), an Office of Naval Research Graduate Fellowship (J.P.S.), an American Chemical Society Petroleum Research Fund Grant (D.J.R.), and a Woods Hole Oceanographic Institution Ocean Ventures Fund Grant (J.P.S.).

29 June 1999; accepted 5 November 1999

Heavy Nitrogen in Carbonatites of the Kola Peninsula: A Possible Signature of the Deep Mantle

Nicolas Dauphas[1]* and Bernard Marty[1,2]

Nitrogen and argon isotopes were measured in carbonatites and associated rocks from the Kola Peninsula in Russia. The Kola mantle source, which is thought to be located in the deep mantle, is enriched in heavy nitrogen (+3 per mil relative to air) as compared to Earth's surface (atmosphere and crust, +2 per mil) and the shallow mantle (−4 per mil). Recycling of oceanic crust (+6 per mil) or metal-silicate partitioning may account for the nitrogen isotopic composition of the deep mantle.

Determining the structure and composition of the mantle is necessary in order to understand current and past mantle dynamics and mantle-to-crust interactions. For example, some have argued that part of the mantle has been isolated from mantle convection for most of Earth's history, allowing the preservation of a primitive component that is only sampled by plumes. Evidence in support of this view arises mainly from noble gases, because plume-derived magmas often show lower radiogenic/primordial isotope ratios than do mid-ocean ridge basalts (MORBs) (*1*). At variance with these models are geophysical (*2*), experimental (*3*), and geochemical (*4*) lines of evidence that suggest that some of the subducting slabs sink through the 670-km-deep seismic discontinuity, implying global stirring of the mantle.

The nitrogen isotopic composition of the shallow mantle that feeds MORs, which is expressed as per mil (‰) deviation relative to the composition of air [in δ^{15}N notation (*5*)], is estimated to be ~−4‰ (*6–13*). This signature may be a remnant of the nitrogen isotopic composition of Earth-forming planetesimals, which later evolved as a result of (i) addition of meteoritic (*14*, *15*) and cometary (*15*) volatiles, or (ii) fractional loss of atmospheric volatiles (*16*), or both. Biologic activity leads to a fractionation of nitrogen isotopes and gives sedimentary rocks a specific composition [δ^{15}N ~ +6‰ (*17*)]. Nitrate is used by denitrifying bacteria as the terminal electron acceptor in energy generation when oxygen is unavailable. Associated with denitrification is a kinetic isotope effect that enriches the residual nitrate in ^{15}N (*18*). Because NO$_3^-$ is the main nitrogen-bearing nutrient, marine organisms and sediments are enriched in ^{15}N relative to the atmosphere (*17*). The oceanic crust thus enriched in ^{15}N is subducted back into Earth at convergent plate margins, which makes nitrogen a potentially powerful tracer of volatile recycling in the mantle.

Mantle plumes, which are assumed to be fixed relative to plate motion, sample a deeper region than that feeding MORs (*19*). The isotopic composition of nitrogen in plumes has not been documented (*20*). Low ^{4}He/^{3}He ratios and a steep ^{20}Ne/^{22}Ne-^{21}Ne/^{22}Ne correlation (*21*) indicate that a mantle plume contributed to the 370-million-year-old (*22*) ultrabasic-alkaline-carbonatite magmatism in the Kola Peninsula in Russia (the eastern segment of the Baltic Shield). The Kola rocks crystallized at depth (*23*), which prevented them from being extensively outgassed, minimizing any subsequent

---

[1] Centre de Recherches Pétrographiques et Géochimiques, CNRS UPR 9046, 15 rue Notre-Dame des Pauvres, Boîte Postale 20, 54501 Vandoeuvre-lès-Nancy Cedex, France. [2] Ecole Nationale Supérieure de Géologie, rue du doyen Marcel Roubault, Boîte Postale 40, 54501 Vandoeuvre-lès-Nancy Cedex, France.

*To whom correspondence should be addressed. E-mail: dauphas@crpg.cnrs-nancy.fr

contamination by atmospheric volatiles. To document the nitrogen isotopic composition of the deep, plume-type mantle, we have measured nitrogen and argon isotopes in carbonatites and associated rocks from the Kola Peninsula [referred to as Kola rocks hereafter (Table 1)]. Volatiles trapped in fluid inclusions were released by stepwise crushing, followed by online nitrogen-argon purification and high-resolution static-vacuum mass spectrometry (*10*, *24*).

The Ne isotopic composition of the mantle is different from that of the atmosphere (*25*), making this element a Rosetta stone when deciphering the isotopic message of terrestrial volatiles. Neon and Ar isotopic ratios correlate in Kola rocks and MORBs, which allows us to estimate the deep and shallow mantle $^{40}Ar/^{36}Ar$ ratios at 4000 to 6000 (*21*) and at 25,000 to 44,000 (*26*), respectively (^{40}Ar is a decay product of ^{40}K, whereas ^{36}Ar is primordial in origin). These ratios are used hereafter to determine the isotopic and elemental characteristics of the mantle.

In Kola rocks [and MORBs (*10*, *13*, *27*)], the $N_2/^{36}Ar$ ratio correlates with the $^{40}Ar/^{36}Ar$ ratio (Fig. 1). The $^{40}Ar/^{36}Ar$ ratio is a reliable indicator of shallow contamination by sediments, air, or air-saturated water. A comparatively K-rich (3.59×10^{-4} mol g^{-1}) ijolite exhibits systematically high $^{40}Ar/^{36}Ar$ ratios at low $N_2/^{36}Ar$ ratios, which may reflect a late (postcrystallization) ^{40}Ar radiogenic ingrowth. A sedimentary contribution is suggested by the high $N_2/^{40}Ar$ ratios (up to 114) of some carbonatites. During partial melting, vesiculation, and formation of fluid inclusions, one might expect a complete extraction of N and Ar and an inheritance of the isotopic and elemental compositions of the source (*28*). When extrapolating the mixing relationships to the source end-member $^{40}Ar/^{36}Ar$ ratios, one can estimate the $N_2/^{36}Ar$ ratios of the deep mantle (from the Kola rocks) and shallow mantle (from the MORBs) at approximately 3×10^5 and 5×10^6, respectively. The $N_2/^{40}Ar$ ratio of the deep mantle (60 ± 5) is lower than that of the shallow mantle [124 ± 20 (*13*)], which leads to a new estimate of the bulk N_2 content of the mantle ($3.6 \pm 1.4 \times 10^{-8}$ mol g^{-1}), as derived from a global K-Ar-N mass balance of the silicate Earth (*27*).

As in the case of MORBs (*10*, *13*), Kola rocks form a triangular array in a N-Ar isotope plot (Fig. 2). This feature is consistent with mixing between air (or air-saturated water), sediments, and mantle gases. The fluid inclusions that host the heavy nitrogen show plume-type $^4He/^3He$ and $^{21}Ne/^{22}Ne$ ratios and comparative-

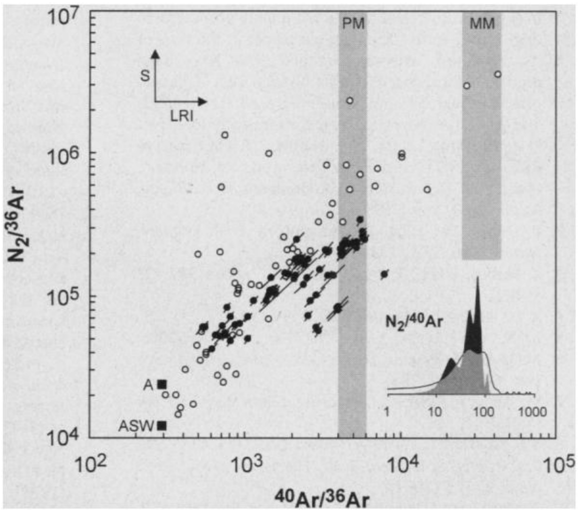

Fig. 1. $N_2/^{36}Ar$-$^{40}Ar/^{36}Ar$ correlations in MORBs [white dots (*10*, *13*, *27*)] and Kola rocks [black dots (Table 1)]. Data points fall on mixing lines between the mantle (PM, plume-type deep mantle; MM, MOR-type shallow mantle) and Earth's surface (A, air; ASW, air-saturated water; S, sediments). This correlation was lately disturbed by ^{40}Ar radiogenic ingrowth (LRI). The uncertainties (depicted as the main axis of standard ellipses) are correlated because they mainly result from the ^{36}Ar blank correction. For the purpose of clarity, uncertainties for MORBs are omitted. The source end-member $^{40}Ar/^{36}Ar$ ratios (shaded regions) are derived from Ar-Ne isotope correlations (*21*, *26*). (Bottom right) Kernel density estimate (*36*, *37*) of the $N_2/^{40}Ar$ ratios in MORBs (black area) and Kola rocks (white area).

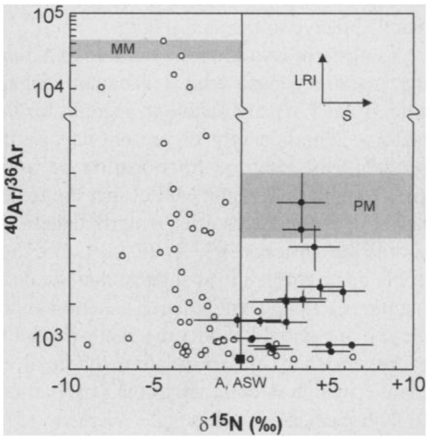

Fig. 2. Nitrogen-argon isotope correlations. Note the change in scale at $^{40}Ar/^{36}Ar = 10^4$. Symbols and abbreviations are as in Fig. 1. MORBs (*10*, *13*) and Kola rocks (Table 1) form triangular mixing arrays between the mantle, air (or air-saturated water), and sediments.

Table 1. N-Ar-K data in carbonatites and associated paragenesis from the Kola Peninsula (additional data are available at www.sciencemag.org/feature/data/1044003.shl). Uncertainties are one sigma.

Complex	Rock (mineral)	N_2 (10^{-9} mol g^{-1})	$\delta^{15}N$ (‰)	^{40}Ar (10^{-11} mol g^{-1})	$^{40}Ar/^{36}Ar$	K (10^{-5} mol g^{-1})
Lesnaya Varaka	Dunite with perovskite and titanomagnetite	3.96 ± 0.10	1.9 ± 1.1	5.68 ± 0.14	612 ± 55	<0.2
	Dunite (magnetite)	1.74 ± 0.05	3.5 ± 1.4	3.89 ± 0.13	5103 ± 899	<0.2
Kovdor	Turjaite	6.06 ± 0.15	3.5 ± 1.1	13.02 ± 0.33	4281 ± 394	3.2 ± 0.3
	Dunite	1.42 ± 0.04	4.6 ± 1.3	2.63 ± 0.07	2497 ± 266	5.1 ± 0.5
	Phoscorite (magnetite)	1.30 ± 0.03	6.0 ± 1.3	2.57 ± 0.06	2376 ± 308	<0.2
	Pyroxenite (diopside)	0.27 ± 0.01	2.7 ± 2.2	0.42 ± 0.01	2062 ± 820	6.2 ± 0.6
Seblyavr	Pyroxenite	3.40 ± 0.09	2.6 ± 1.2	3.93 ± 0.10	2102 ± 209	15.3 ± 0.3
	Pyroxenite (pyroxene)	0.57 ± 0.01	−0.2 ± 2.5	0.63 ± 0.02	1485 ± 201	12.1 ± 0.2
	Calcite carbonatite	7.96 ± 0.20	5.3 ± 1.1	7.00 ± 0.19	532 ± 51	17.6 ± 0.4
	Calcite carbonatite	20.20 ± 0.51	1.7 ± 1.2	27.23 ± 0.69	691 ± 61	0.42 ± 0.04
	Dunite	6.08 ± 0.15	3.6 ± 1.4	5.27 ± 0.14	2144 ± 251	13.4 ± 0.3
	Dolomite carbonatite	2.50 ± 0.06	6.5 ± 1.2	3.38 ± 0.09	745 ± 89	1.5 ± 0.1
	Ijolite	1.75 ± 0.04	4.3 ± 1.5	4.68 ± 0.12	3720 ± 667	35.9 ± 0.7
	Apatite-phlogopite-diopside ore	1.49 ± 0.04	2.6 ± 1.2	2.10 ± 0.05	1415 ± 166	10.2 ± 1.0
	Apatite-diopside-phlogopite ore	6.91 ± 0.17	1.1 ± 1.2	9.23 ± 0.23	1456 ± 132	26.3 ± 0.5
	Clinopyroxenite with perovskite and titanomagnetite	3.52 ± 0.09	0.7 ± 1.1	5.10 ± 0.13	926 ± 86	2.8 ± 0.3
	Dolomite carbonatite	2.83 ± 0.07	5.1 ± 1.2	3.33 ± 0.08	716 ± 68	0.21 ± 0.02

ly high ^{40}Ar/^{36}Ar ratios, which all together indicate a mantle source region (*21*). The coupled Sr and Nd isotope systematics in the Kola Peninsula provide no evidence for crustal contamination (*29*). Independently, preliminary measurements in our laboratory on basalt glasses from the Society Island hot spot yield positive δ^{15}N values, suggesting that heavy nitrogen is a common feature of plume-derived magmas. In contrast to the characteristics of the shallow mantle, which is depleted in heavy nitrogen by ~−4‰ relative to the atmosphere (*6–13*), the deep mantle appears to be enriched by ~+3‰. The δ^{15}N value of the deep mantle outside the range defined by the shallow mantle (*6–13*) and Earth's surface [crust and atmosphere, ~+2‰ (*10*)] suggests that the heavy nitrogen is not primordial in origin. It is noteworthy that the late accretion of extraterrestrial matter depleted in ^{15}N relative to the deep mantle would fail to account for the ^{15}N depletion of the shallow mantle relative to the atmosphere.

Long-term isotopic fractionation of N during magma genesis and subsequent degassing, if any (*28*), are unable to account for the isotopic heterogeneity of present-day Earth. Models of N isotope fractionation between silicate melt and vapor predict that the residual N in the silicates after magma degassing should be enriched in ^{15}N (*7, 30*). Because noble gas isotopic ratios suggest that the deep mantle is less degassed than the shallow mantle (*1*), one should expect the shallow mantle to be enriched in ^{15}N relative to the deep mantle, which is contrary to the observation.

Nitrogen is a siderophile element (*31*), whereas Ar is not (*32*). Hence, uptake of N by the core would lower the $N_2/^{36}$Ar ratio of the mantle. The solubility of N_2 in Fe-Ni alloys follows Sieverts' law (N_2 gas $\rightleftharpoons$ 2N dissolved). Because the ^{14}N-^{14}N bond is weaker than the ^{15}N-^{14}N or ^{15}N-^{15}N bonds, the residual N in the mantle is presumably enriched in ^{15}N relative to its metal counterpart. Such a possibility would require appreciable fractionation of nitrogen isotopes to account for the isotopic stratification of present-day Earth, which calls for experimental as well as theoretical confirmation.

Phanerozoic marine sediments and the deep mantle both exhibit high $N_2/^{36}$Ar ratios and high δ^{15}N values relative to the atmosphere. An appealing possibility is that the nitrogen carried from the deep mantle to the surface of Earth by plumes is of recycled origin. This interpretation is consistent with the recycling of Ar in Earth's interior (*21, 33*) but creates a paradox. If the ^{15}N depletion of the shallow mantle was primordial in origin, as is generally thought (*6–16*), preferential recycling of sediments in the deep mantle would at the same time increase the $N_2/^{36}$Ar ratio and the δ^{15}N value of the deep mantle relative to the shallow mantle, which is apparently not the case. A way to get around this difficulty is to consider that the nitrogen isotopic composition of the shallow mantle is not primordial in origin but rather results from the recycling of Archean, ^{15}N-depleted, sedimentary organic matter (*34*). An alternative explanation is that the $N_2/^{36}$Ar ratio of the primitive mantle was lower than the inferred present-day ratio of the deep mantle (~3×10^5). Early degassing of the shallow mantle would have increased the $N_2/^{36}$Ar ratio to ~5×10^6 as a result of preferential retention of nitrogen in silicates under the reducing conditions prevailing at that time (*35*). Later on, the $N_2/^{36}$Ar ratio of the deep mantle would have increased to its present-day value through recycling of surface nitrogen. Further investigation of the nitrogen isotopic composition of ocean islands such as Hawaii or Iceland will allow this unique stable isotope heterogeneity of Earth to be documented.

References and Notes

1. In the mantle, ^{3}He and ^{22}Ne are mainly primordial in origin (they were trapped in our planet at the time of its accretion), whereas ^{4}He and ^{21}Ne have been produced throughout Earth's history. Less degassed reservoirs exhibit low time-integrated (U+Th)/^{3}He and (U+Th)/^{22}Ne ratios, and consequently low ^{4}He/^{3}He ratios [M. D. Kurz, W. J. Jenkins, S. R. Hart, *Nature* **297**, 43 (1982)] and ^{21}Ne/^{22}Ne ratios [M. Honda, I. McDougall, D. B. Patterson, A. Doulgeris, D. A. Clague, *Nature* **349**, 149 (1991)].
2. R. D. van der Hilst, S. Widiyantoro, E. R. Engdahl, *Nature* **386**, 578 (1997).
3. K. Hirose, Y. Fei, Y. Ma, H.-K. Mao, *Nature* **397**, 53 (1999).
4. A. W. Hofmann, *Nature* **385**, 219 (1997).
5. $\delta^{15}N = [(^{15}N/^{14}N)_{sample}/(^{15}N/^{14}N)_{air} - 1] \times 1000$.
6. M. Javoy, F. Pineau, D. Demaiffe, *Earth Planet. Sci. Lett.* **68**, 399 (1984).
7. M. Javoy, F. Pineau, H. Delorme, *Chem. Geol.* **57**, 41 (1986).
8. S. R. Boyd and C. T. Pillinger, *Chem. Geol.* **116**, 43 (1994).
9. P. Cartigny, S. R. Boyd, J. W. Harris, M. Javoy, *Terra Nova* **9**, 175 (1997).
10. B. Marty and F. Humbert, *Earth Planet. Sci. Lett.* **152**, 101 (1997).
11. P. Cartigny, J. W. Harris, M. Javoy, *Science* **280**, 1421 (1998).
12. P. Cartigny, J. W. Harris, D. Phillips, M. Girard, M. Javoy, *Chem. Geol.* **147**, 147 (1998).
13. B. Marty and L. Zimmermann, *Geochim. Cosmochim. Acta* **63**, 3619 (1999).
14. M. Javoy, *Geophys. Res. Lett.* **24**, 177 (1997); *Chem. Geol.* **147**, 11 (1998).
15. N. Dauphas, F. Robert, B. Marty, *Meteorit. Planet. Sci.* **33**, A38 (1998).
16. I. N. Tolstikhin and B. Marty, *Chem. Geol.* **147**, 27 (1998).
17. K. E. Peters, R. E. Sweeney, I. R. Kaplan, *Limnol. Oceanogr.* **23**, 598 (1978).
18. E. Wada, T. Kadonaga, S. Matsuo, *Geochem. J.* **9**, 139 (1975).
19. Geophysical investigations [L. Bréger and B. Romanowicz, *Science* **282**, 718 (1998); D. V. Helmberger, L. Wen, X. Ding, *Nature* **396**, 251 (1998); S. A. Russell, T. Lay, E. J. Garnero, *Nature* **396**, 255 (1998); H. Bijwaard and W. Spakman, *Earth Planet. Sci. Lett.* **166**, 121 (1999)] together with geochemical investigations [R. J. Walker, J. W. Morgan, M. F. Horan, *Science* **269**, 819 (1995); E. Widom and S. B. Shirey, *Earth Planet. Sci. Lett.* **142**, 451 (1996); R. J. Walker *et al.*, *Geochim. Cosmochim. Acta* **61**, 4799 (1997); A. D. Brandon, R. J. Walker, J. W. Morgan, M. D. Norman, H. M. Prichard, *Science* **280**, 1570 (1998); J. E. Snow and G. Schmidt, *Nature* **391**, 166 (1998); J. M. Bird, A. Meibom, R. Frei, T. F. Nägler, *Earth Planet. Sci. Lett.* **170**, 83 (1999)] suggest that plumes emerge from the core-mantle boundary.
20. R. A. Exley, S. R. Boyd, D. P. Mattey, and C. T. Pillinger [*Earth Planet. Sci. Lett.* **81**, 163 (1986/87)] measured positive δ^{15}N values in basalt glasses from Loihi seamount, but also positive and negative values for MORBs. These results are inconclusive because there was no simultaneous control of shallow contamination by argon isotopes (*10, 13*).
21. B. Marty *et al.*, *Earth Planet. Sci. Lett.* **164**, 179 (1998).
22. U. Kramm, L. N. Kogarko, V. A. Kononova, H. Vartiainen, *Lithos* **30**, 33 (1993).
23. A. A. Kukharenko *et al.*, *The Caledonian Complex of Ultrabasic Alkaline Rocks and Carbonatites of the Kola Peninsula and Northern Karelia* (Nedra, Moscow, 1965).
24. Samples weighing 0.1 to 0.4 g were crushed under ultrahigh vacuum (~2×10^{-9} torr) with a soft iron piston cylinder activated by an external solenoid. Gases were then purified in a glass line where H, C, and S compounds were oxidized (in the presence of Pt foils held at 723 K) with O_2 produced by heating a CuO furnace at 1023 K ($4CuO \rightleftharpoons 2Cu_2O + O_2$). Condensible gases (for example, H_2O, CO_2, and SO_2) were trapped in a cold finger held at 90 K. Excess oxygen was resorbed onto the CuO at 723 K. Nitrogen was then admitted into a Micromass VG5400 static-vacuum mass spectrometer. The trap current of the Nier type source was 20 μA, resulting in a N_2 sensitivity of 2.8×10^{-5} A torr^{-1}. The nitrogen isotopic composition was determined as the 29/28 ion beam ratio on a Faraday collector. Possible isobaric interferences with N_2 of CO, N_2H, and C_2H_x at masses 28 and 29 were monitored at mass 30 and were always negligibly small. Gases left in the purification line were further purified over hot Ti sponge getters. Argon was then admitted to the mass spectrometer, where ^{40}Ar was analyzed with a Faraday collector (with a sensitivity of 5.0×10^{-5} A torr^{-1}) and ^{36}Ar was measured by ion counting after amplification by an electron multiplier.
25. The highest ^{20}Ne/^{22}Ne ratio measured so far in mantle rocks [M. Ozima and S. Zashu, *Geochim. Cosmochim. Acta* **52**, 19 (1988)] is close to the solar ratio [J.-P. Benkert, H. Baur, P. Signer, R. Wieler, *J. Geophys. Res.* **98**, 13147 (1993)] and is much higher than any other known component such as Ne-E [M. H. A. Jungck and P. Eberhardt, *Meteoritics* **14**, 439 (1979)], cosmogenic Ne [E. Mazor, D. Heymann, E. Anders, *Geochim. Cosmochim. Acta* **34**, 781 (1970)], Ne-A [M. Tang and E. Anders, *Geochim. Cosmochim. Acta* **52**, 1245 (1988)], or Ne-Q [R. Wieler, E. Anders, H. Baur, R. S. Lewis, P. Signer, *Geochim. Cosmochim. Acta* **56**, 2907 (1992)].
26. M. Moreira, J. Kunz, C.-J. Allègre, *Science* **279**, 1178 (1998).
27. B. Marty, *Nature* **377**, 326 (1995).
28. The N_2/Ar ratios in mantle vesicles do not correlate with any index of partial melting or degassing, which suggests a comparable behavior of Ar and N. Because Ar is incompatible, this element and by inference N are thoroughly extracted from the mantle during magma genesis and subsequent degassing (*10, 13, 27*).
29. U. Kramm, *Eur. J. Mineral.* **5**, 985 (1993).
30. P. Richet, Y. Bottinga, M. Javoy, *Annu. Rev. Earth Planet. Sci.* **5**, 65 (1977).
31. K. Hashizume, T. Kase, J. Matsuda, H. Sato, *Kazan* **42**, S293 (1997).
32. J. Matsuda *et al.*, *Science* **259**, 788 (1993).
33. P. Sarda, M. Moreira, T. Staudacher, *Science* **283**, 666 (1999).
34. V. Beaumont and F. Robert, *Precambrian Res.* **96**, 63 (1999).
35. F. Humbert, B. Marty, G. Libourel, *Lunar Planet. Sci.* **XXX**, 1955 (1999).
36. S. J. Sheather and M.C. Jones, *J. R. Stat. Soc. B* **53**, 683 (1991).
37. A. W. Bowman and A. Azzalini, *Applied Smoothing Techniques for Data Analysis: the Kernel Approach With S-Plus Illustrations* (Oxford Univ. Press, Oxford, 1997).

38. We thank I. N. Tolstikhin for providing us with these unique samples; K. Hashizume and S. R. Boyd for insightful discussions; and L. Zimmermann, P. Robert, and G. Sauder for help in keeping the mass spectrometer in fine shape. This is contribution 1434 of the Centre de Recherches Pétrographiques et Géochimiques .

28 July 1999; accepted 2 November 1999

Heavy Nitrogen in Carbonatites of the Kola Peninsula: A Possible Signature of the Deep Mantle

Nicolas Dauphas; Bernard Marty

Science, New Series, Vol. 286, No. 5449. (Dec. 24, 1999), pp. 2488-2490.

Stable URL:

http://links.jstor.org/sici?sici=0036-8075%2819991224%293%3A286%3A5449%3C2488%3AHNICOT%3E2.0.CO%3B2-T

This article references the following linked citations:

References and Notes

[11] **Eclogitic Diamond Formation at Jwaneng: No Room for a Recycled Component**
Pierre Cartigny; Jeffrey W. Harris; Marc Javoy
Science, New Series, Vol. 280, No. 5368. (May 29, 1998), pp. 1421-1424.
Stable URL:
http://links.jstor.org/sici?sici=0036-8075%2819980529%293%3A280%3A5368%3C1421%3AEDFAJN%3E2.0.CO%3B2-H

[19] **Three-Dimensional Structure at the Base of the Mantle Beneath the Central Pacific**
Ludovic Bréger; Barbara Romanowicz
Science, New Series, Vol. 282, No. 5389. (Oct. 23, 1998), pp. 718-720.
Stable URL:
http://links.jstor.org/sici?sici=0036-8075%2819981023%293%3A282%3A5389%3C718%3ATSATBO%3E2.0.CO%3B2-B

[19] **Osmium-187 Enrichment in Some Plumes: Evidence for Core-Mantle Interaction?**
Richard J. Walker; John W. Morgan; Mary F. Horan
Science, New Series, Vol. 269, No. 5225. (Aug. 11, 1995), pp. 819-822.
Stable URL:
http://links.jstor.org/sici?sici=0036-8075%2819950811%293%3A269%3A5225%3C819%3AOEISPE%3E2.0.CO%3B2-R

[19] **Coupled ¹⁸⁶ Os and ¹⁸⁷ Os Evidence for Core-Mantle Interaction**
Alan D. Brandon; Richard J. Walker; John W. Morgan; Marc D. Norman; Hazel M. Prichard
Science, New Series, Vol. 280, No. 5369. (Jun. 5, 1998), pp. 1570-1573.
Stable URL:
http://links.jstor.org/sici?sici=0036-8075%2819980605%293%3A280%3A5369%3C1570%3ACAEFCI%3E2.0.CO%3B2-R

LINKED CITATIONS

- Page 2 of 2 -

[26] **Rare Gas Systematics in Popping Rock: Isotpic and Elemental Compositions in the Upper Mantle**

Manuel Moreira; Joachim Kunz; Claude Allègre

Science, New Series, Vol. 279, No. 5354. (Feb. 20, 1998), pp. 1178-1181.

Stable URL:

http://links.jstor.org/sici?sici=0036-8075%2819980220%293%3A279%3A5354%3C1178%3ARGSIPR%3E2.0.CO%3B2-E

[32] **Noble Gas Partitioning Between Metal and Silicate Under High Pressures**

J. Matsuda; M. Sudo; M. Ozima; K. Ito; O. Ohtaka; E. Ito

Science, New Series, Vol. 259, No. 5096. (Feb. 5, 1993), pp. 788-790.

Stable URL:

http://links.jstor.org/sici?sici=0036-8075%2819930205%293%3A259%3A5096%3C788%3ANGPBMA%3E2.0.CO%3B2-J

[33] **Argon-Lead Isotopic Correlation in Mid-Atlantic Ridge Basalts**

Philippe Sarda; Manuel Moreira; Thomas Staudacher

Science, New Series, Vol. 283, No. 5402. (Jan. 29, 1999), pp. 666-668.

Stable URL:

http://links.jstor.org/sici?sici=0036-8075%2819990129%293%3A283%3A5402%3C666%3AAICIMR%3E2.0.CO%3B2-Q

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