Nitrogen and noble gases in micrometeorites

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Abstract—Micrometeorites (MMs) currently represent the largest steady-state mass flux of extraterrestrial matter to Earth and may have delivered a significant fraction of volatile elements and organics to the Earth’s surface. Nitrogen and noble gases contents and isotopic ratios have been measured in a suite of 17 micrometeorites recovered in Antarctica (sampled in blue ice at Cap Prudhomme) and Greenland (separated from cryoconite) that have experienced variable thermal metamorphism during atmospheric entry. MMs were pyrolized using a CO₂ laser and the released gases were analyzed for nitrogen and noble gas abundances and isotopic ratios by static mass spectrometry after specific purification. Noble gases are a mixture of cosmogenic, solar, atmospheric, and possibly chondritic components, with atmospheric being predominant in severely heated MMs. δ¹⁵N values vary between −240 ± 62‰ and +206 ± 12‰, with most values being within the range of terrestrial and chondritic signatures, given the uncertainties. Crystalline MMs present very high noble gas contents up to two orders of magnitude higher than carbonaceous chondrite concentrations. In contrast, nitrogen contents between 4 ppm and 165 ppm are much lower than those of carbonaceous chondrites, evidencing either initially low N content in MMs and/or degradation of phases hosting nitrogen during atmospheric entry heating and terrestrial weathering. Assuming that the original N content of MMs was comparable to that of carbonaceous chondrites, the contribution of nitrogen delivery by these objects to the terrestrial environment would have been probably marginal from 3.8 Gyr ago to present but could have been significant (~10%) in the Hadean, and even predominant during the latest stages of terrestrial accretion.

INTRODUCTION

Independent lines of evidence such as the predominance of carbonaceous chondrites over ordinary chondrites in the asteroid belt (Gradie et al. 1989), the occurrence of carbonaceous chondrite debris in the lunar regolith (Keays et al. 1970) and in meteorites (Gounelle et al. 2003; Zolensky et al. 1996), and remnants of a cometary shower in terrestrial sediments (Farley et al. 1998), strongly suggest that gas-rich extraterrestrial material delivered volatile elements to the surface of the Earth from accretionary stages to the present (e.g., Chyba 1990; Morbidelli et al. 2000). Mass balance considerations based on hydrogen isotopes (Dauphas et al. 1999) and on noble metal and noble gas abundances (Dauphas and Marty 2002) indicate that this flux was dominated by asteroidal material, the mass fraction of comets being less than 1%. Carbonaceous chondrites, comets, and interplanetary dust particles (IDPs) are rich in organic molecules and may have contributed directly to the prebiotic inventory of the Earth (e.g., Anders 1989; Chyba and Sagan 1992; Maurette et al. 2000). Central to the role of extraterrestrial dust as a source of organics on Earth is the fate of trapped volatiles (H, C, N, S) constituting organic molecules during atmospheric entry heating as well as during low temperature alteration at the Earth’s surface.

The flux of cosmic dust measured before atmospheric entry in the near-Earth interplanetary space yields a value of 30,000 ± 20,000 tons/yr (Love and Brownlee 1993). On Earth, the value of the flux is much debated, comprising between ~3,000 and ~35,000 tons/yr, as measured from samples taken in Greenland, Antarctica, of from deep-sea sediments (Duprat et al. 2001; Hammer and Maurette 1996; Peucker-Ehrenbrink 1996; Taylor et al. 1998). Cosmic dust represents the largest contribution of extraterrestrial matter on Earth at present, as the meteorite mass flux over the 10 g to 1 kg interval accounts for only ~3–7 tons/yr (Bland et al. 1996). IDPs collected in the stratosphere by NASA have typical sizes below 50 µm. They probably sample a mixed...
population of debris originating from the asteroidal belt and from the Edgeworth-Kuiper Belt (e.g., Brownlee 1985; Brownlee et al. 1993), with possible contributions from silicates and organics of interstellar origin (Aleon et al. 2001; Aleon et al. 2003; Messenger 2000; Messenger et al. 2003; Messenger et al. 2002). Objects in the size range 25–200 µm (exceptionally up to 400 µm and larger), labeled micrometeorites, dominate the mass flux of cosmic dust onto Earth (e.g., Love and Brownlee 1993). They are mainly collected in ice and snow from Antarctica (e.g., Duprat et al. 2003; IWata and Imae 2001; MAurette et al. 1991; Yada and Kojima 2000). Micrometeorites share mineralogical, chemical, and isotopic similarities with CM and/or CR chondrites (Engrand and MAurette 1998; Kurat et al. 1994; Engrand et al. 1999b), and D/H ratios of MMs point to an extraterrestrial, probably asteroidal (CM-CI-type) origin of trapped water (Engrand et al. 1999a). Two recent noble gas studies (Osawa and Nagao 2002; Osawa et al. 2003) also support a close connection between carbonaceous chondrites and MMs, but they suggest that some of the analyzed MMs could have a cometary origin.

IDPs with sizes <60 µm may be sufficiently decelerated during atmospheric entry to deliver their organics intact (Anders 1989). The fate of volatiles and organics in the larger size range of 50–400 µm dominating the extraterrestrial mass flux is less clear. MMs represent particles that have survived the hypervelocity impact with the Earth’s atmosphere without being volatilized. Depending on the entry velocity and angle, they have suffered various degrees and durations of heating, resulting in morphological changes from coarse-grained crystalline or fined-grained matrix to completely melted cosmic spherule, with scoriaceous intermediate textures being represented. Previous studies have shown that unmelted MMs still contain significant quantities of extraterrestrial noble gases (Olinger et al. 1990; Osawa and Nagao 2002; Osawa et al. 2003; Stuart et al. 1999), although atmospheric entry degassing has been advocated to explain the ~3–5 orders of magnitude difference in the helium content between stratospheric IDPs (Pepin et al. 2000) and MMs (Stuart et al. 1999). Nitrogen is a key element in this context because N₂ is one of the major species in air and because this element is pivotal in the synthesis of organic matter. Recently, Matrajt et al. (2003) presented N and C data for several extraterrestrial objects, including MMs, that was obtained with a nuclear microprobe. They found N concentrations between ≤100 ppm and 900 ppm, which encompasses the values found in carbonaceous chondrites. Here we report the results of a nitrogen and noble gas (He, Ne, Ar) elemental and isotopic study of a suite of MMs presenting various morphologies and therefore degrees of heating, obtained using laser extraction-static mass spectrometry. We aimed to document: 1) the nitrogen isotopic composition of MMs as a potential tracer of their origin, 2) the effect of atmospheric entry heating upon volatile degassing, and 3) the possibility that IDPs and micrometeorites might have supplied a significant fraction of terrestrial volatiles and organics to Earth.

SAMPLES

Osawa et al. (2003) have shown that there is a relation between the amount of extraterrestrial noble gases (e.g., ⁴He) and both the degree of heating during atmospheric entry and that of terrestrial weathering. In this work, 17 particles, which were characterized and kindly supplied by C. Engrand and J. Duprat, were selected in order to represent a wide range of thermal conditions from moderate heating to complete melting (e.g., crystalline, fine-grained, scoria, cosmic spherule) (Fig. 1, Table 1). The extraterrestrial origin of these particles is attested by 1) their chondritic compositions as measured by energy dispersion X-ray (EDX) analysis (Fig. 1) associated with a fine-grained texture for some of them, and 2) the presence of a magnetite rim, which results from atmospheric entry heating (e.g., Olinger et al. 1990; Engrand and Maurette 1998).

Particles from the 99-11 series (Table 1) were extracted from the 100–400 µm size fraction of glacial sand collected from melting and filtering blue ice at Cap Prudhomme during the 1994 Antarctic field expedition (Maurette et al. 1994; Maurette et al. 1991). Each micrometeorite was split into three fragments, one for mineralogical characterization, another one for this work, and the last one for other analyses. Particles labeled 01-08, 01-68, and 01-69 (Table 1) were extracted from Greenland cryoconite collected during the Blue Lake II field expedition (Maurette et al. 1988). Large sizes of the last series (250–550 µm) were selected in order to provide large enough fragments for this work and for the analysis of ²⁶Al and ¹⁰Be by accelerator mass spectrometry on the same individual grains. Unmelted samples of such large sizes are very rare in the flux of micrometeorites. In this series, we could only analyze three unmelted grains, the remaining five samples being cosmic spherules. For the first 99-11 series, the weights of the MM fragments used in this study were calculated from the measurement of the minor and major axis of the grains, assuming an ellipsoid geometry and a density of 2.5 g/cm³. The fragments taken from the larger micrometeorites (01-series) were individually weighed using repetitive measurements with a microscale, resulting in an uncertainty on the MM’s mass of about 1 µg (Table 1).

EXPERIMENTAL

Gases were extracted under ultra-high vacuum using the laser extraction–static mass spectrometry technique developed in CRPG Nancy (Hashizume and Marty 2004; Hashizume et al. 2002; Humbert et al. 2000; Libourel et al. 2003; Wieler et al. 1999). MMs were cleaned in high-grade acetone. Samples were then loaded in pits of the laser
chamber, where they were heated overnight at a mild temperature of 100 °C under high vacuum ($P = 10^{-8}$ Torr). They were then left for six weeks at least in high vacuum ($3 \times 10^{-9}$ Torr) in order to promote further removal of terrestrial contamination. Individual MMs were pyrolyzed using a defocused continuous CO$_2$ laser beam with a wavelength of 10.6 μm. Stepwise heating could not be performed due to the very low amount of nitrogen in the samples, so a single extraction was done at 1600 °C. The evolved gas phase was split volumetrically into two fractions for noble gas and nitrogen analyses. The noble gas aliquot was purified using Ti sponge getters cycled between 723 K and room temperature, and noble gases were analyzed sequentially after cryogenic separation. During the course of this study, the noble gas
Table 1a. Noble gas and nitrogen results for micrometeorites. The mass is that of the analyzed fragment, not that of the whole micrometeorite. Blank/total is the ratio of the blank signal for the isotope over the total signal during sample analysis for the same isotope.

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Texture</th>
<th>Mass µg</th>
<th>$^{4}\text{He}$ $10^{-10}$ mol/g</th>
<th>+/−</th>
<th>Blank/total ($^{4}\text{He}$)</th>
<th>+/−</th>
<th>$^{3}\text{He}/^{4}\text{He}$ $10^{-4}$</th>
<th>+/−</th>
<th>$^{20}\text{Ne}$ $10^{-10}$ mol/g</th>
<th>+/−</th>
<th>Blank/total ($^{20}\text{Ne}$)</th>
<th>+/−</th>
<th>$^{21}\text{Ne}/^{22}\text{Ne}$ +/−</th>
</tr>
</thead>
<tbody>
<tr>
<td>99-11-61</td>
<td>Crystalline</td>
<td>3.0</td>
<td>47.0</td>
<td>3.9</td>
<td>0.45</td>
<td>1.7</td>
<td>0.78</td>
<td>0.07</td>
<td>5.8</td>
<td>0.2</td>
<td>0.13</td>
<td>1.2</td>
<td>1.7</td>
</tr>
<tr>
<td>99-11-13</td>
<td>Crystalline</td>
<td>3.1</td>
<td>47.4</td>
<td>3.8</td>
<td>0.44</td>
<td>208</td>
<td>3.64</td>
<td>0.36</td>
<td>13.1</td>
<td>0.4</td>
<td>0.06</td>
<td>12.9</td>
<td>1.7</td>
</tr>
<tr>
<td>99-11-23</td>
<td>Crystalline</td>
<td>7.7</td>
<td>6.6</td>
<td>1.5</td>
<td>0.70</td>
<td>142</td>
<td>2.16</td>
<td>5.0</td>
<td>8.3</td>
<td>0.3</td>
<td>0.04</td>
<td>11.9</td>
<td>1.6</td>
</tr>
<tr>
<td>99-11-71</td>
<td>Scoria/crystalline</td>
<td>7.7</td>
<td>22.6</td>
<td>1.5</td>
<td>0.40</td>
<td>11.0</td>
<td>0.6</td>
<td>0.487</td>
<td>0.044</td>
<td>0.88</td>
<td>0.05</td>
<td>0.28</td>
<td>16.5</td>
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<td>99-11-21</td>
<td>Scoria/fine-grained</td>
<td>19.4</td>
<td>1.7</td>
<td>0.6</td>
<td>0.78</td>
<td>7.7</td>
<td>0.3</td>
<td>4.56</td>
<td>1.62</td>
<td>0.39</td>
<td>0.02</td>
<td>0.26</td>
<td>11.2</td>
</tr>
<tr>
<td>99-11-53</td>
<td>Scoria</td>
<td>n.m.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>99-11-41</td>
<td>Scoria</td>
<td>3.0</td>
<td>284</td>
<td>5</td>
<td>0.12</td>
<td>34.3</td>
<td>1.6</td>
<td>0.121</td>
<td>0.006</td>
<td>0.83</td>
<td>0.13</td>
<td>0.51</td>
<td>−8.7</td>
</tr>
<tr>
<td>99-11-51</td>
<td>Scoria</td>
<td>10.1</td>
<td>5.6</td>
<td>1.2</td>
<td>0.67</td>
<td>8.5</td>
<td>0.5</td>
<td>1.51</td>
<td>0.32</td>
<td>0.22</td>
<td>0.04</td>
<td>0.54</td>
<td>−9.6</td>
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<tr>
<td>99-11-33</td>
<td>Cosmic spherule</td>
<td>4.0</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>01-69-05</td>
<td>Scoria/cosmic spherule</td>
<td>48.9</td>
<td>7.0</td>
<td>1.0</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
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</tr>
<tr>
<td>01-69-03</td>
<td>Scoria/Xtal (terrestrial?)</td>
<td>14.0</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.235</td>
<td>0.063</td>
</tr>
<tr>
<td>01-69-01</td>
<td>Scoria</td>
<td>5.3</td>
<td>8.8</td>
<td>1.3</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.172</td>
<td>0.098</td>
</tr>
<tr>
<td>01-68-04</td>
<td>Cosmic spherule</td>
<td>45.9</td>
<td>1.3</td>
<td>0.2</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.032</td>
<td>0.015</td>
</tr>
<tr>
<td>01-68-18</td>
<td>Cosmic spherule</td>
<td>66.9</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.037</td>
<td>0.013</td>
</tr>
<tr>
<td>01-08-01</td>
<td>Cosmic spherule</td>
<td>8.0</td>
<td>10.3</td>
<td>1.5</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.423</td>
<td>0.121</td>
</tr>
<tr>
<td>01-68-22</td>
<td>Cosmic spherule</td>
<td>47.4</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.071</td>
<td>0.019</td>
</tr>
<tr>
<td>01-68-03</td>
<td>Cosmic spherule</td>
<td>37.3</td>
<td>0.32</td>
<td>0.05</td>
<td>n.d.</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.056</td>
<td>0.024</td>
</tr>
</tbody>
</table>

n.m. = not measured; n.a. = not analyzed; n.d. = not detected. Errors are 1σ.
Table 1b. Noble gas and nitrogen results for micrometeorites. The mass is that of the analyzed fragment, not that of the whole micrometeorite. Blank/Total is the ratio of the blank signal for the isotope over the total signal during sample analysis for the same isotope.

<table>
<thead>
<tr>
<th>Sample#</th>
<th>Texture</th>
<th>Mass µm</th>
<th>$^{28}$N$_2$ 10$^4$ mol/g</th>
<th>Blank/total N ppm</th>
<th>$^{15}$N‰ +/−</th>
<th>$^{36}$Ar 10$^{-10}$ mol/g</th>
<th>$^{40}$Ar/$^{36}$Ar +/−</th>
<th>$^{38}$Ar/$^{36}$Ar +/−</th>
</tr>
</thead>
<tbody>
<tr>
<td>99-11-61</td>
<td>Crystalline</td>
<td>13.0</td>
<td>3.22 0.13 0.46 90 78 37</td>
<td>0.49 0.01 0.38</td>
<td>48 9</td>
<td>0.216 0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-11-13</td>
<td>Crystalline</td>
<td>3.1</td>
<td>2.85 0.13 0.51 80 −240 62</td>
<td>1.60 0.02 0.15</td>
<td>17 3</td>
<td>0.185 0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>99-11-23</td>
<td>Crystalline</td>
<td>7.7</td>
<td>2.16 0.07 0.27 60 14 16</td>
<td>0.68 0.01 0.15</td>
<td>6.1 2.3</td>
<td>0.198 0.006</td>
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<td></td>
</tr>
<tr>
<td>99-11-71</td>
<td>Scoria/crystalline</td>
<td>7.7</td>
<td>2.06 0.07 0.28 58 75 18</td>
<td>0.10 0.00 0.53</td>
<td>75 16</td>
<td>0.226 0.017</td>
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<tr>
<td>99-11-21</td>
<td>Scoria/fine-grained</td>
<td>19.4</td>
<td>1.71 0.05 0.13 48 81 7</td>
<td>0.058 0.001 0.44</td>
<td>40 11</td>
<td>0.234 0.013</td>
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</tr>
<tr>
<td>99-11-53</td>
<td>Scoria</td>
<td>n.m.</td>
<td>−      −</td>
<td>−</td>
<td>− − −</td>
<td>− − −</td>
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</tr>
<tr>
<td>99-11-41</td>
<td>Scoria</td>
<td>3.0</td>
<td>7.88 0.25 0.19 165 206 12</td>
<td>0.32 0.01 0.48</td>
<td>330 23</td>
<td>0.225 0.015</td>
<td></td>
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</tr>
<tr>
<td>99-11-51</td>
<td>Scoria</td>
<td>10.1</td>
<td>2.51 0.08 0.18 53 91 10</td>
<td>0.098 0.002 0.48</td>
<td>64 13</td>
<td>0.193 0.013</td>
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<tr>
<td>99-11-33</td>
<td>Cosmic spherule</td>
<td>4.0</td>
<td>4.13 0.14 0.27 87 −63 53</td>
<td>0.048 0.003 0.83</td>
<td>−327 −</td>
<td>− − −</td>
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<tr>
<td>01-69-05</td>
<td>Scoria/cosmic spherule</td>
<td>48.9</td>
<td>1.48 0.07 0.08 41.5 −5</td>
<td>10 0.038 0.004 0.23</td>
<td>613 26</td>
<td>0.195 0.007</td>
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<tr>
<td>01-69-03</td>
<td>Scoria/Xtal (terrestrial?)</td>
<td>14.0</td>
<td>0.48 0.19 0.24 13.5 −33 44</td>
<td>0.017 0.005 0.71</td>
<td>5790 977</td>
<td>0.187 0.022</td>
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<tr>
<td>01-69-01</td>
<td>Scoria</td>
<td>5.3</td>
<td>0.29 0.05 0.39 8.2 −</td>
<td>0.056 0.015 0.65</td>
<td>320 41</td>
<td>0.185 0.020</td>
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<tr>
<td>01-68-04</td>
<td>Cosmic spherule</td>
<td>45.9</td>
<td>1.26 0.07 0.09 35.4 −14 12</td>
<td>0.0069 0.0018 0.64</td>
<td>398 42</td>
<td>0.176 0.016</td>
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<tr>
<td>01-68-18</td>
<td>Cosmic spherule</td>
<td>66.9</td>
<td>0.33 0.04 0.36 9.1 −</td>
<td>0.0069 0.0014 0.55</td>
<td>407 32</td>
<td>0.219 0.013</td>
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<tr>
<td>01-08-01</td>
<td>Cosmic spherule</td>
<td>8.0</td>
<td>1.53 0.45 0.08 42.9 −22 9</td>
<td>0.060 0.012 0.54</td>
<td>283 24</td>
<td>0.165 0.012</td>
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</tr>
<tr>
<td>01-68-22</td>
<td>Cosmic spherule</td>
<td>47.4</td>
<td>0.15 0.01 0.42 4.1 −</td>
<td>0.012 0.002 0.49</td>
<td>364 28</td>
<td>0.194 0.013</td>
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<td></td>
</tr>
<tr>
<td>01-68-03</td>
<td>Cosmic spherule</td>
<td>37.3</td>
<td>0.25 0.07 0.46 7.0 −</td>
<td>0.015 0.003 0.50</td>
<td>456 31</td>
<td>0.224 0.012</td>
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<td></td>
</tr>
<tr>
<td>Murchison*</td>
<td>1 grain</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1st step</td>
<td></td>
<td>20.0</td>
<td>0.8 0.0002 560 23.7 2.4 0.227</td>
<td>0.007 0.11</td>
<td>42.7 5.2</td>
<td>0.189 0.013</td>
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<tr>
<td>2nd step</td>
<td></td>
<td>5.82</td>
<td>0.23 0.0006 163 33.7 2.4 0.169</td>
<td>0.005 0.14</td>
<td>21.8 3.2</td>
<td>0.189 0.011</td>
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<td>1.52</td>
<td>0.12 0.18 0.43 67.6 8.0 0.038</td>
<td>0.001 0.43</td>
<td>127.0 26.9</td>
<td>0.180 0.008</td>
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<td>25.8</td>
<td>1.0 723 26.0 3.2 0.430 0.002</td>
<td></td>
<td>30.8 7.9</td>
<td>0.186 0.010</td>
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<td>1st step</td>
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<td>28.0</td>
<td>2.2 0.0001 781 19.9 2.4 0.309</td>
<td>0.009 0.07</td>
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<td>29.6</td>
<td>1.0 828 20.9 2.8 0.511 0.015</td>
<td></td>
<td>20.3 4.2</td>
<td>0.185 0.016</td>
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</tr>
</tbody>
</table>

*aThese analyses were carried out in a previous session during which the analyzer was optimized for N$_2$ analysis, resulting in a N$_2$ blank of 7 × 10$^{-13}$ mol.

n.m. = not measured, n.a. = not analyzed, n.d. = not detected. Errors are 1σ.
blanks were: $^{4}\text{He} = 1.17 \pm 0.12 \times 10^{-14}$ mol (n = 21), $^{20}\text{Ne} = 2.63 \pm 0.37 \times 10^{-17}$ mol (n = 35), $^{36}\text{Ar} = 9.07 \pm 0.37 \times 10^{-17}$ mol (n = 35). Blank noble gas isotopic ratios were atmospheric within uncertainties. The set of samples labeled 01-08, 01-68, and 01-69 was analyzed in different mass spectrometer (MS) conditions. The MS source was optimized to analyze heavy noble gases in addition to N, thus decreasing the helium sensitivity by a factor of $\sim 3$. This setting resulted in the inability to analyze He isotopic ratios because, in addition to the loss of sensitivity, these larger-sized micrometeorites necessarily contained much lower amounts of He compared to the first sample set, due to increased atmospheric entry heating conditions (Table 1). $^{4}$He isotopic ratios were found to be atmospheric within uncertainties and are not reported here.

The nitrogen aliquot was purified statically using a CuO furnace cycled between 723 K and 993 K and a cold trap (a U-shaped glass tube held at 93 K). Purified nitrogen was analyzed using the same on-line MS as the one used for noble gases (Dauphas and Marty 1999; Hashizume and Marty 2004; Hashizume et al. 2002; Humbert et al. 2000; Libourel et al. 2003; Marty and Humbert 1997; Wieler et al. 1999). The best setting of the mass spectrometer source in term of nitrogen blank and reduced interference of C bearing species was obtained using a low-emission current (trap current $\leq 100 \mu$A) (Hashizume and Marty 2004), resulting in extremely low nitrogen blank of $2-7 \times 10^{-13}$ mol $\text{N}_2$ ($6-20 \text{ pg N}$). However, with such low emission current, the analysis of noble gases and particularly of helium was not possible; we compromised by using a higher emission current (trap current of 200 $\mu$A). For the present analyses, special care was taken to ensure a reproducible blank level. Thirty blanks were measured, yielding a mean value of $4.46 \pm 0.28 \times 10^{-12}$ mol $\text{N}_2$, allowing confident blank correction. It nevertheless constituted a significant fraction of the sample signal, which accounts for the large uncertainties on N isotopic ratios (Table 1).

The line and mass spectrometer are routinely calibrated for N abundance and isotopic ratio using a known amount of atmospheric N, which is submitted to exactly the same purification and analysis procedure as the sample gas. This standard gas allows one to compute the analyzer sensitivity for N (typically $3.6 \times 10^{-4}$ A/Torr for a trap current of 200 $\mu$A) (Humbert et al. 2000) and to correct for isotope discrimination (typically 10%). Because the amount of nitrogen extracted during the course of this study varied between $0.81 \times 10^{-11}$ moles and $6.8 \times 10^{-11}$ moles with a mean value of $2.4 \times 10^{-11}$ moles, it was important to check the linearity of the system over the analytical range, especially toward very low values. Figure 2 gives the calibration curve for nitrogen with a trap current of 200 $\mu$A, which is identical to the one used for the analysis of micrometeorites, which encompasses the range of N amounts extracted from MMs. The nitrogen analytical system shows an excellent linearity over two orders of magnitude, demonstrating that the response of this system does not depend on the analyzed amount over the range of abundances relevant to the analysis of microsamples including MMs.

As an independent test of the reliability of the method, a few grains of Murchison (CM2) with individual masses of 200–270 $\mu$g were analyzed for N and Ar (Table 1). Temperature steps were obtained by increasing the power of the laser and correspond roughly to 800 °C (1st step) 1000 °C (2nd step), and 1600 °C (3rd step). The measured nitrogen contents (723 ppm and 828 ppm) are in agreement with those measured previously by either static or dynamic mass spectrometry on larger sample aliquots (345–367 ppm, Lewis et al. 1983; 760 ppm, Robert and Epstein 1982; 830 ppm, Kung and Clayton 1978; 967 ppm, Grady et al. 2002; 968 ppm, Sephton et al. 2003). Our $\delta^{15}$N data of $+21\%$ and $+26\%$ are somewhat lower than most reported values around +40% (although lower values have been found by Grady et al. 2002, and could be attributed to heterogeneous N components). Assuming that part of the N is terrestrial contaminant, a corrected N abundance of 435–465 ppm is still within the range of literature values. To further check the accuracy of the system, we also analyzed a fragment of Orgueil (mass = 90 $\mu$g) during the course of a study aimed to document AMM degassing upon heating (Toppani et al. 2003) and found a concentration of 1295 ± 38 ppm with $\delta^{15}$N = 57 ± 8‰, compatible with literature data (1476 ppm with $\delta^{15}$N = 46‰ and 1360 ppm with $\delta^{15}$N = 39‰; see compilation in Kerridge 1985 and references therein). Finally, we note that some nitrogen could have been lost during acetone cleaning which could have removed indigenous, solvent-soluble organic compounds. As discussed by Wright et al. (1997) in the case of carbon in MMs, these components are comparatively minor by analogy with carbonaceous chondrites and there is a good chance that such components would have been lost by atmospheric heating. The same cleaning technique was applied to the fragments of Murchison and Orgueil analyzed this study without apparent effect on their N content.

RESULTS AND DISCUSSION

Noble Gases in MMs

The He and Ne contents and isotopic ratios (Table 1) of the 99-11 series confirm a predominantly solar origin, likely to be SEP (solar energetic particles) rather than SW (solar wind) (Olinger et al. 1990; Osawa and Nagao 2002; Osawa et al. 2003; Stuart et al. 1999). Some of the samples have lower $^{3}$He/$^{4}$He ratios, suggesting that the trapped $^{3}$He/$^{4}$He ratios could be masked by contribution of in situ produced radiogenic $^{4}$He. Sample 99-11-41 (scoria) has a significantly low $^{3}$He/$^{4}$He ratio of $0.12 \times 10^{-4}$ and a $^{36}$Ar/$^{39}$Ar ratio close to the air value, evidencing extensive interaction with the atmosphere (Table 1). Sample 99-11-23 has a $^{3}$He/$^{4}$He ratio of
21.6 ± 5.0 × 10^-4, which is significantly higher than values expected for solar corpuscular irradiation, thus indicating contribution of 3He of presumably cosmogenic origin. The corresponding cosmic ray exposure (CRE) age is ~2 Myr, assuming galactic cosmic ray (GCR) + solar cosmic ray (SCR) irradiation, which is within the upper range of CRE ages reported for MMs (Olinger et al. 1990; Osawa and Nagao 2002; Osawa et al. 2003; Stuart et al. 1999).

As expected from their large size, particles belonging to the 01-08, 01-68, and 01-69 series present evidence of extensive noble gas degassing and interactions with atmospheric gases. Notably, the He contents of these samples is lower than those of smaller particles such as the 99-11 ones. As noted by one reviewer (R. Becker), however, the smaller He content of large particles could also be the result of a smaller surface/volume ratio. Many micrometeorites presumably spent significant time exposed to solar wind, as evidenced by the solar or SEP nature of Ne isotopes. Larger particles with lower surface/volume ratios will have lower solar-derived gas content for a given exposure time. Sample 01-69-01 presents a clear enrichment in 21Ne, which is presumably of cosmogenic origin (Fig. 3). Uncertainties on the nature of involved cosmic rays (e.g., solar or galactic, Osawa and Nagao 2002) do not allow definite assessment of space exposure duration, which may be within 0.4–5 Myr using the formalism of Osawa et al. (2003). A space exposure duration of ~10^5–10^6 yr is reasonable for particles in this size range of ~200 µm (e.g., Flynn 1989).

The 40Ar/36Ar ratios range from <10, which is typical of unmelted MMs (Osawa and Nagao 2002) up to values similar to air or higher (Table 1). One of the two 99-11 samples having high 40Ar/36Ar ratios is, not surprisingly, a cosmic spherule (99-11-33) in which no He nor Ne was detected and which has a δ15N value indistinguishable from that of air within uncertainty. The other 99-series sample (99-11-41) is a scoria presenting the lowest 3He/4He ratio among MMs of this study. However, it also presents the highest δ15N value, suggesting a mixed origin for volatile elements. The 01-series MMs have particularly high 40Ar/36Ar ratios. Sample 01-69-03 which presents an exceptionally high 40Ar/36Ar ratio of 5,800 together with Ne and N isotopic ratios not resolvable from atmospheric ones (Table 1). There is suspicion based on petrological observations that this specific particle only could have a terrestrial origin (Engrand, personal communication).

3He, 20Ne, and 36Ar contents of the 99-series samples correlate well (see Fig. 4 for 20Ne and 36Ar), with correlations coefficients (R^2) of 0.938, 0.914, and 0.910 for the 20Ne, 36Ar, 3He, 20Ne, and 3He, 36Ar correlations, respectively. These correlations are not a result of atmospheric contamination, because: 1) air contribution to 36Ar (and by consequence to 20Ne) is limited as judged from 40Ar/36Ar ratios often lower than the atmospheric value, and 2) 36Ar correlates with 3He (not shown) and with 20Ne (Fig. 4), for which purely atmospheric origins are unlikely. They instead represent variable loss of a MM noble gas component. Ne isotopic ratios as well as the 20Ne versus 36Ar correlation suggest that the trapped component is formed from a mixture of solar noble gases and chondritic (Q-type) noble gases (Fig. 4).
Although this mixed origin is consistent with previous noble gas studies of MMs showing the occurrence of Q-like noble gases (Osawa and Nagao 2002; Osawa et al. 2003), it must also be noted that He, Ne, and Ar abundance ratios are consistent with a fractionated solar composition enriched in Ar relative to He and Ne, as proposed in the case of IDPs (Kehm et al. 2002).

The abundances of trapped $^3$He, $^{20}$Ne, and $^{36}$Ar vary according to the degree of atmospheric entry heating. They decrease in the following order (Fig. 4): crystalline > scoria > cosmic spherule. Notably, the $^3$He, $^{20}$Ne, and $^{36}$Ar contents of crystalline MMs ($^{36}$Ar up to $1.6 \times 10^{-10}$ mol/g and $^{20}$Ne up to $13 \times 10^{-10}$) (Table 1) are up to two orders of magnitude higher than the average CI-CM compositions (Fig. 4). The fact that these particles have suffered to varying extent heating suggests that the pre-entry contents were even higher. For example, one scoria/crystalline AMM (99-11-71) has a close-to-chondritic noble gas content. The morphological transition of carbonaceous chondritic material towards scoriaceous structure requires flash heating during atmospheric entry (Alexander and Love 2001; Greshake et al. 1998; Love and Brownlee 1991; Toppani et al. 2001). Heating of Orgueil fragments for 5–10 sec at 1350 °C with log fO$_2 = -3.26$ can reproduce the textures observed for scoriaceous MMs (Toppani et al. 2001). Under these conditions, chips of Orgueil have lost 80%–90% of their original Ne and Ar contents (Toppani et al. 2003). It is therefore likely that this particle contained up to one order of magnitude more noble gases than the observed contents. High Ne contents of MMs, together with $^{20}$Ne/$^{22}$Ne ratios between solar wind and SEP values, are due to implantation of a solar-derived component during space exposure of the MMs. However, these MMs also present very high $^{36}$Ar contents (for which the $^{40}$Ar/$^{36}$Ar ratios rule out a purely atmospheric origin) which, together with $^{20}$Ne/$^{36}$Ar ratios intermediate between solar and chondritic (Fig. 4) and the identification of Q-like noble gases in MMs (Osawa and Nagao 2002), support the occurrence of a gas-rich material (although light noble gases could also derive from a fractionated solar component; see above).

The possibility that some of the MMs analyzed here were originally extremely rich in gases compared to gas-rich meteorites such as carbonaceous chondrites suggests that some of these particles could be cometary in origin. Comets are likely to be rich in volatile elements including noble gases as they originate from greater heliocentric distance than asteroids (although a definite assessment of the volatile content of cometary material will have to wait for the return of the Stardust spacecraft). A cometary origin for some of the MMs recovered on Earth is consistent with only ~50% of cosmic dust in the 10–100 µm size range coming from the asteroid belt (Dermott et al. 1996), thus requiring other sources of dust. Comet P/Halley may contribute of the order of 1% of the zodiacal dust during its maximum life of $10^5$ years, and estimates of the Edgeworth-Kuiper Belt (EKB) parent body population suggest that the surface density of EKB dust produced by collisional events might be
comparable to that of the zodiacal cloud present in the inner solar system (Backman et al. 1995), depending on the efficiency of contribution of EKB dust in the inner solar system. Independently, studies of IDPs suggest that some of these objects are cometary (Aléon et al. 2003; Bradley 1994; Brownlee et al. 1995; Messenger 2000; Thomas et al. 1992).

Nitrogen in MMs

The nitrogen content of MMs from 4 ppm to 165 ppm (Table 1) is one to two orders of magnitude lower than the one observed in CI, CM, and CR chondrites (300–2000 ppm, e.g., Kerridge 1985). Furthermore, there is no systematic variation with the degree of heating, contrary to the case of noble gases. Matrajt et al. (2003) analyzed the nitrogen content of a suite of MMs using nuclear microprobe analysis (NM). On eleven MM samples analyzed by these authors, six belonged to the same Antarctic 99-series, allowing direct comparison of results from two different analytical techniques. Aliquots from two common samples were analyzed by both NM and static MS: sample 99-11-61 gave compatible results (below the detection limit of 100 ppm for NM and 90 ppm for MS) but sample 99-11-21 yielded 500 ppm by NM and 48 ppm by MS. Overall, the mean N content of 99-series MM analyzed by Matrajt et al. (2003) is 370 ppm, whereas it is only 50 ppm in the present study. This discrepancy could result from sampling heterogeneity in the 99-series or from internal heterogeneity of samples due to the fact that the NM analyzes the surface of the MMs within a depth of ~3 µm, whereas MS is a bulk analysis technique. However, the systematic bias between the two techniques suggests that sample heterogeneity may not be the only source of discrepancy. It is possible that the nuclear microprobe analysis used by Matrajt et al. (2003) might have led to overestimation of the N content of MMs. We note that the nitrogen standard used by Matrajt et al. (2003) was TiN (equivalent to 220,000 ppm N), whereas the range of N contents in MMs is three orders of magnitude lower. Matrajt et al. (2003) analyzed fragments of Murchison and Tagish Lake and reported 1400 ppm N for the former, to be compared with the range of 365–968 ppm N found by laboratories using mass spectrometry, and 1500–2200 ppm N for the latter, to be compared with 1200 ppm measured by Grady et al. (2002). These differences suggest an offset of a few hundreds of ppm for the analysis of N by NM in the hundreds of ppm range.

The low abundances of N in Antarctic and Greenland MMs are in line with low C contents in MMs reported by Wright et al. (1997), attributed to degradation of organics during atmospheric entry and terrestrial residence. Alternatively, it is possible that the MMs did not contain N (and C) in chondritic proportion, and that the noble gas load was from contribution of a solar or solar-nebula-like component. Indeed, the solar (and presumably the solar nebula) component presents a nitrogen to noble gas ratio (solar $^{14}$N/$^{36}$Ar = 37) (Anders and Grevesse 1989) 3–4 orders of magnitude lower than the range of chondritic values ($^{14}$N/$^{36}$Ar $\sim$3 $\times$ 10$^6$ for Orgueil). This possibility is, however, not supported by evidence for a genetic relationship between MMs and carbonaceous chondrites (Engrand and Maurette 1998; Kurat et al. 1994), and by the occurrence of Q-like noble gases in fresh MMs (Osawa and Nagao 2002; Osawa et al. 2003). If nitrogen initial abundance was similar to that of carbonaceous chondrites, then the drastic loss of nitrogen from MMs, compared to the case of noble gases, requires that nitrogen and trapped noble gases are hosted in different phases, or in sites having different activation energies. A major fraction of noble gases is from the solar corpuscular irradiation and is therefore implanted in silicates. If MMs contain significant amounts of Q noble gases, the different behavior of noble gases and nitrogen must have another origin. In primitive meteorites, the main host phase of nitrogen is a major carbonaceous component (Robert and Epstein 1982) thought to be aromatic organic matter (Engel and Macko 2001; Epstein et al. 1987). Degradation of this phase is promoted by heating under high fO2 (Robert and Epstein 1982). Chondritic (Q-type) noble gases are trapped in an acid-resistant, highly evolved carbon-rich phase (Lewis et al. 1975) and their release requires heating at high temperature (>1000 °C under vacuum) (e.g., Verchovsky et al. 2002 and references therein). Noble gases are thought to be physically trapped in a complex network of cage-like structures (Zadnik et al. 1985), whereas nitrogen is part of the aromatic structure of a presumably different type of organic matter. In a recent study of the siting and degassing behavior of C and noble gases from a suite of enstatite chondrites, Verchovsky et al. (2002) concluded that for these meteorites, and probably for other chondritic groups, the major carbonaceous component is not the carrier of trapped noble gases. Our study suggests that the nitrogen in MMs may be associated with a major carbon component prone to degradation during heating under oxidative condition, whereas the noble gases trapped in MMs could better survive oxidative degradation, as they may be hosted by a Q-like, structurally different, phase.

The $^{15}$N values of MMs (Table 1, Fig. 5) are within the range of values observed in carbonaceous chondrites, and are compatible with a relationship with CM and CR chondrites inferred from petrological and geochemical analogies (Kurat et al. 1994; Engrand and Maurette 1998). N isotope data also evidence extensive contribution of terrestrial N, especially those of the 01-series. Even for the less-degraded MMs, terrestrial contamination cannot be ruled out since no stepwise heating experiment was possible (although pre-cleaning of the samples in acetone is likely to have removed a major fraction of contaminants, as indicated by a carbon study of MMs; Wright et al. 1997). The interpretation of MM data in terms of a genetic relationship to potential precursor phases is therefore extremely difficult because it is impossible to
assess quantitatively the fraction of contaminant N and because uncertainties on $\delta^{15}N$ values are large due to important blank corrections. The restricted present set of data nevertheless suggests that several meteoritic signatures have survived. The low N content of MMs, compared to carbonaceous chondrites, suggests that MMs might have lost their more labile N components while keeping the refractory ones, which have been shown to present highly variable $\delta^{15}N$ values (e.g., Robert and Epstein 1982; Lewis et al. 1983). Meteoritic nitrogen is mostly hosted by (e.g., Sephton et al. 2003 and references therein): 1) free organic matter soluble in most solvents and which makes a minor fraction, this component might have been lost through atmospheric entry heating, terrestrial alteration and/or sample cleaning, 2) macromolecular, insoluble organic matter resistant on Hf/HCl treatment, part of this matter has probably been highly degraded, 3) refractory organic matter that resists most treatments and which should be more prone to survive in MMs, and 4) specific nitrogen components characterized by extreme isotopic compositions and hosted by nanodiamonds and several types of presolar phases (e.g., SiN, TiN...). MM data show that there exists a $^{15}$N-rich ($\delta^{15}N > 50\%$) component that might be reminiscent of macromolecular, CR-type nitrogen (e.g., Kerridge 1985; Grady et al. 2002; Sephton et al. 2003), and/or of the $^{15}$N-rich end-member often seen at both low and high temperature in residues of carbonaceous chondrites (Grady et al. 2002; Sephton et al. 2003). Sample 99-11-13 (crystalline) has a very negative $\delta^{15}N$ value of $\sim -240\%$, which could represent the very light N component found in acid resistant residues of carbonaceous chondrites ($\delta^{15}N$ down to $-271\%$; Lewis et al. 1983) and later on identified in nanodiamonds ($\delta^{15}N$ down to $-350\%$; Russell et al. 1996). The abundance of nanodiamonds in carbonaceous chondrites is 400 ppm and that of N in nanodiamonds from these meteorites is $\sim 4,000$–$10,000$ ppm (Russell et al. 1996). The abundance of light N in carbonaceous chondrites should be around 2–5 ppm, whereas the one observed in particle 99-11-13 is 80 ppm. Therefore, a factor of $\sim 20$ enrichment in nanodiamonds is required for this MM to account for the data, which is quite extreme but not impossible. Alternatively, the light $\delta^{15}N$ signature of this MM could point out to a predominantly solar composition for trapped nitrogen ($\delta^{15}N \leq -240\%$, Hashizume et al. 2000; $\delta^{15}N = -370\%$, Owen et al. 2000), or, in line with the highest noble gas content of this particle among all analyzed MMs, a cometary origin for nitrogen, as a light N component has been documented in comet Hale-Bopp (Jewitt et al. 1997).

**Micrometeorites as a Source of Terrestrial Nitrogen?**

The present study suggests strongly that nitrogen originally trapped in MMs with a size range of 100–400 $\mu$m is efficiently delivered to the Earth’s atmosphere and hydrosphere. This range corresponds to the maximum mass delivery of meteoritic matter to Earth. An estimate of the nitrogen delivery flux can be assessed by assuming an initial N content of $\sim 1,000$ ppm, characterizing carbonaceous chondrites and in particular CM chondrites. This value may be a lower limit, since some of the micrometeorites might contain a larger initial N content, as suggested by high trapped noble gas contents of some of the MMs. IDPs can contain N at the percent level (Aléon et al. 2003), but their
mass flux is ~0.01 times that of micrometeorites (Love and Brownlee 1993), so that their nitrogen contribution appears at best comparable to the MM flux. Comets contain about 10,000–40,000 ppm N (see Dauphas and Marty 2002 and references therein) and might be the parent bodies of a significant fraction of cosmic dust. However, mass balance considerations involving volatile and siderophile elements together with D/H ratios of the terrestrial oceans suggest that the bulk cometary contribution to the terrestrial inventory of volatile elements was very limited, of the order of $10^3$ relative to the total mass of contributors (Dauphas et al. 1999). Available N isotope data for comets ($\delta^{15}$N = −160 ± 120‰ for HCN in the coma of Hale-Bopp, Jewitt et al. 1997; $\delta^{15}$N ~ +940±30−340‰ in CN radicals of Hale-Bopp and C2000 WM1, Arpigny et al. 2003) do not support extensive contribution from these objects, although a combination of the different N components could in principle produce the terrestrial value. We make the conservative hypothesis that the initial nitrogen content of cosmic dust is on the order of ~1000 ppm, probably within a factor of 2. It must be noted that the nitrogen content of cosmic dust necessary to account for N isotope variations in lunar soils has been estimated at ~1000 ppm on average over most of the lunar history (Hashizume et al. 2002).

The micrometeorite flux might not have varied dramatically since 3.8 Gyr ago, except for a possible increase in the last 0.5 Gyr (Culler et al. 2000; Hashizume et al. 2002). A near-constant planetary contribution within a factor of 2 since 3.8 Gyr ago is also consistent with the cratering record at the lunar surface (Hartmann et al. 2000). The present-day mass ratio between dust and meteorites is of the order of $10^2–10^3$, but little is known for the past. Although highly imprecise, the mass contribution due to large objects, which is dominated by rare events of kilometer or more sized objects, might have been comparable to the cosmic dust flux, averaged over the last 3 Gyr (Anders 1989; Kyte and Wasson 1986; Trull 1994). A constant cosmic dust mass flux similar to the present-day one (~30,000 tons/yr) integrated over 3.8 Gyr could have supplied $4 \times 10^{15}$ mol N$_2$ to the atmosphere, which makes only $3 \times 10^{-5}$ times the amount of atmospheric N$_2$ (1.38 × 10$^{20}$ mol N$_2$, Ozima and Podecek 2002). Such a limited contribution is unlikely to have had discernible isotopic effects on atmospheric nitrogen, a view consistent with available data for Archen and Proterozoic sediments, indicating that the atmospheric N isotope composition has been near-constant since 3.5 Gyr ago (Pinti 2002; Sano and Pillinger 1990).

There is an active debate about past fluxes before 3.8 Gyr. Although some argue a steep decline of the cratering rate between 4.5 Gyr and 3.8 Gyr, there is compelling evidence that a spike of bombardment took place 4.0–3.8 Gyr ago; but that in the time interval 4.4–4.0 Gyr ago, the impacting flux was not drastically high (Hartmann et al. 2000). The total mass of impactors during the last spike of bombardment around 3.9 Gyr is ~6 × 10$^{21}$ g (Hartmann et al. 2000). The content of siderophile elements in the ancient highlands suggests that the amount of interplanetary mass accumulated by the Moon in the 4.4–4.0 Gyr period is about the same as that required to form the 3.9 Gyr basins, so that the post 4.4 Gyr contribution to the lunar surface might have been ~1.2 × 10$^{22}$ g. This is 20 times less than the contribution suggested by models with a declining bombardment since 4.4 Gyr ago (Hartmann et al. 2000). This contribution included both bolides (evidenced by remnants of the lunar cataclysm) and cosmic dust, all of them being integrated in the siderophile element record. A lower limit for the Earth’s efficiency over the Moon in collecting cosmic dust is given by the ratio between the surfaces of the two bodies, which is equal to 13. Gravitational focusing of cosmic dust (Kortenkamp et al. 2001) possibly increases the collection efficiency of the Earth by a factor of ~3 relative to the Moon (Hashizume et al. 2002). Therefore, the range of extraterrestrial material collected by Earth between 4.4 Gyr and 3.8 Gyr might have been ~(2.4–7.2) × 10$^{23}$ g. This represents a contribution of (0.07–2.1) × 10$^{19}$ mol N$_2$, that is, 6–18% of present-day atmospheric nitrogen. Nitrogen has been actively exchanged between the surface and the mantle (Marty and Dauphas 2003), so that it is more appropriate to consider the total nitrogen budget of the Earth, which is 2.8 ± 1.0 × 10$^{20}$ mol N$_2$ (Marty 1995; Marty and Dauphas 2003). Thus the total post-4.4 Gyr contribution of nitrogen to Earth might have been ~10% of total terrestrial N.

An upper limit for the nitrogen contribution by extraterrestrial matter to Earth can be set from the highly siderophile element (HSE) budget of our planet, which might have been delivered after metal/silicate differentiation towards the end of terrestrial accretion (e.g., Chyba 1991 and references therein). If nitrogen trapped in the protomantle acted as a siderophile element (Hashizume et al. 1997) and nitrogen from a primordial atmosphere was lost, as noble gas models suggest (e.g; Hunten et al. 1987; Sasaki and Nakasawa 1988; Porcelli and Pepin 2000; Pepin 1991), the amount now seen in the mantle and the atmosphere might have been delivered after core formation during “late veneer” events. The amount of HSE present in the mantle corresponds to the contribution of 1 × 10$^{25}$ – 4 × 10$^{25}$ g of chondritic material (Chyba 1991), thus to a delivery of (3–14) × 10$^{20}$ mol N$_2$. This is clearly in the range of the nitrogen budget of the Earth (3 × 10$^{20}$ mol N$_2$), thus suggesting that cosmic dust, which dominates now the extraterrestrial flux of matter onto Earth, could have been a considerable source for the terrestrial nitrogen inventory during the late accretion stages of the Earth.

CONCLUSIONS

We have analyzed nitrogen and noble gases in a suite of MMs presenting different degrees of atmospheric entry heating. Crystalline MMs are rich in trapped noble gases and concentrations can exceed those of carbonaceous chondrites.
In contrast, nitrogen is depleted by about one order of magnitude relative to chondritic values in moderately to strongly heated MMs, suggesting that phases hosting this element were highly degraded upon atmospheric entry heating and/or during subsequent terrestrial weathering. To understand the role of each process, it will be important in the future to analyze nitrogen in MMs having a short terrestrial residence time collected in fresh snow, such as those collected around the Dome Fuji station (Osawa and Nagao 2002).

The contribution of nitrogen to the Earth’s atmosphere by cosmic dust has been marginal since 3.8 Gyr ago. In the time interval 4.4–3.8 Gyr ago, the contribution to the terrestrial nitrogen budget could have been ~10% of total terrestrial N. A budget involving highly siderophile elements suggests that the nitrogen present in the mantle and the atmosphere could have been supplied by late accreting matter, among which cosmic dust might have been a significant contributor.

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