15. C. E. Junge and R. T. Werby, *J. Meteorol.* **15**, 417 (1958). Samples were collected from July 1955 through June 1956.
16. Estimated Mg^{2+} concentration represents 32% of the 1955–1956 C_β value. If the Mg^{2+} concentration were zero, which is unrealistic, the C_β value would be 36.2 μeq liter^{-1}, or about three times the current value.
17. Sulfate in pre–Industrial Revolution (PIR) (around 1800) stream water was estimated at 20 μeq liter^{-1} [T. J. Sullivan *et al.*, *Nature* **345**, 54 (1990); T. J. Sullivan, in *Acidic Deposition and Aquatic Ecosystems*, D. F. Charles, Ed. (Springer-Verlag, New York, 1991)], and NO_3^- was estimated at 5 μeq liter^{-1}, equaling 25 μeq liter^{-1} for SO_4^{2-} + NO_3^-. PIR values of ANC were probably about 20 μeq liter^{-1}, resulting in a C_β estimate of about 45 μeq liter^{-1}. Initially, in response to increases in emissions of SO_2 and consequent atmospheric deposition of SO_4^{2-}, C_β concentrations in drainage water probably increased stoichiometrically with increases in SO_4^{2-}. Empirical relations between SO_2 emissions and stream SO_4^{2-} at HBEF suggest stream concentrations of SO_4^{2-} + NO_3^- of 96 μeq liter^{-1} in 1940. If C_β increased stoichiometrically with increases in SO_4^{2-}, C_β and ANC would have been 116 and 20 μeq liter^{-1}, respectively, in 1940.
18. The weathering rate of Ca^{2+} was estimated from Ca:Na (molar ratio) in bedrock, assuming that all streamwater Na^+ was derived from rock weathering. Calcium release from weathering before 1963 was assumed to be the same as the average from 1963 to 1993, 105 eq ha^{-1} year^{-1}. Before 1973, net biomass storage was assumed to be constant (718 eq ha^{-1} year^{-1}) [on the basis of F. H. Bormann and G. E. Likens, *Pattern and Process in a Forested Ecosystem* (Springer-Verlag, New York, 1979)], and after 1973, its value came from a logistic curve fitted to data from 1965 to 1992. Although a logistic curve can be fitted to bulk precipitation input from 1956 to 1994 ($r^2 = 0.87$), we used linear trends and projected the 1955–1956 value (350 eq ha^{-1} year^{-1}) to 1940. Estimated streamwater Ca^{2+} output was based on a relation between SO_2 emissions and concurrent SO_4^{2-} + 5 μeq liter^{-1} of NO_3^-. Before 1963, the amount of precipitation and streamflow was taken as the average for 1963 to 1993.
19. G. B. Lawrence, M. B. David, W. C. Shortle, *Nature* **378**, 162 (1995).
20. E. K. Miller, J. D. Blum, A. J. Friedland, *ibid.* **362**, 438 (1993). Strontium was measured as a surrogate for calcium.
21. The total depletion of Ca^{2+} from labile soil pools during 1940 to 1995 was estimated at 42,200 eq ha^{-1} (Fig. 3). If Ca^{2+} bulk precipitation concentrations were low from 1940 to 1995, such as currently observed (3.6 μeq liter^{-1}), depletion of soil Ca^{2+} would have been 50,400 eq ha^{-1}. In contrast, if Ca^{2+} precipitation concentrations were high from 1940 to 1995, such as observed in 1955–1956 (25 μeq liter^{-1}), soil depletion of Ca^{2+} would have been 34,400 eq ha^{-1}. As a result, reductions in atmospheric deposition of Ca^{2+} associated with particulate emission control (5) contributed some 20% of the apparent depletion of soil Ca^{2+} at HBEF.
22. Total Ca^{2+} and Mg^{2+} concentrations in Oie and Oa soil horizons for Watershed 6 of HBEF declined by 30 to 40% between 1970 and 1987 [R. D. Yanai, T. G. Siccama, M. A. Arthur, *Bull. Ecol. Soc. Am.* **74**, 496 (1993)]. Elsewhere in the region, Ca^{2+} in forest floors declined by 22% on average during 1979 to 1994, and Mg^{2+}, by 14% [R. D. Yanai, M. A. Arthur, T. G. Siccama, C. A. Federer, *Bull. Ecol. Soc. Am.* **76**, 290 (1995); (*19*)].
23. C. A. Federer *et al.*, *Environ. Manage.* **13**, 593 (1989).
24. C. O. Tamm and L. Hällbacken, *Water Air Soil Pollut.* **31**, 337 (1986); *Ambio* **17**, 56 (1988).
25. E. A. Bondietti, N. Monroshima, W. C. Shortle, K. T. Smith, *Can. J. For. Res.* **20**, 1850 (1990); W. C. Shortle and E. A. Bondietti, *Water Air Soil Pollut.* **61**, 253 (1992).
26. C. S. Cronan and D. F. Grigal, *J. Environ. Qual.* **24**, 209 (1995). Mean Ca:Al molar ratios for spruce, fir, and white birch stands at HBEF (elevation, 750 m) were 1.27 in Oa horizon leachate, decreasing to 0.40 in Bh and 0.27 in Bs horizon solutions. In high-elevation (730 m) deciduous stands, Ca:Al decreased from 1.21 in Oa to 0.59 in Bh and 0.39 in Bs horizon soil water.
27. We used current NO_3^- plus 50% of the 1980 SO_4^{2-} values to estimate the minimum trajectory of strong acid anion concentrations after 1999 in Fig. 2 (*5*).
28. "National Air Pollutant Emission Estimates 1940–1990," EPA-450/4-91-026 (U.S. Environmental Protection Agency, Research Triangle Park, NC, November 1991).

29. Financial support was provided by the National Science Foundation and the A. W. Mellon Foundation. We thank the various contributions of M. A. Arthur, C. Eagar, C. E. Johnson, C. W. Martin, T. G. Siccama, and R. D. Yanai. The HBEF is operated by the U.S. Department of Agriculture Forest Service, Radnor, Pennsylvania.

13 November 1995; accepted 18 January 1996

History of Ancient Copper Smelting Pollution During Roman and Medieval Times Recorded in Greenland Ice

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Determination of copper concentrations in Greenland ice dated from seven millennia ago to the present showed values exceeding natural levels, beginning about 2500 years ago. This early large-scale pollution of the atmosphere of the Northern Hemisphere is attributed to emissions from the crude, highly polluting smelting technologies used for copper production during Roman and medieval times, especially in Europe and China. This study opens the way to a quantitative assessment of the history of early metal production, which was instrumental in the development of human cultures during ancient eras.

Most emissions of pollutants to the global atmosphere of our planet occurred after the Industrial Revolution, driven by the combination of unprecedented growth in the population of the Earth and massive technological and economic development. The only exception reported so far is lead emission. Time series recently obtained from Greenland ice (*1*) and Swedish lake sediments (*2*) indicate that there was early hemispheric-scale atmospheric pollution from lead during Greek and Roman times. The importance of this early lead pollution remained relatively limited, however; cumulative lead deposition to the Greenland ice cap during the eight centuries of the flourishing of the Greek and Roman civilizations (~400 metric tons) was about an order of magnitude lower than lead deposition from post–Industrial Revolution fallout [~3200 metric tons (*3*)]. Here we report evidence that cumulative early atmospheric pollution from copper before the Industrial Revolution was one order of magnitude greater than that from the Industrial Revolution to the present.

We analyzed copper in 23 sections of the 3028.8-m Greenland Ice Core Project (GRIP) deep ice core (*4*), drilled in central Greenland at Summit (72°34′N, 37°37′W; elevation 3238 m above sea level). Twenty-one sections were selected from ice dated from 2960 to 470 years ago (from depths of 619.3 to 129.3 m) in order to cover the Greek and Roman civilizations, barbaric and medieval times, and the Renaissance. Two sections were chosen from ice dated from 7260 and 7760 years ago (depths of 1230.4 and 1286.5 m, respectively) to assess natural Holocene copper concentrations during times before copper production. We mechanically decontaminated each core section using ultraclean procedures by chiseling successive veneers of ice from the outside to the central part as described in detail elsewhere (*5*). Copper concentrations were then determined with a precision of ±10% by graphite furnace atomic absorption spectrometry (GFAAS) after preconcentration. Each value was blank-corrected (*5*). The accuracy of the data depends on the efficiency of the decontamination procedure. This was systematically checked for all sections by investigation of radial changes in copper concentrations from the outside to the center of each individual core section (*6*). Copper concentrations measured in the central parts of the

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23 sections ranged from 0.8 to 6.4 pg/g. These are the first reliable copper data ever obtained for ancient Greenland ice.

Changes in the copper/aluminum ratio (*7*) as a function of the age (*8*) of the ice are shown in Fig. 1. Before the beginning of the production of copper by man ~7000 years ago, the copper/aluminum ratio was about 2×10^{-4} (Fig. 1) All copper originated from various natural sources (*9*). The copper/aluminum ratio remained unchanged until ~2500 years ago. From ~2500 to 1800 years ago, the lowest values remained close to the natural level of $\sim 2 \times 10^{-4}$ but part of the samples had higher values, up to $\sim 6 \times 10^{-4}$. From ~1800 years ago, all values were above natural levels (range $\sim 3 \times 10^{-4}$ to $\sim 17 \times 10^{-4}$).

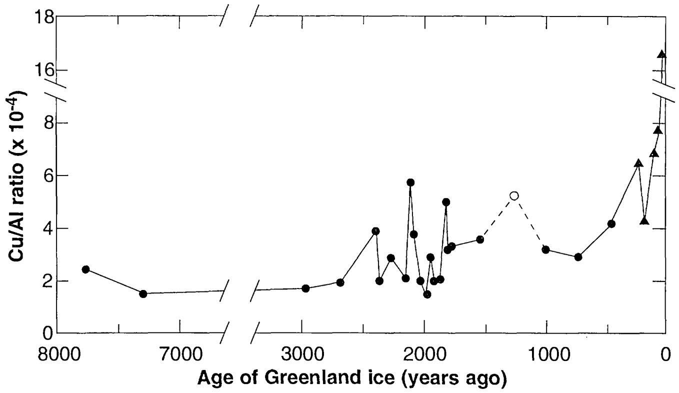

Fig. 1. Changes in the copper/aluminum ratio in ice from Summit, central Greenland, dated from 7760 to 470 years ago (black circles). An open circle is used for the core section dated from 1248 years ago, because no plateau of concentration was obtained for copper in that section (*6*). The copper/aluminum ratio of that section was calculated with the use of the copper value extrapolated from the radial profile (*6*) and should therefore be considered as an upper limit of the original ratio in the ice. Also shown (triangles) are representative mean values from (*3*) for ice and snow dated from the Industrial Revolution to the present, collected at the same location.

The high values in the samples from ~2500 years ago are not due to uncontrolled contamination of the corresponding core sections, because the radial concentration profiles for copper (and aluminum) across all but one (*6*) section show excellent plateaus of concentration, which confirms that transfer of outside contamination to the inner parts of the cores cannot be responsible for the observed high values. The high concentrations cannot be explained by changes in contributions from natural sources. Ancillary measurements of aluminum, sodium, sulfate, and ammonium (*10*) show (*11*) that copper from natural sources such as rock and soil dust, sea salt spray, volcanoes, and biomass burning is not responsible for the observed high values. We interpret these concentrations to be the result of early large-scale copper pollution of the atmosphere of the Northern Hemisphere long before the Industrial Revolution.

During ancient and recent times, copper emissions mainly originated from copper mining and smelting activities, with only rather minor contributions from other human activities [such as production of iron and other nonferrous metals, wood combustion, and so on (*12*)]. As a first step toward obtaining a time series for copper emissions to the atmosphere that can be used to interpret our Greenland ice data, we reconstructed past changes in copper production (Fig. 2) from a comprehensive review (*13*) of available literature.

Copper was first produced from native copper ~7000 years ago (*14*). Its production became substantial ~5000 years ago, after the development of techniques for smelting carbonate and oxide ores (*15*) and the introduction of tin-bronze, which heralded the real Bronze Age. Production then continuously increased after the development of new techniques for smelting sulfide ores ~4500 years ago (*14–16*). Cumulative production from ~ 4000 to 2700 years ago was ~500,000 metric tons (*17*).

The Roman period marked the beginning of a sharp rise in the production of copper in response to the rapidly increasing use of copper alloys for military and civilian purposes, especially in coinage (*17, 18*). Total production peaked at over ~15,000 metric tons per year ~2000 years ago (Fig. 2). The main production districts were in Spain (which accounted for more than half of worldwide production during Roman times), Cyprus, and central Europe (*15, 18*). Cumulative production from ~2250 to 1650 years ago was ~5 million metric tons.

After the fall of the Roman Empire, copper production greatly declined in Europe and world production remained low at ~2000 metric tons per year until about the eighth century (*16, 19*). It started to increase again during medieval times. In Europe, this increase was linked with the mining of new German ores beginning in the ninth century and of Swedish ores (especially in the Falun area) beginning in the 13th century (*16, 19, 20*). But during medieval times, the largest share of the production originated in China (*21, 22*), especially during the Northern Sung period (10th to 12th century). During that period, Chinese production reached a maximum of ~13,000 metric tons per year ~900 years ago (*21*), which gives a worldwide production peak of ~15,000 metric tons per year ~900 years ago, which is comparable to the Roman peak ~2000 years ago.

Production then fell to a lower level for several centuries (~2000 metric tons per year in the 14th century), before increasing greatly from the Industrial Revolution to the present, when it was strongly stimulated by the development of electrical industries. Present-day production is ~9 million metric tons per year.

Atmospheric emissions related to this production varied considerably during the past seven millennia because of substantial changes in production technologies (*16, 23*). During ancient times, emission factors were prob-

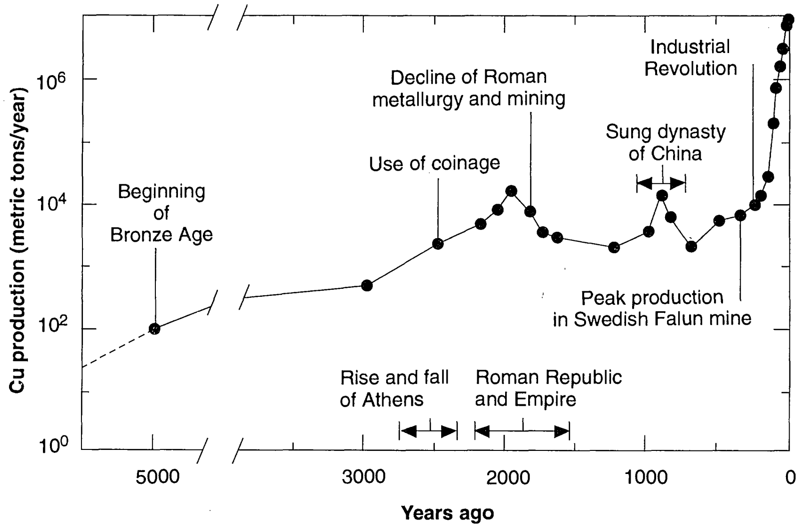

Fig. 2. Variations in the copper production rate during the past 5000 years as reconstructed from an extensive review of available literature.

ably as high as $\sim$15% because of uncontrolled and wasteful smelting procedures. Smelting of sulfide ores required numerous roasting, smelting, oxidizing, and refining steps (*24*) performed in crude open furnaces. Emissions remained uncontrolled until the Industrial Revolution (*16*), when improved furnaces and metallurgical techniques began to be used. By the middle of the 19th century, smelting procedures were reduced to only five steps (*16*). These improvements resulted in a sharp decrease in emission factors, which were probably reduced to $\sim$1% at the beginning of the 20th century. Further improvements were subsequently made, resulting in present-day emission factors of $\sim$0.25% (*25*).

Combination of these emission factors with the production data (Fig. 2) shows that copper emissions to the atmosphere were as high as $\sim$2100 to 2300 metric tons per year at the peak of the Roman Empire $\sim$2000 years ago and of the Northern Sung dynasty in China $\sim$900 years ago (Table 1). These emissions were higher than those for the mid-18th and 19th centuries and represent as much as $\sim$10% of present-day emissions.

The high copper/aluminum ratios observed in our ice samples dated from Roman times onward (Fig. 1) show that these emissions were intense enough to produce substantial copper pollution of the middle troposphere of the Arctic. Pollutant copper was probably emitted to the atmosphere as small-sized aerosols during the high-temperature steps of copper production processes. These aerosols were easily transported to the Arctic by well-known atmospheric pathways (*26*) from the mid-latitude areas where they were emitted (mainly in the Mediterranean basin, especially Spain, during Roman times; and in China during medieval times).

Table 1. Estimated copper emissions to the atmosphere, linked with copper production. These estimates were derived from the production data shown in Fig. 2, with the assumption that the copper emission factor was $\sim$15% until the Industrial Revolution and then declined linearily to $\sim$1% in 1900 and to $\sim$0.25% at present.

Date (years ago)	Copper emission to the atmosphere (metric tons/year)
5000	5‡
3000	20‡
2500	300
2000*	2,300
1250	300
900†	2,100
500	800
250	1,500
150	1,500
50	16,000
5	23,000

*Peak of Roman copper production. †Peak of Chinese copper production during the Northern Sung dynasty. ‡Calculated with an assumed emission factor of $\sim$5% for oxide and carbonate ores.

Changes in copper/aluminum ratios in Greenland ice appear to be in general agreement with the estimated changes in anthropogenic copper emissions (Table 1). The Greenland ice data show low (natural) values until $\sim$2500 years ago, then medium values from Roman times to the Industrial Revolution, and finally a sharp increase in recent times (Fig. 1). We do not have enough data points for medieval times to confirm the peak of emissions during the 11th century (Table 1) and the periods of low emissions that preceded and followed this peak. Of interest is the high variability of the data during the Roman period. It might be a consequence of the fact that copper production during Roman times varied greatly over short time periods (decades) as a result of pronounced changes in the need for copper, especially for coinage. The variability probably does not reflect changes in atmospheric transport from mid-latitude areas to the Arctic because it was not observed for lead (*1*) (lead production did not suffer such large short-term changes).

Changes in the fallout flux of copper at Summit during the past seven millennia can be obtained from copper concentrations measured in the ice and from the mean local ice accumulation rate of 23 g of H_2O cm^{-2} year^{-1}. Copper ranges from $\sim 0.17 \times 10^{-10}$ g cm^{-2} year^{-1} (in the pre-Roman period, $\sim$3000 years ago) to $\sim 2.2 \times 10^{-10}$ g cm^{-2} year^{-1} (in the present day). Cumulative fallout of anthropogenic copper to the whole Greenland ice cap (surface of 1.4×10^6 km^2; mean annual accumulation rate of 34 g of H_2O cm^{-2} year^{-1}) after correction for copper flux from natural sources (*27*) was $\sim$800 metric tons during the Roman period ($\sim$2500 to 1500 years ago). From the fall of the Roman Empire to the Industrial Revolution ($\sim$1500 to 220 years ago), $\sim$2000 metric tons were deposited. The cumulative deposition from 2500 years ago to the Industrial Revolution is then $\sim$2800 metric tons. These values are much higher than the cumulative deposition of copper to the Greenland ice cap from the Industrial Revolution to the present [$\sim$200 metric tons (*3*)]. This means that cumulative large-scale copper pollution of the atmosphere of the Northern Hemisphere was much larger before the Industrial Revolution than after it.

This evidence of pronounced, early, large-scale atmospheric pollution is not the only interest of the ice data presented here. They open up the possibility of future quantitative studies of the history of metal production during antiquity. Our present knowledge of this history, which was a crucial factor in social and cultural development, is essentially qualitative. It will be especially interesting to analyze concentrations of arsenic and tin to obtain quantitative estimates of when the process of smelting copper alloyed with arsenic to make hard weapons and tools began, as well as the process of smelting copper alloyed with tin, which marked the onset of the Bronze Age.

REFERENCES AND NOTES

1. S. Hong, J. P. Candelone, C. C. Patterson, C. F. Boutron, *Science* **265**, 1841 (1994).
2. I. Renberg, M. W. Persson, O. Emteryd, *Nature* **368**, 323 (1994).
3. J. P. Candelone, S. Hong, C. I. Pellone, C. F. Boutron, *J. Geophys. Res.* **100**, 16605 (1995).
4. W. Dansgaard *et al.*, *Nature* **364**, 218 (1993).
5. J. P. Candelone, S. Hong, C. F. Boutron, *Anal. Chim. Acta* **299**, 9 (1994).
6. Substantial copper contamination was found in the outermost layer of the core sections. Concentrations then decreased in the second or third layers. Good plateaus of concentrations were obtained from the second or third layers for all but one of the investigated core sections; this indicates that the plateau concentration value represents the original concentration in the ice. The only exception was the section from a depth of 294.25 m (dated 1248 years ago). For this section, we used a value extrapolated from the radial profile, which showed a continuous decrease from the outside to the inside.
7. Aluminum and sodium were measured by GFAAS with a precision of 10%. Aluminum is used to normalize copper concentrations in order to compensate for year-to-year changes in parameters such as atmospheric transport or precipitation rates.
8. S. J. Johnsen, D. Dahl-Jensen, W. Dansgaard, N. Gundestrup, *Tellus* **47B**, 624 (1995).
9. J. O. Nriagu, *Nature* **338**, 47 (1989).
10. Sulfate and ammonium were measured by ion chromatography with a precision of 10%.
11. S. Hong, J. P. Candelone, C. F. Boutron, in preparation.
12. J. O. Nriagu and J. M. Pacyna, *Nature* **333**, 134 (1988).
13. S. Hong, J. P. Candelone, M. Soutif, C. F. Boutron, in preparation.
14. C. C. Patterson, *Am. Antiq.* **36**, 286 (1971).
15. A. S. Darling, in *An Encyclopaedia of the History of Technology*, I. McNeil, Ed. (Routledge, London, 1990), pp. 47–145.
16. R. F. Tylecote, *A History of Metallurgy* (Mid-County, London, 1976).
17. C. C. Patterson, *Econ. Hist. Rev.* **25** (2nd ser.), 205 (1972).
18. J. F. Healy, *Mining and Metallurgy in the Greek and Roman World* (Thames and Hudson, London, 1988).
19. M. Lombard, *Les Métaux dans l'Ancien Monde du Ve au XIe siècle* (Mouton, Paris, 1974).
20. N. J. G. Pounds, *An Historical Geography of Europe* (Cambridge, London, 1990).
21. Archaeometallurgy Group, Beijing University of Iron and Steel Technology, *A Brief History of Metallurgy in China* (Science Press, Beijing, 1978).
22. J. Ch'en, *Bull. Sch. Orient. Afr. Stud.* **28**, 613 (1965).
23. R. F. Tylecote, *The Early History of Metallurgy in Europe* (Longman, London, 1987).
24. R. J. Forbes, in *A History of Technology, Vol. II.*, C. Singer, E. J. Holmyard, A. R. Hall, T. I. Williams, Eds. (Clarendon Press, Oxford, 1956), pp. 48–80.
25. J. O. Nriagu, in *Copper in the Environment*, J. O. Nriagu, Ed. (Wiley, New York, 1979), pp. 43–75.
26. W. E. Raatz, in *Pollution of the Arctic Atmosphere*, W. T. Sturges, Ed. (Elsevier, London, 1991), pp. 13–42.
27. Natural copper flux was calculated as the arithmetic mean of the fluxes obtained from the data points at 7760, 7260, 2960, and 2670 years ago. The value obtained was 0.25×10^{-10} g cm^{-2} year^{-1}.
28. This work is a contribution of GRIP organized by the European Science Foundation. We thank B. Stauffer and J. P. Steffensen for their assistance in ice core selection; M. Soutif, R. J. Delmas, and C.

Domergue for helpful discussions; and the national funding agencies and organizations in Belgium, Denmark, France, Germany, Iceland, Italy, Switzerland, and the United Kingdom, as well as the XII Directorate of the Commission of European Communities, for financial support. Supported by the French Ministry of the Environment (grants 92295 and 94074), the Institut National des Sciences de l'Univers, the University Joseph Fourier of Grenoble, and the Institut Universitaire de France.

20 December 1995; accepted 22 February 1996

Extraterrestrial Helium Trapped in Fullerenes in the Sudbury Impact Structure

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Fullerenes (C_{60} and C_{70}) in the Sudbury impact structure contain trapped helium with a $^3He/^4He$ ratio of 5.5×10^{-4} to 5.9×10^{-4}. The $^3He/^4He$ ratio exceeds the accepted solar wind value by 20 to 30 percent and is higher by an order of magnitude than the maximum reported mantle value. Terrestrial nuclear reactions or cosmic-ray bombardment are not sufficient to generate such a high ratio. The $^3He/^4He$ ratios in the Sudbury fullerenes are similar to those found in meteorites and in some interplanetary dust particles. The implication is that the helium within the C_{60} molecules at Sudbury is of extraterrestrial origin.

Fullerenes (C_{60} and C_{70}) have recently been identified in a shock-produced breccia (Onaping Formation) associated with the 1.85-billion-year-old Sudbury impact structure (*1*). The presence of 1 to 10 parts per million (ppm) (*1*) of fullerenes in these samples from the Onaping Formation raises questions about the origin of fullerenes and about the potential for delivery of intact organic material to Earth by a large bolide (for example, an asteroid or comet). Because the Sudbury target rocks are poor in carbon (C), we have suggested that the fullerene C was extraterrestrial in origin (*1*). There are two possible scenarios for the presence of fullerenes in the Sudbury impact deposits: (i) that fullerenes are synthesized within the impact plume from the C contained in the bolide (*1*), or (ii) that fullerenes were already present in the bolide and survived the impact event. We examine here these possible sources of the Sudbury fullerenes by searching for noble gases trapped inside the fullerene molecule.

The correlation of C and trapped noble gas atoms in meteorites is well established (*2*). Primitive meteorites contain several trapped noble gas components that have anomalous isotopic compositions. For example, Black and Pepin (*3*) found anomalous Ne values in several primitive unmetamorphosed meteorites, and Anders and co-workers (*4*) reported Kr and Xe values in the Murchison and Allende meteorites that are indicative of a presolar origin. Several C-bearing phases have been recognized as carriers of trapped noble gases, including SiC, graphite, and diamond (*5*). Fullerenes have been suggested as a carrier of noble gas components in carbonaceous chondrites (*6*); however, so far, the identification of fullerenes (C_{60} and C_{70}) is limited to a single occurrence in the Allende meteorite (*7*).

The C_{60} molecule is large enough to enclose the noble gases He, Ne, Ar, Kr, and Xe but is too small to contain diatomic gases such as N_2 or triatomic gases such as CO_2. Recent experimental work has demonstrated that (i) He is incorporated into C_{60} during fullerene formation in a He atmosphere and (ii) noble gases of a specific isotopic composition can be introduced into synthetic fullerenes at high temperatures and pressures; these gases can then be released by the breaking of one or more C–C bonds during step-heating under vacuum (*8*). The unique thermal release patterns for He encapsulated within the C_{60} molecule (He@C_{60}) are similar to the patterns for acid-resistant residues of carbonaceous chondrites (*9*), suggesting that fullerenes could be a carrier of trapped noble gases in meteorites.

To determine the noble gas abundances and isotopic ratios for the fullerenes, we undertook a systematic study of acid-resistant residues generated from samples collected at the Dowling and Capreol townships within the C-rich layer (Black Member) of the Onaping Formation (*10*). If the fullerenes were formed in the impact plume, then the isotopic ratios of the trapped gases would reflect the composition of Earth's atmosphere (that is, terrestrial) at the time of the impact. If, on the other hand, the fullerenes were present in the bolide before impact, then the isotopic ratios of the trapped gases would have an extraterrestrial signature (*3, 4, 11*).

We demineralized samples using HF-BO_3, and the carbonaceous residue was refluxed with toluene to extract fullerenes (*1, 12, 13*). An ultraviolet-visible absorption spectrum of the toluene fractions revealed a peak at 330 nm indicative of C_{60} (*14*). The toluene fractions were then analyzed by laser desorption (linear and reflectron) time-of-flight mass spectrometry (*1, 15*). All of the toluene fractions showed a strong peak at mass-to-charge ratio (m/z) of 720 atomic mass units (amu), which corresponds to C_{60}^+, and a peak at 840 amu, which corresponds to C_{70}^+ (Fig. 1A). In addition, the mass spectrum of the Capreol toluene fraction (Fig. 1B) showed a strong peak at 720 amu corresponding to C_{60}^+ and a peak at 724 amu corresponding to ^{4}He@C_{60}^+. The mass spectrum (Fig. 1B) of this sample indicates that not only are fullerenes present in the Sudbury deposits, but they contain trapped He (*16*).

Synthetic He@C_{60} molecules release He upon heating (*8*). We evaporated a separate toluene fraction from Sudbury (containing fullerenes) to dryness, heated the residues incrementally, and measured the ^{3}He and ^{4}He concentrations (Table 1) using a mass spectrometer (*17, 18*). The He concentrations in the Dowling sample correspond to 67 atoms of ^{4}He per 10^7 fullerene molecules and 37 atoms of ^{3}He per 10^{10} fullerenes. The ^{3}He release pattern for the Capreol sample (Fig. 2) is similar to the release pattern determined for synthetic fullerenes (*8*). The release of ^{3}He from the Dowling sample (Fig. 2) is somewhat greater at lower temperatures and is attributed to the preferential release of He from C_{70}. These measurements suggest that the He was released from fullerenes because no other acid-resistant He carrier phase, such as carbides or microdiamonds (*19*), was observed in our samples nor would such phases produce the release pattern characteristic of He@C_{60} that we found upon heating.

The $^3He/^4He$ ratio (sum of all heating steps) was 5.88×10^{-4} for Capreol and 5.46×10^{-4} for Dowling. These ratios are higher than the accepted solar wind value of 4.4×10^{-4} (*20*) and higher by an order of magnitude than the maximum mantle value of 4.4×10^{-5} (*21*). Some meteorites have been reported to contain He with a higher $^3He/^4He$ ratio, produced by a combination of implantation and cosmic-ray bombardment (*20*). The $^3He/^4He$ ratios measured for the Sudbury fullerenes are higher than the 3.0×10^{-4} value reported for interplanetary dust particles collected in the stratosphere and in deep-sea sediments (*22*). The implication of the $^3He/^4He$ results for the Sudbury fullerenes is that the He within the

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