PRIMORDIAL NOBLE GASES IN FIVE LL CHONDrites:
HOST PHASES, ABUNDANCE PATTERNS, ORIGIN

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Most of the primordial noble gases in C2 and C3 chondrites reside in a small, 0.5-2% residue remaining when the meteorite is dissolved in HCl-HF (1,2). To determine whether the gases in ordinary chondrites are similarly localized, we examined 5 LL-chondrites of petrologic types 6 to 3 by the same technique. All gave residues consisting mainly of chromite (Table 1).

Table I. HCl-HF-insoluble residues from LL-chondrites

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>FeO*</th>
<th>Fe</th>
<th>Cr</th>
<th>Cr/Fe</th>
<th>Chromite*</th>
<th>Cr,Fe</th>
<th>Weight</th>
<th>Cr,Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>LL5</td>
<td>St. Séverin</td>
<td>0.62</td>
<td>35.3</td>
<td>22.1</td>
<td>98</td>
<td>7.4</td>
<td>0.21</td>
<td>2.7</td>
<td></td>
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<tr>
<td>LL5</td>
<td>Olivenza</td>
<td>0.60</td>
<td>34.2</td>
<td>23.7</td>
<td>90</td>
<td>4.10</td>
<td>0.14</td>
<td>1.3</td>
<td></td>
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<tr>
<td>LL4</td>
<td>Hamlet</td>
<td>0.54</td>
<td>30.9</td>
<td>17.6</td>
<td>76</td>
<td>11.21</td>
<td>0.32</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>LL4</td>
<td>Parnelle</td>
<td>0.37</td>
<td>25.8</td>
<td>18.9</td>
<td>56</td>
<td>11.22</td>
<td>0.32</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>LL6</td>
<td>Krymka</td>
<td>0.26</td>
<td>19.1</td>
<td>13.1</td>
<td>47</td>
<td>4.12</td>
<td>1.22</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>LL3</td>
<td>Allende</td>
<td>0.40</td>
<td>15.3</td>
<td>33.2</td>
<td>70</td>
<td>6.40</td>
<td>1.27</td>
<td>2.67</td>
<td></td>
</tr>
</tbody>
</table>

*Percent mean deviation of Fe content of olivine (Fe) from equilibrium; a measure of disequilibrium. Chromite contents were calculated from Cr analyses, using reported values for chromites from individual meteorites or group means (4). Samples were etched twice, to remove Q as completely as possible. Figures refer to weight losses in the first and second treatments; they have substantial errors for the smaller samples (Krymka, Olivenza). Cr and Fe data in the next 2 columns (determined by INAA) refer to first treatment only. The Fe values have errors of ±0.5 ppm.

Portions of the residues were etched with fuming HNO₃, to remove any "Q" (a minor phase containing most of the noble gases in Allende and Murchison; presumably a mixture of Fe,Ni- and Fe,Cr-sulfides; 1,2,5). Both the etched and unetched samples were analyzed for noble gases. The results are summarized in Fig. 1. Allende data from (1) are shown for comparison.

Gross Patterns. All 5 unetched residues are enriched in noble gases relative to the bulk meteorites. The enrichment factor for the 3 heavy gases rises from 8 for St. Séverin to 100 for Hamlet, and then levels off. Interestingly, trapped (planetary) Ne is clearly present even in the LL4-LL6 residues, though it has never been detected in the bulk meteorites, or, for that matter, in any ordinary chondrite of petrologic type 4 or higher. Srinivasan et al. (2) have previously shown the value of this technique for detecting small amounts of trapped Ne in C4 and E4 chondrites.

Phase Q. Etching with HNO₃ reveals some close parallels to Allende (Fig. 1). Most of the heavy gases are lost, from ~50% for St. Séverin to >99% for Hamlet. Only a small amount of each sample dissolves in this treat-
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ment, as shown by the weight loss and the Cr,Fe content of the etch solutions (Table 1). And the Fe/Cr ratio of the dissolved phase(s) is high, as in a recent, more detailed study on Allende (5). Apparently the bulk of the gases in the LL residues is located in a minor phase of essentially the same properties as "phase Q" in Allende and Murchison: insoluble in HCl and HF but soluble in HNO₃, comprising less than 0.05% of the meteorite, and consisting mainly of Fe and Cr.

Chromite and Carbon. The etched samples (light, solid lines in Fig. 1) show some interesting trends. The gas contents increase steadily by some 3 orders of magnitude from St. Severin to Krymka, and the Ar/Xe ratios are higher than those in the unetched or bulk samples. Krymka is unique in its high Ne/Ar ratio, and resembles Allende both in this respect and in its high gas concentrations. This difference may be due to the presence of carbon, and/or to a high Fe³⁺ content of the chromite. [Allende chromite has some 30 mol% Fe³⁺ in the M⁵⁺ sites (1), and the chromite of unequilibrated ordinary chondrites shows an increase in Fe³⁺ with PMD (4)].

Material Balance. Though Q is the most gas-rich mineral in both C and LL-chondrites, it accounts for a smaller fraction of the total gas in the latter, especially for the higher petrologic types (Fig. 2). Here the gas contents are expressed per gram of original meteorite, so that residues and bulk samples can be directly intercompared. The xenon plot typifies the situation for heavy gases. Unetched samples, represented by half-filled symbols, account for 60% the total Xe in Allende and ~90% in Murchison (2), but only 5% in St. Severin, 14% in Olivenza, and 36-31% in Parnallee and Krymka. Only Hamlet, with 75%, resembles the C-chondrites, but this figure is based on an old bulk analysis (6).

Condensation or Metamorphism? Space does not permit discussion of all conceivable explanations for this trend. In our judgment, the most likely reason is that the higher petrologic types condensed/accreted at higher temperatures, where formation of Q from its parent material (FeNiCr grains?) was progressively less complete, in common with other metal-sulfide equilibria (7,8).

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With less Q available, the contribution of other, acid-soluble phases looms larger.

Some support for this view comes from the Ne$^{20}$/Ar$^{36}$ ratios (Fig. 3). Because Ne has a smaller heat of solution than does Ar (e.g. -2.2 vs -15 kcal/mole in magnetite; 9), the Ne/Ar ratio in a given mineral falls with decreasing condensation temperature, whereas the Ar content rises. Qualitatively, this is just the trend shown by the first 4 meteorites in Fig. 3, whose Ne and Ar are largely soluble in HNO$_3$ (Fig. 1) and hence reside mainly in Q. An even steeper trend, in closer agreement with theoretical curves, would be obtained if the points were corrected for Ne,Ar in chromite and for differences in Q content. The upturn for the last two meteorites is no embarrassment, because most of their Ne is located in HNO$_3$-insoluble phases, not in Q (Fig. 1).

Figure 3 contradicts the popular hypothesis that the decreasing gas contents of higher petrologic types reflect losses during metamorphism, not higher condensation temperatures. Because Ne diffuses more rapidly than does Ar, Ne/Ar ratios should fall rather than rise with decreasing Ar content, in direct contrast to observation (Fig. 3). Again, only the first 4 meteorites, with a single host phase for Ne and Ar, are relevant.

**Isotopic composition of xenon.** The xenon from unetched samples seems to be slightly but consistently enriched in the heavy isotopes, compared to trapped xenon [e.g. mass fractionated solar Xe (1) or Xe from the Kenna ureilite (10)], and approaches AVCC Xe in this respect. However, in contrast to Allende and Murchison, etching with HNO$_3$ gave no further enhancement of the heavy isotopes, except for Krymka, where the Xe$^{136}$/Xe$^{132}$ ratio rose from 0.32 to 0.46. Apparently, such enhancement requires low-temperature phases peculiar to these meteorites: Fe$^{3+}$-substituted chromite and/or amorphous carbon (1,11). Fe$^{3+}$-rich chromite presumably forms near the stability field of Fe$_2$O$_4$, i.e. at temperatures slightly above 400 K in a solar gas, and is therefore found only in the most primitive chondrites (12).

These trends can be explained, perhaps not uniquely, in terms of the superheavy element hypothesis (1,8). Volatiles, including noble gases and a superheavy element, condensed on Q, in amounts dependent on temperature and amount of Q (itself a function of temperature). In low-temperature meteorites, Q became associated with ferri-chromite and carbon, which acted as catchers for recoiling fission fragments. In other meteorites, Q was surrounded by chemically less resistant catcher phases that did not survive HCl-HF treatment.

The etched Krymka sample, like its counterparts from Allende and Murchison, is enriched in light xenon isotopes along with the heavy ones. However, on a 124/132 vs 136/132 plot, it falls appreciably below the mixing line of Allende Q and chromite-carbon (1). Taken at face value, this suggests independence of the excess light and heavy xenon components.