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# Primordial Rare Gases in Meteorites

General lines of evidence suggest the presence of components of different origins.

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Meteorites have always been objects of great interest to mankind. Today this interest is due less to the spectacular manner of their arrival on earth than to their bearing on the ancient question of the origin of the solar system. The development of science during the 19th and 20th centuries stimulated an increasingly intensive and comprehensive study of meteorites. It is now generally accepted that they consist of extraterrestrial material, that they originate from some source within the solar system itself, and that they must have formed very early in the history of the solar system, long before any geological structure in the crust of the earth.

The meteorites can be classified according to their macroscopic appearance into iron, stony-iron, and stone meteorites. Metallurgical and mineralogical characteristics, together with differences in the fine structure of the chemical composition, give criteria for a sophisticated subclassification within each major group. Despite their wide variety of structures and compositions, meteorites are the most primitive objects at present accessible for detailed study. They constitute a complex record of the early history of material in the solar system. Known terrestrial material, on the other hand, has apparently gone through more extensive processes of separation and fractionation, and geochemical examination of the crust of the earth gives few clues about the very early stages of the development of matter. The meteorites offer much more hope in this respect because mineralogical, chemical, and isotopic studies indicate that, in at least some classes of meteorites, formative processes were halted at much earlier stages than they were in even the oldest terrestrial rocks. Investigations by scientists from almost every discipline have revealed many basic facts concerning the physical and chemical aspects of meteorites, but the present state of knowledge is still far from being able to account unambiguously for the early history of the earth and the planetary system. It is our purpose in this discussion of primordial rare gases in meteorites to summarize the present situation in one phase of this broad scientific effort.

The rare gases are of particular interest in the attempt to unravel the life history of matter. Their abundances in most meteorites are so low that extremely small contributions of rare gases from nuclear transformations and other processes can be detected. The chemical inertness of these elements permits description of their behavior in terms of diffusion and other physical processes, rather than in terms of complex chemical reactions. The inertness of the rare gases simplifies analytic procedures, and the volume of data concerning their abundances in meteorites exceeds that for most other elements. With modern techniques a determination of rare-gas concentrations can be carried out with high precision in samples as small as a few tenths of a gram —a decided advantage in view of the scarcity of meteoritic material.

The first attempts to investigate meteoritic rare gases—helium, in particular—go back as far as 1928, to Paneth and his group. These pioneering scientists concluded that the detected helium was of radiogenic origin (*1*). However, in 1948 Bauer (*2*) and Huntley (*3*) independently suggested that some of the helium in meteorites could have been produced by interaction of the cosmic radiation with meteoritic matter. Experimental evidence in support of this suggestion came a few years later (*4*) from mass spectrometric analysis of meteoritic helium, which indicated that $He^3$ constituted some 20 percent of the total helium extracted from iron meteorites. It is now known that the helium in most iron meteorites consists predominantly of cosmogenic (*5*) helium.

Shortly after the discovery of cosmogenic helium, cosmogenic neon and argon were found (*6*), and a large number of data on all these cosmogenic rare gases in meteorites have since been accumulated. In the latter half of the last decade the belief that meteoritic rare gases are of either cosmogenic or radiogenic origin became generally accepted. In the light of accumulating data, obtained by the potassium-argon technique, on the ages of terrestrial minerals, it became apparent that radiogenic argon is lost from minerals during major metamorphic processes, and therefore it seemed reasonable to assume that any primeval rare gases trapped in matter during the initial condensation had long since been lost. However, Gerling and Levskii (*7*) in 1956 found rare gases in the meteorite

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Pesyanoe which occurred in abundances that were far too high, and which were much too anomalous in isotopic composition, to permit the conclusion that these gases were of either cosmogenic or radiogenic origin. In 1960 Zähringer and Gentner (*8*) reported similar results for the achondrite Kapoeta. Since then a considerable number of stone meteorites with anomalous rare-gas contents have been discovered. Some of them contain these gases in relative abundances quite similar to those for Pesyanoe and Kapoeta and belong with them in a small group of meteorites having a very characteristic appearance. Others, however, exhibit very different helium, neon, and argon abundance patterns. The first reports of light rare-gas patterns of this second type, now known to be present in almost all carbonaceous and enstatite chondrites, were made by Reynolds (*9*) and Stauffer (*10*).

New impetus was given to the study of meteoritic rare gases in 1960 when Reynolds (*9, 11*) reported the discovery of anomalous xenon in two stone meteorites, Richardton and Murray. He showed that the differences in isotopic composition between the xenon in these meteorites and the xenon in the terrestrial atmosphere could not be attributed to cosmic-ray irradiation of the meteorites. Over the past 5 years, investigations in several laboratories have shown that all stone meteorites examined so far, belonging to all major subclasses, contain at least some krypton and xenon which definitely derives from a source quite distinct from radioactive decay or cosmic-ray reactions.

All meteoritic rare gases which are of neither radiogenic nor cosmogenic origin have come to be called *primordial* rare gases. It is important to point out that the term *primordial* cannot be taken to imply an identity between the elemental and isotopic abundances occurring in meteorites and the composition of *primeval* rare gases occurring in the solar nebula very early in the history of the solar system. The abundances of these primeval gases may well have been modified during their incorporation into primitive matter and throughout intermediate stages of accretion and metamorphism that preceded the formation of the meteorite bodies we observe today. Although one must be wary of attaching undue significance to the word *primordial* and to primordial abundances in meteorites, these meteoritic rare gases nevertheless provide valuable clues to the development of the solar system.

## Concentrations of Primordial Helium, Neon, and Argon

Several years after the first reports on primordial gases appeared in the literature, a group of investigators at the Max-Planck-Institut in Mainz, Germany (*12*), discovered a third meteorite which contained large amounts of primordial helium and neon—the chondrite Pantar. This report was particularly significant because Pantar has a distinct dark-light structure and it was observed that the primordial gases are contained only in the dark matter. This dark-light structure (Fig. 1) consists of light-colored nodules a few millimeters to centimeters in diameter embedded in a darker matrix. The light and dark components of this structure are identical in major chemical composition (*13, 14*). The light inclusions contain radiogenic $He^4$ and all cosmogenic helium and neon isotopes in concentrations typical of the majority of chondrites. Shortly after correlation of this macroscopic structure with the distribution of these primordial gases was observed, two other meteorites, Breitscheid (*15*) and Tabor (*16*), were found to exhibit this characteristic dark-light structure and to contain primordial helium and neon in the dark fraction.

Signer and Suess (*17*) have investigated these same meteorites and have included in their study determination of argon, krypton, and xenon abundances. Their findings not only confirmed the results of the group in Mainz concerning the distribution of primordial helium and neon but showed that the dark matrix contained large amounts of primordial argon. Signer and Suess also reported that Kapoeta contains light-colored inclusions which are essentially free of primordial gases. Suess has since noted another meteorite with this dark-light structure, and analyses of both light and dark components to determine rare-gas content (*18–21*) reveal that this meteorite, the Fayetteville chondrite, contains light-weight primordial rare gases in the highest abundances ever observed. Here again, these primordial rare gases are confined strictly to the dark fraction. It is most surprising to find a concentration of primordial $He^4$ of $2,250,000 \times 10^{-8}$ $cm^3/g$ at standard temperature and pressure (about 4 parts of $He^4$ per million) in the dark part of the Fayetteville chondrite and, a few millimeters away, in the light fraction, a concentration of only about $200 \times 10^{-8}$ $cm^3/g$—a concentration lower by a factor of some $10^4$ (*22*). No other trace-element abundances are known to exhibit variations of this magnitude, especially in materials of virtually the same chemical composition.

The fact that the light-weight primordial gases occur only in the dark material of these gas-rich meteorites is of great significance because this systematic pattern must reflect a very specific mechanism of incorporation of the primordial gases. The occurrence of two components of different appearance in the same meteorite is not new. Other meteorites show the same structure but do not contain any noticeable amounts of primordial gases. In fact, subsequent studies of Pantar, a known gas-rich meteorite, have shown that the dark material in this meteorite is not invariably gas-rich. Pantar fell in the Philippines in 1937, and several separate fragments were found. After the exciting reports from Mainz on one of these fragments (Pantar I), a second fragment (Pantar II) was made available for scientific investigations and it was discovered (*17, 21*) that the material of Pantar II contained virtually no primordial light rare gases, in either the dark- or light-colored part.

Seven gas-rich meteorites are now known. All seven have the dark-light structure, and in all of them the light-weight primordial gases are strictly confined to the dark fraction. Although some of these meteorites contain very high concentrations of the light gases, the group is better characterized by a recurrent pattern of the *relative* abundances of primordial helium, neon, and argon. The abundances of the primordial rare gases in these seven meteorites are listed in Table 1 (meteorites 1 to 7) and summarized in Fig. 2 (top). The concentrations vary by factors of up to 300, whereas the $He^4/Ne^{20}$ and $Ne^{20}/Ar^{36}$ ratios vary only by factors of 5 and 2, respectively.

Other stone meteorites which contain primordial rare gases, but in relative abundances quite different from those in the gas-rich meteorites, are represented in Table 1 (meteorites 8 to 21) and Fig. 2 (middle). This second group contains all the carbonaceous and enstatite chondrites investigated so far. Since no precise correction for radiogenic and cosmogenic helium can be applied in the absence of a known fraction free of primordial gases, the helium concentrations given are upper limits. The most remarkable difference between the abundance patterns of the meteorites in this group and those of meteorites 1 to 7 in Table 1 is the predominance of argon over neon in all the group-2 meteorites but Mokoia. According to Stauffer (*10*), Mokoia contains neon and argon in relative abundances typical for gas-rich meteorites. An analysis of a fragment of Mokoia at the Minnesota laboratory (*23*) failed to yield the expected high helium and neon concentrations; the primordial rare gases found in this sample of Mokoia have an abundance pattern similar to that of primordial rare gases in the other carbonaceous chondrites. It is quite possible that this meteorite, like the gas-rich meteorites, contains two fractions. The lack of a notable dark-light structure is not surprising in view of the dark appearance of the carbonaceous meteorites. However, the classification of Mokoia as a gas-rich meteorite must await confirmation of these results.

Carbonaceous and enstatite chondrites are comparatively rare. The great majority of stone meteorites are hypersthene and bronzite chondrites, often called ordinary chondrites. Ordinary chondrites typically contain only very small amounts of light rare gases (*24*), and these are predominantly of radiogenic and cosmogenic origin. However, some ordinary chondrites contain detectable traces of primordial light rare gases. The amounts of these traces cannot be evaluated with an accuracy comparable to that of the values given in Table 1, partly because contamination with atmospheric noble gases becomes a severe problem at these low concentrations. Figure 2 (bottom) shows estimates of the concentrations of primordial light rare gases in several ordinary chondrites (*25*).

At this time, some 140 stone meteorites have been analyzed. About 5 percent of these are gas-rich meteorites. This group includes representatives of subclasses of widely different chemical composition and mineralogical structure —for example, an enstatite achondrite, a calcium-rich achondrite, and several bronzite chondrites. The fact that no hypersthene chondrites, which outnumber bronzite chondrites almost two to one (*26*), belong to the group of seven known gas-rich dark-light-structured meteorites may be statistically significant. All the carbonaceous chondrites and enstatite chondrites analyzed contain primordial neon and argon and at least indications of primordial helium. Some 10 percent of the ordinary chondrites contain detectable amounts of primordial neon and argon; coexistent

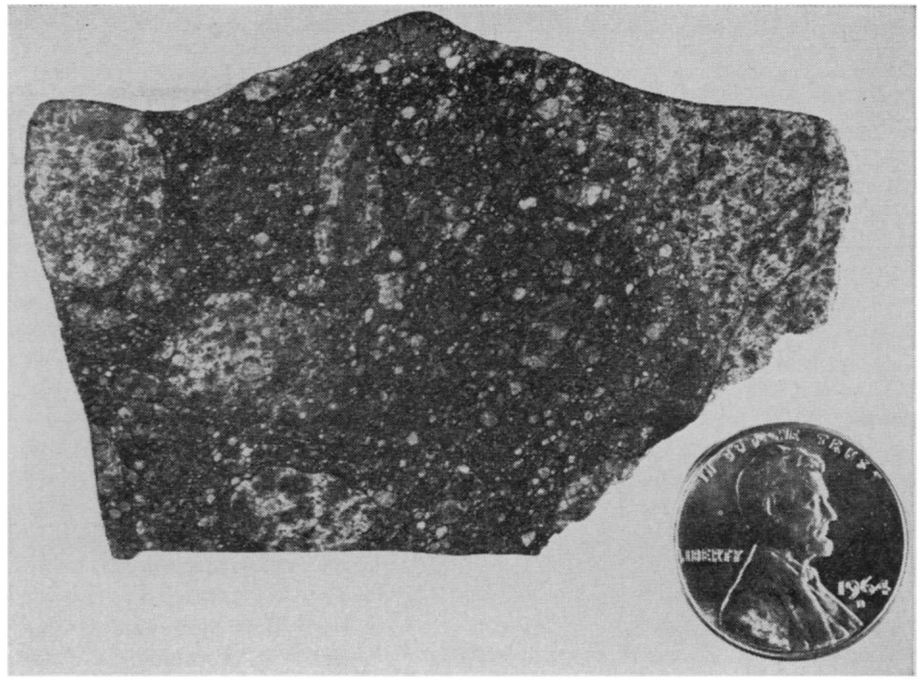


Fig. 1. A fragment of the gas-rich chondritic meteorite Pantar (*59*). The dark-light structure is characteristic of all known gas-rich meteorites. The $He^4$ concentrations in the dark matrix of Pantar are about 50 times greater than in the large light inclusions (*17*). In addition to the rare gases, other trace elements, such as carbon (*14*), bismuth (*60*), and almost certainly iodine (*32*), are enriched in the dark material of this meteorite. The numerous small spherical inclusions are chondrules. The diameter of the penny is 19 millimeters.

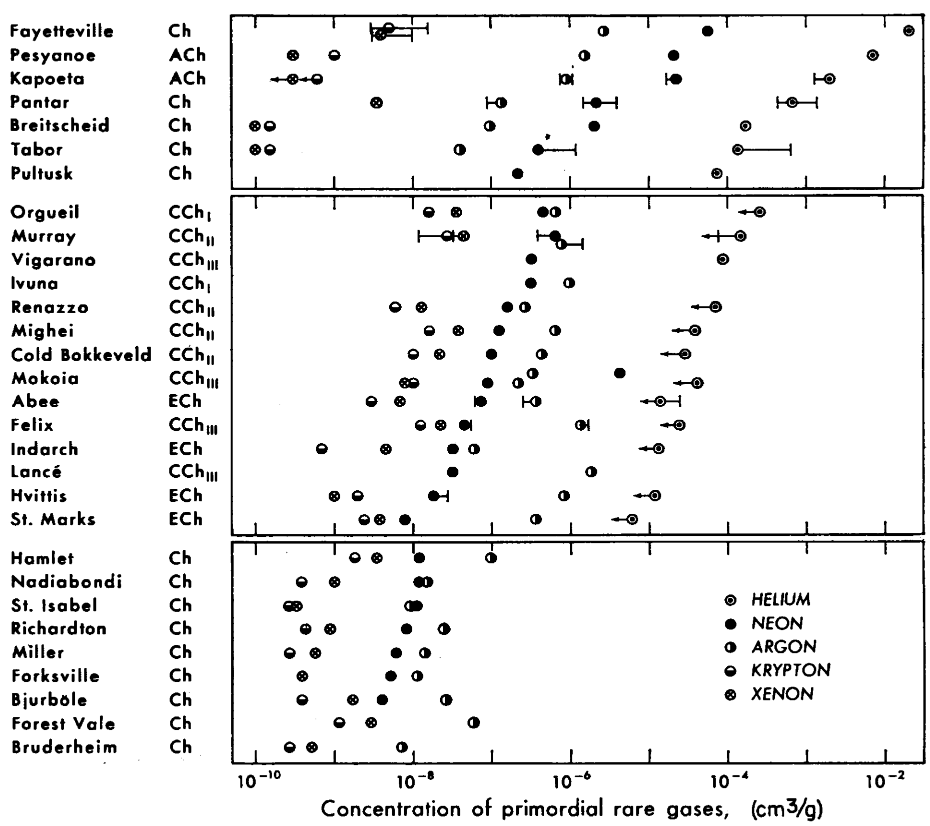



Fig. 2. Plots of selected primordial-rare-gas abundances from Table 1. (Top) Gas-rich meteorites; (middle) carbonaceous and enstatite chondrites; (bottom) ordinary chondrites. Meteorites in each group are listed in order of decreasing $Ne^{20}$ concentration; the upper limits are indicated by arrows. *Ch*, *Ach*, *CCh*, and *ECh* designate chondrites, achondrites, carbonaceous chondrites, and enstatite chondrites, respectively; subscripts I, II, and III refer to subclasses of the carbonaceous chondrites (*56*). Note the striking inversion of neon and argon abundances which distinguishes the gas-rich meteorites from all others.

Table 1. Abundances of primordial rare gases in meteorites at standard temperature and pressure. The meteorites are listed in order of decreasing $Ne^{20}$ concentration. Numbers 1 through 7 are the known gas-rich meteorites, the others are carbonaceous and enstatite chondrites. Where no corrections for content of radiogenic and cosmogenic $He^4$ were possible, the total $He^4$ concentrations are given as upper limits. Neon and argon concentrations in these cases have been corrected for cosmogenic nuclides according to the following values: $Ne^{20} : Ne^{21} : Ne^{22} = 0.9 : 0.95 : 1.00$; $Ar^{36}/Ar^{38} = 0.65$; $Ne^{21}/Ar^{38} = 9.1$.

| Meteorite sample* | Abundance (× $10^{-8}$ $cm^3/g$) | | | | | Isotopic abundance ratio | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $He^4$ | $Ne^{20}$ | $Ar^{36}$ | Kr | Xe | $He^3/He^4$† | $Ne^{20}/Ne^{22}$ | $Ar^{36}/Ar^{38}$ | $He^4/Ne^{20}$ | $Ne^{20}/Ar^{36}$ |
| *1, Fayetteville* | | | | | | | | | | |
| 20 | | | 660 | 1.60 | 1.04 | | | 5.05 | | |
| 20 | | 30,700 | 345 | 0.49 | 0.37 | | 10.6 | 5.04 | | 89 |
| 20 | | 16,400 | 173 | 0.29 | 0.33 | | 10.8 | 5.14 | | 95 |
| 21 | 2,030,000 | 5,040 | | | | 3.55 | 12.6 | | 402 | |
| 22 | 2,250,000 | 6,240 | 280 | | | 2.95 | 12.3 | 5.30 | 360 | 22 |
| 22 | 2,100,000 | 5,500 | 250 | | 0.4 | 3.35 | 12.1 | 5.20 | 380 | 22 |
| 22 | 700,000 | | 76 | | | 2.85 | 12.0 | 5.35 | | |
| *2, Pesyanoe* | | | | | | | | | | |
| 7 | 730,000 | 2,200 | 159 | | | 1.8 | 12.1 | 5 | 385 | 11.2 |
| 58 | 705,000 | 2,160 | 148 | | | 2.15 | 12.0 | 5.35 | 325 | 14.6 |
| 27 | 630,000 | 2,060 | 148 | 0.1 | 0.03 | 2.55 | 12.5 | 5.35 | 305 | 13.9 |
| 10 | | 1,890 | 159 | | | | 12.2 | 5.46 | | 11.9 |
| *3, Kapoeta* | | | | | | | | | | |
| 8 | 136,000 | 2,400 | 107 | 0.1 | 1.3 | 2.80 | 14.0 | 5.15 | 56.5 | 22.5 |
| 24 | 222,000 | 2,300 | 88 | | | 2.35 | 12.8 | 5.20 | 96.5 | 26.0 |
| 27 | 204,000 | 2,220 | 88 | ≤0.06 | ≤0.03 | 2.45 | 13.5 | 5.20 | 91.0 | 25.0 |
| 17 | 132,000 | 1,930 | 78 | ~0.06 | ~0.03 | 2.95 | 12.8 | 5.20 | 68.5 | 24.5 |
| 21 | 156,000 | 1,720 | | | | 3.42 | 13.0 | | 91.0 | |
| *4, Pantar* | | | | | | | | | | |
| 12 | 109,000 | 394 | | | | 3.50 | 12.6 | | 275 | |
| 32 | 146,000 | 178 | 11.0 | | 0.35 | 3.15 | 12.7 | 5.50 | (820) | 16.2 |
| 17 | 45,000 | 147 | 9.1 | | | 2.80 | 11.5 | 5.35 | 305 | 16.2 |
| 17 | 68,000 | 214 | 13.1 | | | 3.10 | 12.5 | 5.95 | 320 | 16.3 |
| 17 | 44,000 | 142 | 10.2 | | | 3.25 | 12.5 | 6.00 | 310 | 14.0 |
| *5, Breitscheid* | | | | | | | | | | |
| 15 | 18,000 | 204 | | | | 4.30 | 13.6 | | 88 | |
| 17 | 16,600 | 200 | 9.5 | ~0.015 | ~0.01 | 3.60 | 13.0 | 4.75 | 83 | 21.0 |
| *6, Tabor* | | | | | | | | | | |
| 16 | 66,300 | 123 | | | | 2.55 | 12.8 | | 540 | |
| 17 | 13,800 | 39.2 | 3.9 | ~0.02 | ~0.01 | 3.05 | (10.9) | 4.9 | (350) | 11 |
| 21 | 66,000 | 124 | | | | 1.98 | 12.5 | | 532 | |
| *7, Pultusk* | | | | | | | | | | |
| 21 | 7,340 | 20.9 | | | | 8.75 | 11.2 | | 350 | |
| 21 | 7,720 | 20.8 | | | | 8.00 | 12.9 | | 370 | |
| *8, Orgueil* | | | | | | | | | | |
| 27 | 24,800 | 46.5 | 67 | 1.6 | 3.7 | | 11.3 | 5.6 | 530 | 0.7 |
| *9, Murray* | | | | | | | | | | |
| 9 | 14,200 | 63.2 | 76.5 | 2.7 | 4.3 | | 9.2 | 5.47 | 225 | 0.83 |
| 10 | | 53.8 | 137 | | | | 10.6 | 5.37 | | 0.39 |
| 27 | 8,900 | 39.7 | 68 | 1.2 | 3.2 | | 9.7 | 5.53 | 225 | 0.5 |
| 21 | 7,560 | 38.9 | | | | | 9.9 | | 195 | |
| *10, Vigarano* | | | | | | | | | | |
| 21 | 8,480 | 31.8 | | | | 4.50 | 12.7 | | 270 | |
| *11, Ivuna* | | | | | | | | | | |
| 10 | | 20.9 | 96 | | | | 9.8 | 5.37 | | 0.22 |
| *12, Renazzo* | | | | | | | | | | |
| 44 | 6,800 | 15.8 | 27 | 0.6 | 1.3 | | 7.9 | 5.5 | 430 | 0.6 |
| *13, Mighei* | | | | | | | | | | |
| 27 | 3,700 | 12.4 | 62 | 1.6 | 3.8 | | 8.3 | 5.4 | 300 | 0.2 |
| *14, Cold Bokkeveld* | | | | | | | | | | |
| 27 | 2,800 | 9.9 | 43 | 1.0 | 2.2 | | 9.0 | 5.5 | 280 | 0.2 |
| *15, Mokoia* | | | | | | | | | | |
| 10 | | 309 | 34 | | | | 13.2 | 5.39 | | 9.1 |
| 23 | 3,000 | 8.9 | 21.3 | 1.0 | 0.8 | | 6.4 | 5.0 | 300 | 0.4 |
| *16, Abee* | | | | | | | | | | |
| 8 | 2,360 | 6.3 | 25.2 | | | | 9 | 5.2 | 375 | 0.25 |
| 27 | 1,320 | 7.4 | 37 | 0.3 | 0.7 | | 10.6 | 5.4 | 175 | 0.20 |
| *17, Felix* | | | | | | | | | | |
| 10 | | 5.6 | 167 | | | | | 5.40 | | 0.03 |
| 27 | 2,400 | 4.6 | 135 | 1.3 | 2.3 | | | 5.2 | 520 | 0.03 |
| *18, Indarch* | | | | | | | | | | |
| 27 | 1,270 | 3.3 | 6.0 | 0.07 | 0.47 | | | 4.0 | 300 | 0.68 |
| *19, Lancé* | | | | | | | | | | |
| 10 | | 3.3 | 174 | | | | | 5.36 | | 0.019 |
| *20, Hvittis* | | | | | | | | | | |
| 17 | 1,100 | 1.8 | 82 | ~0.2 | ~0.1 | | ~9 | 5 | 610 | 0.022 |
| 21 | 1,190 | 2.8 | | | | | | | 420 | |
| *21, St. Marks* | | | | | | | | | | |
| 27 | 600 | 0.8 | 36 | 0.74 | 0.37 | | | 5.6 | 750 | 0.022 |

* Each sample is here designated by the number of the reference in which the analysis is discussed. Sample 20 refers to work of Manuel and Kuroda (*20*), and so on. † The value given has been multiplied by $10^4$. To obtain the computed value, multiply by $10^{-4}$. Thus, the value 3.55 means $3.55 \times 10^{-4}$.

traces of primordial helium, totally masked by radiogenic and cosmogenic helium, may also be present. The observed concentrations of each of the light rare gases range over three to four orders of magnitude, from the highest values in the Fayetteville chondrite to the ambiguously small traces in chondrites such as Bruderheim. Of particular significance is the lack of any strict correlation between the concentrations of light primordial gases and the chemical and mineralogical structure of the host material. Very similar types of chondritic material, such as the dark- and light-colored fractions of the gas-rich meteorites, incorporate the light-weight rare gases in very different concentrations. On the other hand, carbonaceous chondrites and enstatite chondrites are mineralogically distinctly different, but they contain comparable concentrations of primordial helium, neon, and argon. It is apparent that any successful explanation of the origin and history of meteoritic material must account for these remarkable distributions as well as for both abundance patterns of the light rare gases.

## Light-Rare-Gas Abundance Patterns

The relative abundances of the isotopes of primordial helium, neon, and argon are listed in Table 1. The $He^3/He^4$ ratios for the gas-rich meteorites (with the exception of Pultusk) appear to vary by no more than a factor of 2, despite enormous variability in helium content. Primordial $He^3$ has never been detected unambigously in other than gas-rich meteorites. For neon, there is a systematic decrease in $Ne^{20}/Ne^{22}$ ratios, from the gas-rich meteorites to the carbonaceous and enstatite chondrites, with a difference of more than 40 percent between the extreme values. Only Vigarano and Stauffer's sample of Mokoia are exceptions to this trend. In sharp contrast, the $Ar^{36}/Ar^{38}$ ratio is constant to within about 10 percent over the entire range of meteorites of Table 1, there being *no* systematic difference in the ratios for the gas-rich meteorites and for others.

Stauffer (*10*) was the first to note a significant relationship between the abundances and isotopic compositions of the light primordial rare gases. He discovered a correlation between the isotopic composition of primordial neon and the $Ne^{20}/Ar^{36}$ ratio in five carbonaceous chondrites and two ureilites, and suggested that diffusive loss of neon from meteoritic material could account for this correlation. For most of the meteorites 8 to 21 of Table 1, low $Ne^{20}/Ne^{22}$ ratios are related to low $Ne^{20}/Ar^{36}$ ratios. This is just what would be expected as a consequence of gas loss by diffusion. Diffusion constants for isotopes of a given element are inversely proportional to the square root of mass; light isotopes therefore diffuse away more readily, leaving behind an isotopic mixture which is depleted of light isotopes. However, relative diffusion constants for different elements depend not only on mass but also on factors such as atomic radii and the lattice dimensions of the crystals in which the diffusing atoms are trapped. The constancy of the $Ar^{36}/Ar^{38}$ ratios and the relatively small variations in argon concentrations in the meteorites examined by Stauffer led him to conclude that neon must have diffused from this material much more effectively than argon.

Zähringer (*27, 28*) has extended this concept of diffusive loss to the gas-rich meteorites. He suggests that all primordial-rare-gas abundances observed in meteorites have been derived by simple diffusion from one initial abundance pattern very similar to that now present in the dark fraction of a gas-rich meteorite such as Kapoeta. According to this view, the dark material of Kapoeta has retained most of its original complement of rare gases, carbonaceous chondrites and enstatite chondrites have been outgassed to progressively greater extents, while ordinary chondrites and the light fractions of the gas-rich meteorites—which intimately coexist with the dark material within the same meteorite body—have lost practically all their light noble gases.

In Fig. 3 (top and bottom) the isotopic ratio $Ne^{20}/Ne^{22}$ and the $Ne^{20}$ concentration for all meteorites listed in Table 1 are plotted against the $Ne^{20}/Ar^{36}$ ratio. The linear dependencies noted by Stauffer for the carbonaceous chondrites appear to extend to the gas-rich meteorites as well. The wide range of these broad correlations certainly suggests the operation of some rather simple mechanism. Nevertheless, there are a number of observations concerning the abundances and distributions of primordial rare gases in meteorites which cannot be accounted for by pure volume diffusion without the invoking of additional, complex mechanisms. A serious difficulty arises when one calculates the amount of neon which must have been lost from a meteorite such as Mighei (see Table 1), in which the original $Ne^{20}/Ne^{22}$ ratio has presumably been fractionated by about 40 percent (*28*). It can be shown that the neon now in Mighei can be no more than a few parts in $10^5$ of its initial concentration, and that helium, which diffuses much more easily than neon, must have been present initially in exceedingly large amounts—larger by several orders of magnitude than the amounts present in Fayetteville or Kapoeta. Furthermore, the pure volume diffusion model cannot itself account for, or provide clues to, the remarkable phenomenon of the gas-rich meteorites. It offers no explanation for the chemically and structurally similar dark-light fractions in these meteorites, for the take-up of large amounts of light rare gases, and for the strict confinement of these gases to the dark fractions. In this context, Fredriksson and Keil (*13, 29*) have proposed that shock phenomena, occurring *in situ* after the formation of the meteorite bodies, may have produced the dark-light structure and the correlated rare-gas distributions in the gas-rich meteorites. Laboratory experiments (*30*) show that severe shock can darken meteoritic material and firmly trap ambient noble gases. However, Suess, Wänke, and Wlotzka (*31*), in arguments based on the structure, mineralogy, and rare-gas content and composition of the gas-rich meteorites, have strongly criticized this theory of their origin.

A different approach to the problem of meteoritic abundances of rare gases, one which appears capable of resolving the major difficulties inherent in the pure diffusion scheme, has been proposed by Signer and Suess (*17*). They find strong indications in the data of Table 1 that meteorites in general contain a mixture of two *independent* kinds of primordial light rare gases, rather than a single component in various stages of diffusive loss, and that one of these two types is predominant in the gas-rich meteorites, the other in the carbonaceous and enstatite chondrites. According to this view, gases have been lost by diffusion in progressively greater amounts in this latter group of meteorites, but the rare-gas abundances originally present in these chondrites did *not* resemble those now found in the gas-rich meteorites.

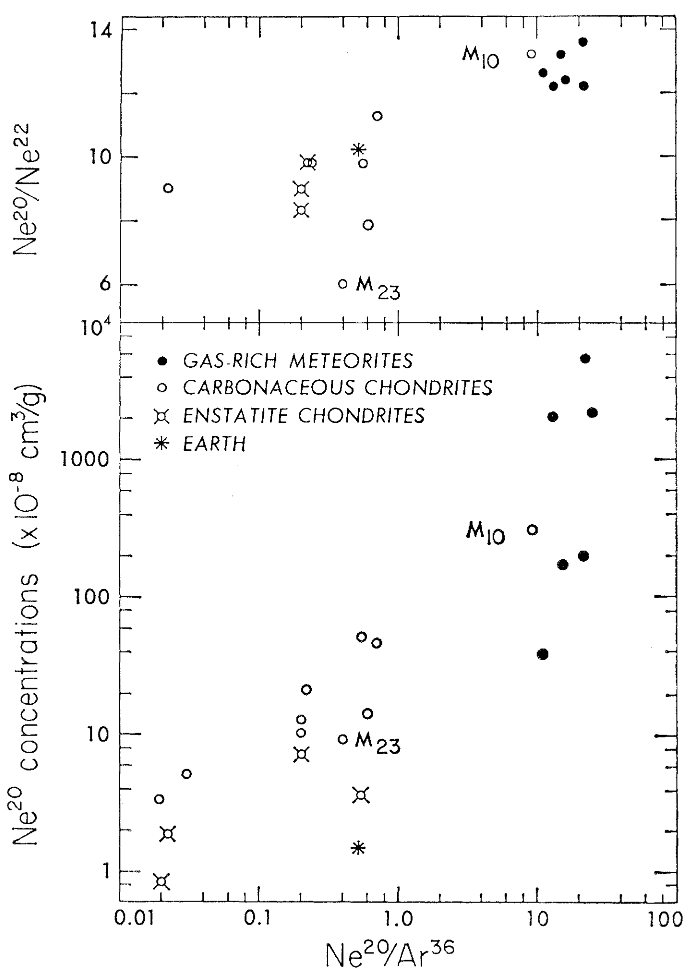
It is interesting to reexamine the data of Fig. 3 in terms of this two-component model. It is apparent that the points cluster in two distinct groups separated by a rather wide gap. The group with large $Ne^{20}/Ar^{36}$ values contains only gas-rich meteorites, except for the interesting Mokoia sample analyzed by Stauffer. All carbonaceous and enstatite chondrites, including the second sample of Mokoia, form the other group. This pattern certainly suggests the presence of two distinct kinds of light rare gases. In addition, note that the range of neon concentrations for the gas-rich meteorites is comparable to that for the carbonaceous and enstatite chondrites. If diffusive losses alone are responsible for these ranges, the range of $Ne^{20}/Ne^{22}$ ratios in the gas-rich group should also be comparable. This is not the case, as may be seen in Fig. 3 (top). However, if we assume that the individual gas-rich meteorites originally incorporated different amounts of rare gases of approximately uniform composition, there is no longer any reason why the abundances and isotopic compositions of neon should correlate.

The presence in meteorites of two light-rare-gas components of different composition makes it unnecessary to conclude, as one must with the single-component diffusion model, that the carbonaceous and enstatite chondrites originally contained extraordinarily large amounts of helium and neon. If the component initially present in these meteorites had a $Ne^{20}/Ne^{22}$ ratio comparable to that for the earth's atmosphere, 10.2, and not to that for Kapoeta, the fractionation of meteoritic neon by diffusive loss has been relatively small. In this case, Mighei has retained about one part in 100 of its original neon rather than a few parts in $10^5$.

## The Heavy Rare Gases

Krypton and xenon are present in meteoritic material only in very small concentrations, on the order of $10^{-3}$ to $10^{-6}$ parts per million. Both are usually more abundant in meteorites than in the earth, as are the light rare gases. Unlike meteoritic helium, neon, and argon, which frequently contain substantial cosmogenic and radiogenic contributions masking the possible presence of traces of primordial gases, krypton and xenon in stone meteorites appear to be predominantly primordial.

*All* stone meteorites examined so far contain detectable amounts of the heavy rare gases. Concentrations in a number of ordinary, enstatite, and carbonaceous chondrites, and in gas-rich me-



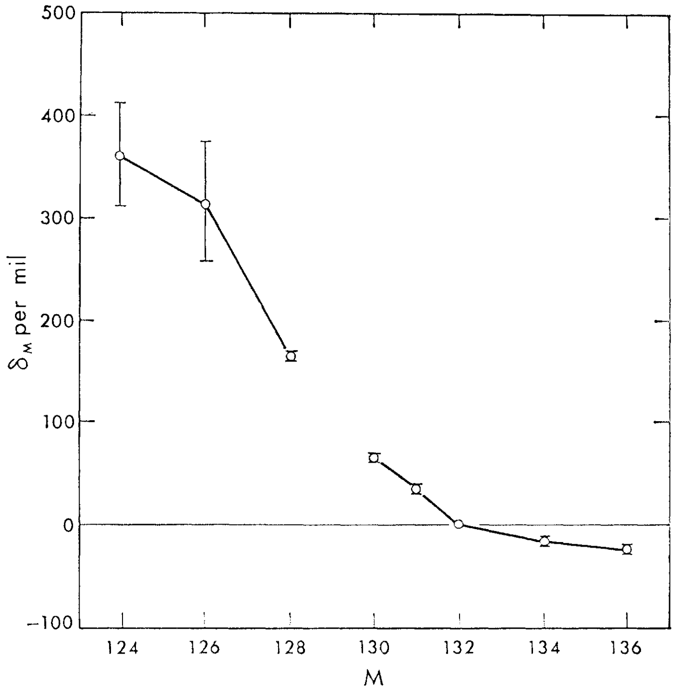




Fig. 3 (left). Plots of $Ne^{20}/Ne^{22}$ ratios and neon concentrations versus $Ne^{20}/Ar^{36}$ ratios for all meteorites for which data are available, and for the earth. $M_{10}$ and $M_{23}$ designate Stauffer's (*10*) and Signer's (*23*) analyses of Mokoia. The values for the three meteorite groups and for the earth correlate in a systematic way. Note the absence of points for values of $Ne^{20}/Ar^{36}$ between approximately 1 and 10. Fig. 4 (above). Average isotopic anomalies in xenon from the carbonaceous chondrites Murray, Mighei, and Orgueil, plotted against isotopic mass number ($M$). Xenon in the earth's atmosphere, taken as the reference in calculating these anomalies, is represented by the horizontal line at $\delta_M = 0$ (see *61*).

teorites, are shown in Fig. 2. The first three of these classes of meteorites typically contain more xenon than krypton, in sharp contrast to the earth's atmosphere, where krypton is more abundant by more than an order of magnitude. The available data suggest that in the gas-rich meteorites krypton may be slightly more abundant than xenon, although the Xe/Kr ratio is still far above the terrestrial value.

Ordinary chondritic stone meteorites such as Richardton and Bjurböle contain about $0.1 \times 10^{-8}$ cm$^3$ of xenon per gram (at standard temperature and pressure); enstatite chondrites contain roughly five times this amount, while the highest concentrations are found in the carbonaceous chondrites [up to about $4 \times 10^{-8}$ cm$^3$/g in Murray (*9*)]. The heavy rare gases clearly follow the trend displayed by the light primordial gases of Fig. 2—that of increases in concentration as one goes from ordinary chondrites to carbonaceous chondrites. It is equally clear that this trend does *not* extend to the group of gas-rich meteorites. Despite the large amounts of helium and neon in several of these unusual stones, krypton and xenon are unmistakably less abundant in these meteorites than in carbonaceous chondrites. In this respect the gas-rich meteorites are very similar to the ordinary chondrites, a fact of fundamental importance in any consideration of possible origins of their abundant helium and neon.

Comparatively little is yet known about the relative distribution of the heavy rare gases in the light- and dark-colored fractions of the gas-rich meteorites. Measurements on Fayetteville (*20*) and Pantar (*32*) show xenon to be more abundant in the dark material by factors ranging from 2 to 12. In Fayetteville, krypton also appears to be more abundant in the dark fraction (*20*).

Of the two meteoritic heavy noble gases, xenon has been studied far more intensively than krypton. Stimulated by Reynolds' discoveries in 1960, investigations at the Berkeley laboratory and elsewhere have firmly established that the isotopic composition of xenon in stone meteorites is systematically different from that of xenon in the earth's atmosphere. No corresponding systematic difference has been found for meteoritic krypton. While isotopic anomalies are known to exist in krypton from at least two chondrites (*33*), the meteorites with the largest abundances of the heavy rare gases—the carbonaceous chondrites—contain krypton which is isotopically very similar to terrestrial krypton (*34*).

The most characteristic of the isotopic anomalies in meteoritic xenon is an excess of $Xe^{129}$. This enrichment occurs in varying degrees in all chondritic stone meteorites. There is conclusive evidence that the excess $Xe^{129}$ is a radiogenic contribution, produced very early in the history of meteorite bodies by *in situ* decay of $I^{129}$, an extinct radioactivity no longer present in nature, with a mean life of only 24 million years (*11, 35–37*). The presence of substantial amounts of $I^{129}$ in the parent bodies of the meteorites indicates a rapid time scale for the early evolution of the solar system, since the interval between the end of $I^{129}$ synthesis and the formation and cooling of large bodies in the solar nebula could have been only a few mean lives of $I^{129}$.

A complete examination of iodine-xenon chronology, its implications, and the several points of view taken by various investigators are beyond the scope of this article. Discussions have been presented by Reynolds (*36*), Cameron (*38*), Fowler *et al.* (*39*), Zähringer (*28*), and others.

The relative abundances of *all* meteoritic xenon isotopes, not only of $Xe^{129}$, are anomalous in comparison with abundances of terrestrial xenon. In analyses where samples are melted and their total xenon contents are examined, one particular pattern of isotopic anomalies is found in several different types of stone meteorites. This recurrent pattern is best represented by the average isotopic composition of xenon from the three carbonaceous chondrites Murray, Mighei, and Orgueil, shown in Figure 4 (*34*). A per mil notation, defined by

$$\delta_M = 1000 \left\{ \frac{(Xe^M/Xe^{132})_{meteorite}}{(Xe^M/Xe^{132})_{atmosphere}} - 1 \right\}$$

is used to represent these anomalies, where $M$ is the mass number of any particular isotope. Anomalies at mass 129, presumably dominated by radiogenic $Xe^{129}$ from $I^{129}$ decay, are omitted from Fig. 4.

The isotopic compositions of xenon from sources as different as the bronzite chondrite Richardton (*11*), chondrules from the hypersthene chondrite Bjurböle, the dark fraction of the gas-rich Pantar meteorite (*32*), and the three carbonaceous chondrites of Fig. 4 are virtually identical. Xenon from the enstatite chondrite Abee (*40*) and from one sample of the hypersthene chondrite Bruderheim (*41*) is very similar, differing only in the relative abundances of the extremely rare isotopes $Xe^{124}$ and $Xe^{126}$. Heavy-isotope anomalies in xenon from the light-colored, gas-poor fraction of Pantar also fit the pattern of Fig. 4 (*32*); light-isotope abundances have not yet been measured.

These meteorites include representatives from all three groups of Fig. 2. Xenon concentrations in Bruderheim and Murray differ by two orders of magnitude. On the basis of the available data, it seems clear that there is no correlation of xenon isotopic composition with either xenon abundance or meteorite type. There is no evidence for more than one basic kind of *primordial* xenon in meteorites (although we shall see that there is evidence for at least two additional, nonprimordial xenon components). This situation is unlike that for the light rare gases, where the presence of two primordial components appears quite probable.

The difference in isotopic composition between meteoritic and terrestrial xenon is one of the major puzzles in the interpretation of abundances of primordial rare gases. It cannot be due to diffusive loss of gas from the meteorites (although the regularity of the pattern in Fig. 4 does suggest a mass-fractionation mechanism) because the light meteoritic xenon isotopes are enriched, not depleted, with respect to the heavy isotopes. Krummenacher and his associates (*34*) have suggested that the anomalies may derive in part from a severe fractionation of *terrestrial* xenon. If this were the case one would expect krypton to have been lost from the earth and therefore fractionated to an even greater extent than xenon. Apparently this has not occurred, since the Kr/Xe ratio for the atmosphere is higher by more than an order of magnitude than the ratio for meteorites, and since terrestrial and meteoritic krypton are isotopically similar. Nevertheless, we suspect that the quantitative similarity of the four light-isotope anomalies shown in Fig. 4 to a mass-fractionation pattern is no accident, but is in fact an important clue to the origin of the xenon anomalies.

Two other quite different mechanisms have been proposed to explain these anomalies. Kuroda (*42*) and Cameron (*38*) suggest that meteoritic xenon is essentially primordial, while terrestrial xenon has been modified over geologic time by the addition of xenon components from spontaneous fission and from the solar wind. Fowler, Greenstein, and Hoyle (*39*) regard terrestrial xenon as primordial, and propose that the isotopic composition of meteoritic xenon was altered early in the evolution of the solar system by an intense irradiation of high-energy particles from the primitive sun. Each of these models can account for the principal features of the pattern in Fig. 4 in a qualitative way; however, a number of problems exist in both theories (*34, 43*). As yet there is no really satisfactory explanation for these xenon anomalies.

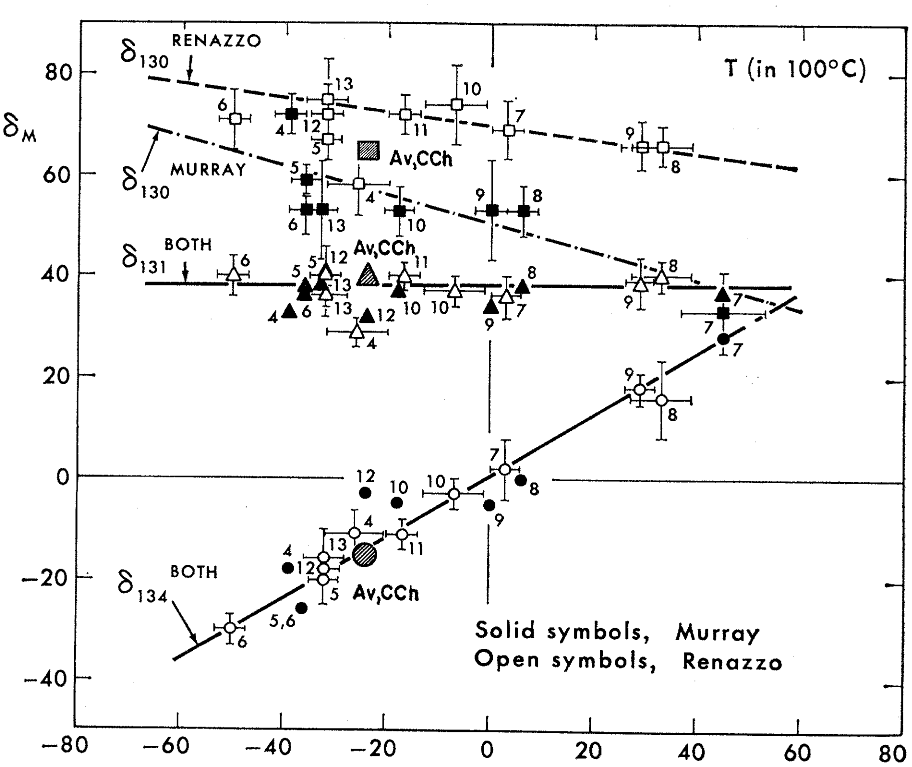



Fig. 5. Anomalies in the heavy isotopes of xenon outgassed at various temperatures (*T*) from single samples of meteorites Murray and Renazzo (*36, 44, 46*). Within limits of experimental error, the data points lie quite accurately on straight lines, indicating two component mixtures. The points labeled *Av,CCh* are taken from Fig. 4. These points fall on or close to the correlation lines, which suggests that carbonaceous chondrite xenon is in general a mixture of these two components.

## Krypton and Xenon from Fission and Irradiation

As more and more analyses have been made of krypton and xenon in stone meteorites, it has become very clear that these gases are not always of uniform isotopic composition. Although xenon resembling that found in carbonaceous chondrites has been observed in individuals from all major subclasses of chondrites, many meteorites display xenon anomalies which differ from this recurrent pattern. Of even greater interest has been the discovery that a single meteorite often contains xenon of more than one isotopic composition. If a meteorite is heated to its melting point in steps of roughly 100°C, with the temperature at each stage held constant for 1 hour, about 15 separate rare-gas fractions, one at each temperature, are obtained, instead of a single total-gas sample. Analyses of these individual temperature fractions reveal that xenon outgassed from almost any meteorite varies in composition as a function of temperature. A striking example of such isotopic fluctuations is shown in Fig. 5, where heavy-xenon-isotope anomalies are plotted against $\delta_{136}$ for a number of temperature fractions from two carbonaceous chondrites, Murray and Renazzo (*36, 44*). On this plot, the average anomalies in total-xenon samples from carbonaceous chondrites, shown in Fig. 4, are represented by the large shaded points labeled *Av,CCh*. Rather large departures from this composition are evident in both meteorites, particularly in the temperature range 700° to 900°C.

The fact that the anomalies in Fig. 5 are not randomly distributed but lie in every case along straight lines is significant. Such a pattern can arise only if two isotopically different kinds of xenon are present in these meteorites, mixed in varying proportions in each gas fraction. Furthermore, it can be argued quite convincingly from these data that one of the two xenon components, the one released preferentially between 700° and 900°C, where $\delta_{134}$ and $\delta_{136}$ are largest, must have been produced by fission (*43*). This argument rests on the observation that this component is enriched in $Xe^{134}$ and $Xe^{136}$; fission is the only known nuclear mechanism capable of producing substantial amounts of these neutron-rich isotopes.

The detection of fission products in Murray and Renazzo was followed by the discovery that most other stone meteorites also contain at least traces of fission-produced xenon. Results of isotopic analyses of total xenon from 17 stone meteorites are available in the literature or as unpublished data; $Xe^{134}$ and $Xe^{136}$ anomalies for these samples are plotted in Fig. 6. The tendency of the points to fall along the line defined by the Renazzo-Murray data is clear: of the 25 points, all but one lie on this line, within the limits of experimental error. This suggests very strongly that fission-produced xenon is widely distributed in meteorites.

Definitive experimental evidence for the presence of this component in meteoritic xenon was recently obtained by Rowe and Kuroda (*45*), who found values for $\delta_{134}$ and $\delta_{136}$ of 225 and 290 per mil, respectively, in total xenon from the calcium-rich achondrite Pasamonte. Within the limits of experimental error, this point falls on the line of Fig. 6, far to the right of the diagram. Pasamonte is rich in uranium and poor in xenon, and fission-produced xenon comprises a much more substantial fraction of the total xenon content than it does in any meteorite previously analyzed. Fission-produced krypton should also be observable in this meteorite, though it has not yet been reported.

The isotopic compositions of the fission-produced components in Murray and Renazzo can be deduced from the slopes of the correlation lines in Fig. 5 (*44, 46*). The calculated values for the fission mass yields of these components, and the values derived by Rowe and Kuroda for Pasamonte, all normalized with respect to $Xe^{136}$, are plotted in Fig. 7. Mass-yield curves for the fission of four heavy nuclides are shown for comparison (*47*). The general agreement between the calculated relative yields for these meteoritic xenon components and the relative yields for xenon from fission processes appears to be the decisive evidence for the presence of fission-produced xenon in meteorites. In view of the errors involved in these calculations, it is entirely possible that the fission-produced components in all three meteorites of Fig. 7 have identical mass-yield curves, and that they were produced from the same parent nuclide.

A few meteorites exhibit anomalous patterns of isotopic abundances which suggest that another component, entirely unrelated to fission processes, occurs in some meteoritic heavy rare gases. Definitive evidence for a third kind of xenon in meteorites appears in

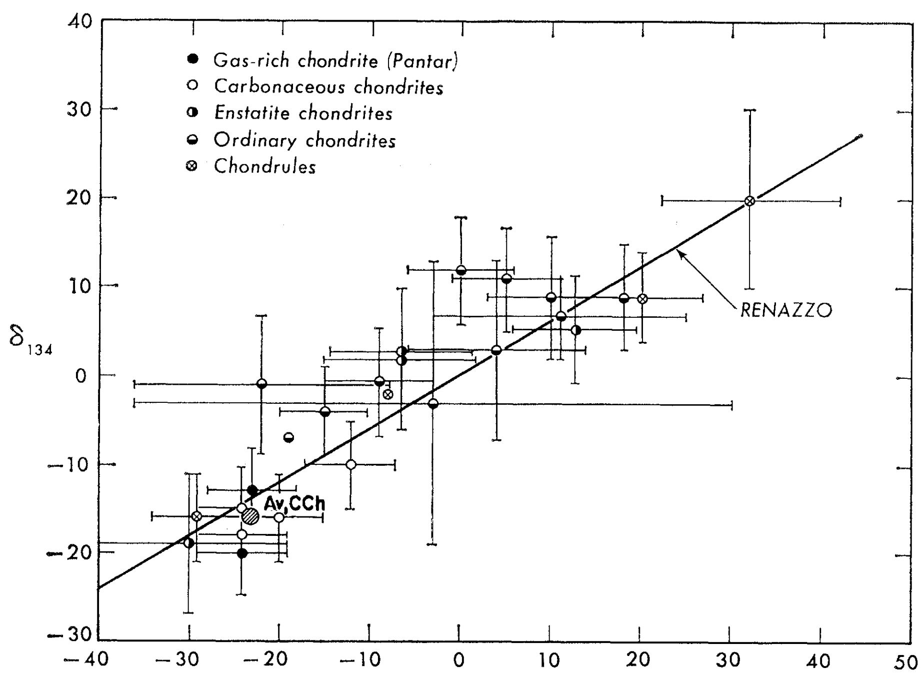
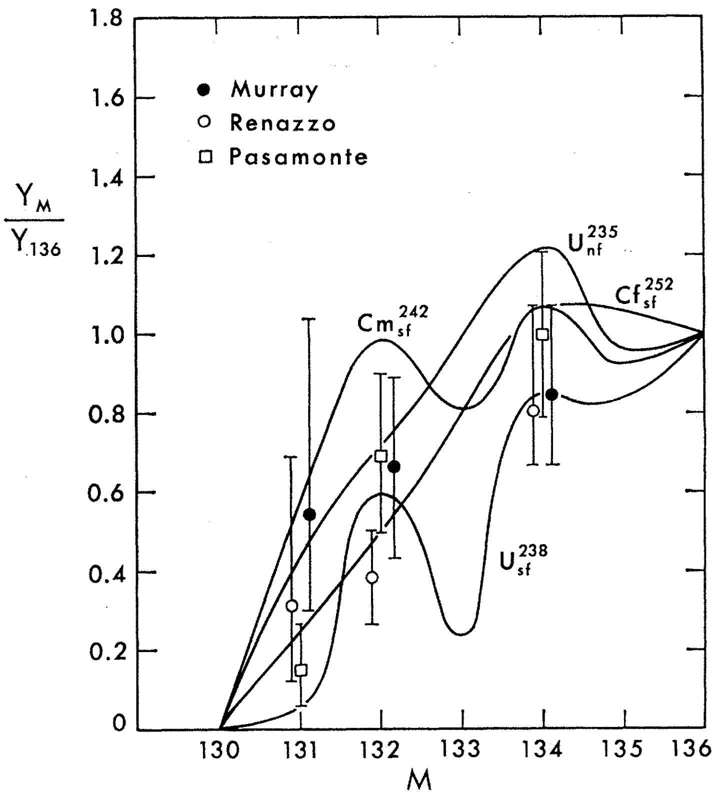



Fig. 6. Anomalies in $Xe^{134}$ and $Xe^{136}$ from stone meteorites. One gas-rich meteorite, four carbonaceous chondrites, three enstatite chondrites, and nine ordinary chondrites are represented. The chondrule samples are from Bruderheim (*37, 48*) and Bjurböle (*36, 46*). The remaining data are from references *32, 34, 36, 37, 40, 44,* and *48*, or are unpublished results from the Berkeley laboratory. The "Renazzo" line is taken directly from Fig. 5.



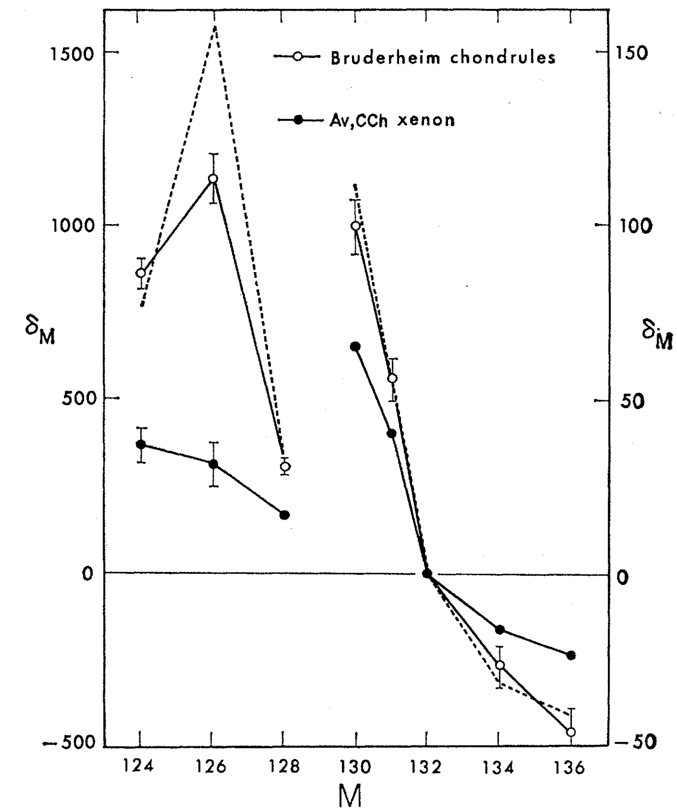



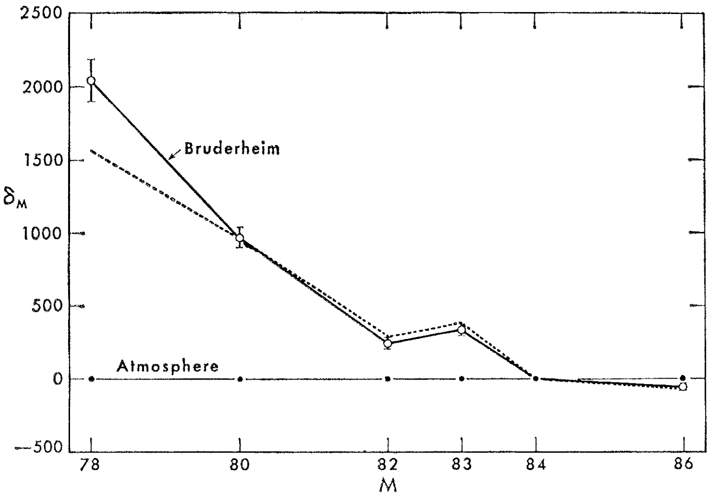

Fig. 7 (left). Xenon yields relative to $Xe^{136}$ for the fission-product components from the Murray, Renazzo, and Pasamonte stone meteorites, and for xenon from four heavy fissioning nuclides, plotted against isotopic mass number (*M*). The isotope $Xe^{130}$, which is shielded from production by spontaneous fission (*sf*) or fission induced by neutron bombardment (*nf*), is assumed to be absent in meteoritic fission-produced xenon. [Data for Pasamonte, from Rowe and Kuroda (*45*)] Fig. 8 (right). The composition of xenon released from Bruderheim chondrules of about 1 millimeter in diameter at 1100°C (*37*), compared with the average composition of xenon from carbonaceous chondrites (*Av,CCh*). The dashed line represents the estimated composition of a mixture of such average xenon and spallation-produced xenon; a small amount of fission-produced xenon has been subtracted from the mixture. It appears that these chondrules could contain such a mixture.

Merrihue's (*37, 48*) study of rare gases in the Bruderheim chondrite. Figure 8 shows the isotopic composition of xenon released at 1100°C from chondrules separated from this meteorite (*37*). In Fig. 8, values for $\delta_{124}$, $\delta_{126}$, and $\delta_{128}$ are read on the scale at left, values for other isotopes, on the scale at right. The anomalies in this fraction, which are among the largest ever observed, differ from the carbonaceous-chondrite pattern of Fig. 4, particularly for the two light isotopes. While the heavy-isotope anomalies of the Bruderheim chondrules can be derived quantitatively from xenon from carbonaceous chondrites by assuming that the chondrules contain a slightly smaller percentage of the fission component than the carbonaceous chondrites, fission-produced xenon cannot account for these large enrichments of $Xe^{124}$ and $Xe^{126}$.

An interesting possibility is that xenon produced by particle bombardment has contributed to the Bruderheim chondrules (*48, 49*). High-energy particles can produce all xenon isotopes from $Xe^{124}$ to $Xe^{132}$ by spallation of barium and heavier elements. One can estimate the isotopic composition of both krypton and xenon produced in spallation reactions in meteoritic material (*43*). The dashed line in Fig. 8 represents the anomaly pattern produced by adding 1 percent of this approximate spallation-produced component to carbonaceous-chondrite xenon and subtracting a trace of fission-produced xenon. The computed pattern agrees essentially with the pattern observed in the chondrules.

Spallation reactions would also be expected to produce observable effects in the krypton mass spectrum. Complete results of an analysis of krypton composition in Bruderheim chondrules are not yet available, but Clarke and Thode (*33*) have reported large anomalies in krypton from a bulk sample of Bruderheim which are of particular interest in the context of possible spallation contributions in this meteorite. The anomaly pattern which they report, normalized relative to $Kr^{84}$, is shown in Fig. 9. The anomalies are computed with respect to atmospheric krypton, which, as mentioned, is isotopically similar to the krypton in the carbonaceous chondrites. Also displayed in Fig. 9 are the anomalies produced by mixing with terrestrial krypton 6.5 percent of the meteoritic krypton component estimated to result from the spallation of rubidium, strontium, and heavier elements. There is no evidence for fission-produced krypton in this sample of Bruderheim, not a surprising result in view of the fact that fission produces considerably less krypton than xenon (*47*). The close agreement of the two patterns in Fig. 9 indicates that the Bruderheim anomalies are fully consistent with the presence of heavy rare gases created by high-energy irradiation.

Spallation, while perhaps the most probable, is not the only nuclear mechanism able to give rise to such an irradiation component. Alpha-particle reactions in selenium and tellurium yield all krypton and xenon isotopes except $Kr^{86}$, $Xe^{134}$, and $Xe^{136}$. It has been estimated that irradiation of meteoritic



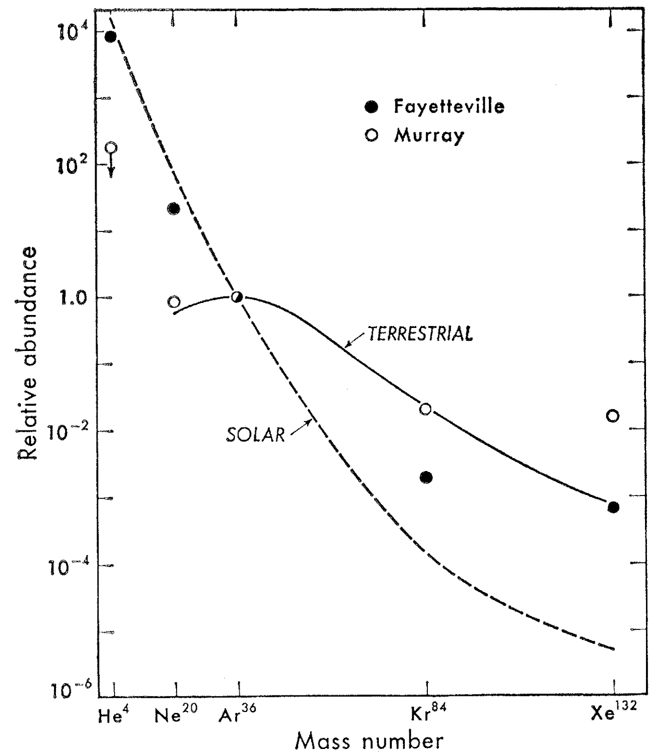




Fig. 9 (above). The composition of krypton from the Bruderheim meteorite. A mixture of terrestrial krypton with spallation-produced krypton produces a very similar pattern, indicated by the dashed line. [Data for Bruderheim, from Clarke and Thode (*33*)] Fig. 10 (right). Relative abundances of primordial rare gases in a gas-rich meteorite, Fayetteville, and a carbonaceous chondrite, Murray, compared with the solar (*51*) and terrestrial (*17*) abundance patterns. All abundances are normalized with respect to $Ar^{36}$. [Data for Fayetteville, from Manuel and Kuroda (*20*) and Signer (*22*); for Murray, from Reynolds (*11*)]

material with ~ 20 Mev $\alpha$-particles would produce, through these reactions, a heavy-rare-gas component which fits the Bruderheim data of Figs. 8 and 9 fully as well as a component formed in spallation (*43*). However, this model is quite restrictive and requires a highly specific combination of astrophysical circumstances.

In addition to spallation and $\alpha$-capture, a large variety of nuclear reactions involving protons, neutrons, and less common particles such as deuterons and $He^3$ can produce certain krypton and xenon isotopes. Irradiation products in the heavy rare gases probably arise from complex interactions of several of these particles with meteoritic matter.

A question immediately arises as to the extent to which these fission and irradiation components in the heavy rare gases may be considered primordial rare gases. The radioactive heavy elements which produced the fission gas must have been incorporated into certain meteoritic mineral structures when they formed, so this xenon is essentially another type of radiogenic contribution. There is considerable speculation as to the source of fission-produced xenon in meteorites. Murray contains more of this component, by at least three orders of magnitude, than could have been produced within the meteorite over the last 4.5 billion years by spontaneous fission of $U^{238}$ (*46*). An early, intense neutron irradiation, as suggested by Fowler *et al.* (*39*), could have produced abundant fission xenon by neutron-induced fission of $U^{235}$. More experimental studies are required to determine whether mass yields for meteoritic fission xenon are consistent with the mass yield curve for neutron-induced fission of $U^{235}$. The data of Fig. 7 suggest that at mass 134 they are not. The most likely source of this component so far suggested is the spontaneous fission of extinct radioactivities in the early history of meteoritic material. In this context, considerable attention has been focused on the transuranium isotope $Pu^{244}$ (*42*). This nuclide has a half-life of 75 million years, and decays comparatively frequently (about one atom in 300) by spontaneous fission. A simple model of element synthesis in the galaxy gives an abundance of $Pu^{244}$ about 1/60 the abundance of $U^{238}$, in the earliest history of the solar system (*36*). This relative abundance of $Pu^{244}$ is more than adequate to produce the amounts of fission xenon estimated to be present in Pasamonte (*45*) and in a chondrule from Bruderheim (*37*). However, it is insufficient—by factors of at least 5 to 10—to account for the fission-product xenon in the carbonaceous chondrites Renazzo and Murray (*44, 46*). Either these meteorites originally contained much higher concentrations of extinct radioactivities than one estimates from their present uranium contents, or their abundant fission-produced xenon derives from some other source.

The heavy-rare-gas component detected in Bruderheim and attributed to irradiation may have been produced by recent cosmic-ray bombardment. Bruderheim contains very little krypton and xenon and has been exposed to cosmic-ray bombardment for about 25 million years (*21*); it is just possible that cosmogenic effects might be observable in this meteorite. If this proves not to be the case, the Bruderheim anomalies may be evidence of a very ancient irradiation of meteoritic material before the formation of meteorite parent bodies (*37, 43*).

## Discussion

The basic premise in any attempt to understand the variations in isotopic and elemental abundances of primordial rare gases is the assumption of certain initial compositions common to all premeteoritic matter. Even at a very early stage these compositions could have differed considerably from the composition of primeval gases in the solar nebula, according to prevailing conditions and the specific processes responsible for their trapping in the first solid matter. Suess (*50*), for example, has successfully invoked hydrodynamic loss and subsequent gravitational separation of gases to explain the difference between terrestrial and solar abundances of rare gases.

The trapping of energetic particles, or diffusive equilibrium between gas and liquid or solid phases, are mechanisms which might have led to the original emplacement of the rare gases in primitive matter. Adsorption on the surfaces of small grains in intermediate stages of accretion and compaction of this material may also have been of primary importance. Each of these processes undoubtedly resulted in very specific fractionations, which may have further depended on variable, local conditions. Later in the history of matter, formative and metamorphic alterations were certainly paralleled by diffusive changes in the rare-gas abundances, and it is conceivable that this diffusion depended on numerous complicating parameters difficult to evaluate billions of years later. Radioactive decay and nuclear reactions induced by radiation have superimposed additional components on the primordial rare gases throughout the entire lifetime of material in the solar system. It is not surprising that many details of rare-gas abundance patterns as they exist today have eluded explanation.

Nevertheless, a number of general conclusions may be drawn from the data presented in the preceding sections. Two different kinds of elemental and isotopic abundance patterns exist for the light primordial rare gases in meteorites. Diffusion calculations strongly suggest that these patterns arise from the presence of two distinct, independent types of light rare gases rather than from diffusive fractionation of a single component. The strict confinement of one of these types to the dark fractions of gas-rich meteorites implies an intimate genetic relationship between this structural phenomenon and its gas content, which must somehow be explained.

Meteoritic krypton and xenon have been modified in varying degrees by the addition of supplementary components created by fission and irradiation, a situation analogous to the alteration of primordial helium, neon, and argon by radiogenic and cosmogenic contributions. These two components appear to be superimposed on one basic heavy-rare-gas abundance pattern for all meteorites, in which krypton is isotopically similar to terrestrial krypton, xenon differs from terrestrial xenon, and Xe/Kr ratios are substantially larger than the ratio for the atmosphere. When, in addition, abundances of the light rare gases in the carbonaceous and enstatite chondrites are compared with abundances in the atmosphere, an extremely interesting fact emerges: except for xenon (and helium, for which primordial abundances are not known), the relative elemental *and isotopic* abundances of all primordial rare gases in these meteorites are very similar to abundances in the earth. One case where this resemblance is particularly striking is shown in Fig. 10, where abundances in the earth and in the Murray meteorite are plotted relative to $Ar^{36}$. Alone among the rare gases, xenon is anomalous in both abundance and isotopic composition.

This similarity was noted by Merrihue and his associates (*32*), who also pointed out that the relative abundances of the other type of light rare gases, found in the dark fractions of gas-rich meteorites, resembled abundances in the sun. Abundances of the rare gases in Fayetteville and in the sun (*51*) are also shown in Fig. 10, again plotted relative to $Ar^{36}$. The agreement for the light gases is evident. However, present data indicate that the primordial heavy gases, while relatively less abundant in Fayetteville than in Murray, are similar, isotopically and in Xe/Kr ratio, to krypton and xenon in Murray and in all other meteorites.

On the basis of comparisons like those of Fig. 10, Signer and Suess (*17*) proposed the terms *planetary*, to describe the abundance patterns of the light gases in carbonaceous and enstatite chondrites and in the earth, and *solar*, for the pattern in the gas-rich meteorites. It is evident from Fig. 10 and from isotopic compositions that the planetary rare gases include meteoritic and terrestrial krypton, while xenon is a special case. These designations raise immediately the fundamental question of the origin of the two kinds of primordial gases. Planetary rare gases are widely distributed, occurring not only in the carbonaceous and enstatite chondrites but in ordinary chondrites, where they are difficult to detect, and in the earth. Traces of these gases undoubtedly exist in both light- and dark-colored fractions of the gas-rich meteorites, although the planetary-type light gases are overwhelmed by the abundant solar-type component. The presence of the highest known abundances of planetary gases in the carbonaceous chondrites is particularly significant, since these are meteorites which in many ways appear to be extremely primitive aggregates of matter. The common occurrence of this type of abundance pattern, and its association with relatively unaltered material, suggests very strongly that planetary rare gases are residues of the primeval gases.

If this is the case, what is the origin of the solar-type light gases in the gas-rich meteorites? Several authors (*19, 31, 52*) have suggested that a particle irradiation such as the solar wind would have been a uniquely suitable agent for supplying these gases; in particular Wänke (*52*) has strongly advocated this hypothesis. Suess, Wänke, and Wlotzka (*31*) have pointed out that not only is the solar wind easily capable of supplying, in reasonably short times, the amounts of light rare gases observed in the gas-rich meteorites, but that it can account in a natural way for both the dark-light structure and the confinement of the gases to the dark material. In their view, the dark appearance of the gas-bearing fraction could be due to the deposition of carbon along with the rare gases in this material when it was in a dispersed, dust-like state, to the presence of volatile carbon compounds in the material itself, or to darkening under irradiation by solar-wind hydrogen, a process experimentally demonstrated by Hapke (*53*). The light-colored gas-free inclusions in a gas-rich meteorite were formed from common meteoritic material which was effectively shielded from this irradiation. They became embedded in the dark matrix at some later time, but before or during the ejection of the meteorite from its parent body.

Hintenberger, König, and Wänke (*54*; see also *31*), working with the Pantar meteorite, and Eberhardt, Geiss, and Grögler (*55*), who very recently discovered a new gas-rich meteorite, the achondrite Khor Temiki, have demonstrated that in the gas-rich material of these two meteorites the light rare gases are most highly concentrated on the *surfaces* of mineral grains. Since the rare gases in a low-energy particle bombardment would have been stopped in the surface layers of irradiated grains, these observations very strongly support the solar-wind hypothesis.

The abundances of rare gases in the solar wind are a matter of some speculation. As a first approximation one might assume them to be characteristic of the sun as a whole. In this case, a few percent of the total krypton in Fayetteville would have been added with the solar rare-gas component, as may be seen in Fig. 10, and a multistage temperature experiment might reveal evidence for two isotopically different kinds of krypton in this meteorite. However, the assumption of solar abundances in the solar wind, combined with the observation that the pattern for abundances of light rare gases in Fayetteville is also approximately solar, requires the conclusion that Fayetteville has lost almost no gases by diffusion. Helium escapes so much more readily than neon that initial abundance ratios cannot be maintained in the event of diffusive loss. It is interesting to speculate that the solar wind may be fractionated to some extent, with resultant preferential enrichment of light elements—and isotopes—relative to heavy ones. A slight gravitational separation of ions, or some other mechanism which discriminates against the emission from the solar corona of species of high mass or of high mass-to-charge ratio, could account for such a fractionation. In this case Fayetteville must have lost some of its light gases after implantation, and the resemblance of their present abundances to a solar abundance pattern is coincidental. Relative abundances of the heavy rare gases in a fractionated solar wind would be very low, so that virtually all krypton in the gas-rich meteorites would derive from the residual planetary rare gases.

The question of when the solar-type gases were added to the gas-rich meteorites is an interesting one. It seems clear that because these gases at present exist in well-defined and characteristic abundance patterns in meteorites which presumably have quite different metamorphic histories, they must have been added after the primary evolutionary stages of meteoritic material were completed. This conclusion will be strengthened still further if either Mokoia or Vigarano proves to be a gas-rich meteorite, since the development of these carbonaceous chondrites and an enstatite achondrite like Pesyanoe must have been radically different.

The high $Ne^{20}/Ne^{22}$ ratio for Vigarano certainly suggests that this meteorite may contain predominantly solar rather than planetary neon. Determination of the $Ne^{20}/Ar^{36}$ ratio should settle the question of whether or not the Vigarano sample in Fig. 2 belongs in the gas-rich meteorite group. If it does, a nearly perfect systematic relation appears in Fig. 2 between the carbonaceous chondrite subclasses I, II, and III (*56*) and their contents of planetary neon. This correlation holds in a general way for all the rare gases except for argon in Felix and Lancé. Anders (*57*) has pointed out that the abundances of many other trace elements in carbonaceous chondrites show systematic lessening from type I to type III. He suggests that these meteorites may be variable mixtures of two kinds of material with very different thermal histories: one kind which originated at high temperature and lost its volatile elements, and another which was never severely heated and retained such elements. The data for the primordial rare gases are generally consistent with this view, although some light gases were undoubtedly lost from the low-temperature material by diffusion.

The presence of two distinct kinds of primordial rare gases in terrestrial and meteoritic material, one a widely distributed residue of primeval gases modified to varying extents by diffusive loss and the other a relatively late addition, from the solar wind, to the group of gas-rich meteorites, accounts reasonably well for all major lines of observational evidence except one: the abundance and composition of meteoritic xenon. This gas does not belong to the planetary neon, argon, and krypton family of noble gases, as is shown convincingly in Figs. 4 and 10. Xenon is relatively more abundant in meteorites than in the earth and is consistently anomalous in isotopic composition. It is tempting to regard these two observations as related clues to some process which essentially affected only meteoritic xenon among all the planetary rare gases.

The adsorption of gas on the surface of finely divided premeteoritic material might account for the high abundance of xenon in meteorites. It is conceivable that within a certain critical temperature range, xenon would selectively adsorb on such surfaces, while most of the lighter rare gases would not. Adsorption of all gases would have been less effective in material which later formed the earth, since it was presumably closer to the sun and at a higher temperature. This process could have occurred during an intermediate stage in the development of meteoritic and terrestrial matter, after the planetary-type rare gases had been incorporated and most of the primeval gases had escaped from the nebula but before large solid bodies had aggregated. If most of the ambient gases in the solar nebula at this stage had been supplied by gross hydrodynamic outflow from the sun, mass fractionation might have occurred when they escaped from the solar corona. Xenon subsequently adsorbed on premeteoritic dust particles would have been richer in light isotopes and poorer in heavy isotopes than planetary xenon. It has already been noted that the four light-xenon-isotope anomalies of Fig. 4 are fully consistent with a simple mass-fractionation mechanism of this type. Krummenacher and his associates (*34*) also pointed out that *all* these xenon anomalies could be accounted for quantitatively if one assumed both fractionation and the addition of fission-produced xenon to meteorites. Since their report appeared, fission-produced xenon has been discovered in meteorites. As yet we cannot say exactly how much is there or where it came from, but in this context its presence appears especially significant.

There are many fine details in the observations of primordial rare gases in meteorites which we have not discussed. There are details which the two-component model considered here cannot as yet explain. However, general lines of evidence appear to fit the principal features of this model, even though many of the discussions and conclusions are necessarily speculative. More data are needed here as in every aspect of meteorite research, especially in such areas as investigation of rare-gas abundances in the solar wind, where satellite and space-probe experiments offer the principal immediate hope. The data are complex and will increase in complexity as old techniques are improved and new ones are invented, but basic underlying patterns have appeared, and in these patterns are clues to the origin and evolution of matter.

**References and Notes**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# Respiratory Chains and Sites of Coupled Phosphorylation

## Studies in a bacterial system give further evidence of a basic biochemical unity between different forms.

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Oxidative phosphorylation, a vital cellular process for the synthesis of adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and inorganic phosphate was discovered during a period when many other biosynthetic processes were also being recognized. However, while the biosynthesis of many types of small molecules and even macromolecules has come to be understood in fairly close detail, the mechanism of generating the terminal high-energy phosphate of ATP during the respiratory process is still unclear. We understand rather well the biosynthesis of the adenine ring, and of the ribose moiety. But we do not understand in chemical terms how the stepwise downhill process of electron transport may be coupled to the production of "high-energy" phosphate bonds. Basically the reason for this gap in our knowledge is that structure at the intermacromolecular level is essential to the functioning of the complicated electron transport coupling process, and that most of our methods for studying biochemical processes depend on the resolution of the process into its component parts. When we apply the "gentlest" sorts of methods to fractionation of mitochondria we tend to lose the very reactions we wish to study.

The biochemical processes of bacteria and of mammalian tissues differ mainly in the pathways concerned with specialized activities. At a more basic biochemical level—such as glycolysis, the Krebs cycle, and protein synthesis—these widely diversified biological forms exhibit similar processes. Thus, bacterial systems have been investigated, not with the object of finding a radically new or different sort of coupling process, but with the hope of finding that at the mechanistic level the coupling process in bacteria is similar to that in mammalian mitochondria, yet sufficiently different in the fine details of structural organization to allow a meaningful and informative comparison between the two systems. As we discuss later, the chemical composition of the respiratory chains of *Mycobacterium phlei*, an organism capable of coupling phosphorylation to oxidation, as well

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