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The noble gas record of the terrestrial planets

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The noble gas record of the terrestrial planets

The Earth's atmosphere was produced by exhaustive degassing of the upper mantle during the first 200My, but the lower mantle has retained an appreciable fraction of its initial inventory of primordial ^{3}*He. The lower mantle has retained most of its initial inventory of the heavy noble gases, and it is presently accumulating radiogenic* ^{4}*He and* ^{40}*Ar. Most of the radiogenic* ^{40}*Ar in air was produced in the crust during the first 2.5Gy. Extinct radionuclides have augmented the atmospheric inventory of* ^{136}*Xe by less than 1% and that of* ^{129}*Xe by about 5%. Terrestrial Ar, Kr, and Xe are type-Y, but the He and Ne are of solar wind origin. Terrestrial Xe may not be isotopically unique in the solar system; its composition can be related to that in meteorites by consideration of nucleogenetic heterogeneities and mass dependent fractionation.*

The atmospheres of the terrestrial planets were produced by exhaustive degassing of specific regions. Observed similarities in the abundance patterns of noble gases in meteorites and in the terrestrial planets rule out elemental fractionation in the evolution of their atmospheres. The degassed portions of Mars, Earth, and Venus are estimated to be 1-2%, 17% and 100%, respectively. The iron cores of these bodies were produced by heterogeneous accretion.

INTRODUCTION

Investigations of noble gases in meteoritic and lunar samples have played a key role in our understanding of the formation and early history of these extraterrestrial bodies (BOGARD, 1971; REYNOLDS, 1977; PODOSEK, 1978). Recently it has been realized that differences in the elemental and isotopic compositions of the noble gases in these objects may also contain important information on the synthesis of the chemical elements and the birth of the solar system (SABU and MANUEL, 1980a).

Studies of terrestrial noble gases resulted in several important findings, but no comprehensive understanding of these discoveries has emerged. In this report we review the available data and suggest an outline of the basic features that seem to be emerging for the noble gas record of the terrestrial planets.

Early attempts to decipher the Earth's noble gas record were hampered by the following set of widely-accepted assumptions about the distribution of the chemical elements and their isotopes in the primitive nebula: (i) the solar system condensed under conditions of thermodynamic equilibrium from a well-mixed batch of elements (UREY, 1952; LORD, 1965; LARIMER and ANDERS, 1967). (ii) The elemental and isotopic composition of the primitive nebula represents an average of all previous galactic nucleosynthesis events (UREY, 1954; SUESS and UREY, 1956; BURBIDGE et al., 1957; REYNOLDS, 1967). (iii) Differences between the abundances of elements in carbonaceous chondrites and in the Earth were produced by the selective loss of volatiles from the latter (UREY, 1952, 1954). (iv) The internal structures of the terrestrial planets were generated by partial melting and geochemical differentiation (UREY, 1952; RINGWOOD, 1966).

The finding of nucleogenetic anomalies in the isotopic abundances of several of the elements in meteorites (REED and JOVANOVIC, 1969; MANUEL et al., 1972; CLAYTON et al., 1973; JOVANOVIC and REED, 1976; ARDEN, 1977; WASSERBURG et al., 1977; LUGMAIR et al., 1978; SRINIVASAN and ANDERS, 1978; MCCULLOCH and WASSERBURG, 1978; LEE et al., 1978) clearly demonstrate that even the isotopes of individual elements were not homogenized prior to the formation of planetary solids. The discovery that meteorites also contain the *in situ* decay products of the short-lived radionuclides, ^{129}I (REYNOLDS, 1960a), ^{244}Pu (ROWE and KURODA, 1965), ^{26}Al (GRAY and COMPSTON, 1974), ^{107}Pd (KELLY and WASSERBURG, 1978) and ^{247}Cm (TATSUMOTO and SHIMAMURA, 1980), indicates that there was a relatively short time interval ($\sim 10^7$ years) between the end of nucleosynthesis and the condensation of planetary solids. Further, a recent finding that the inclusions of some iron meteorites started to retain radiogenic ^{129}Xe as early as the chondrites (NIEMEYER, 1979) suggests that these iron meteorites were formed primarily by nebular processes (WASSON, 1970; BILD, 1977) rather than by differentiation in a parent body (KELLY and LARIMER, 1977). The results of this I-Xe study on inclusions of iron meteorites provide additional support for an earlier suggestion that iron and silicates of the terrestrial planets and meteorites condensed as separate phases from a chemically zoned protoplanetary nebula (EUCKEN, 1944; TUREKIAN and CLARK, 1969; VINOGRADOV, 1975; MANUEL and SABU, 1975).

However, the finding in meteorites which has the greatest implication for our attempt to decipher the terrestrial noble gas record is the correlation between elemental and isotopic ratios of these elements. The results of analyses on noble gases in meteorites were the subject of a recent review (SABU and MANUEL, 1980a) in which it was shown that the primitive nebula contained basically two isotopically and chemically distinct types of noble gases, X and Y.

Type Y noble gases contain only the three heavy members, Ar, Kr, and Xe, and these are dominant in bulk meteorites and in the inner planets. Thus, the isotopic compositions of type-Y Ar, Kr, and Xe appear “normal” to the inhabitants of an inner planet. Type-X noble gases contain all five noble gases, He, Ne, Ar, Kr, and Xe. Type-X gases were concentrated in the outer regions of the primitive nebula. These account for all of the He and Ne originally trapped in meteorites during condensation, and the He and Ne therefore appear to be isotopically “normal”. But type-X Ar, Kr and Xe seem to be isotopically “strange” because these constitute only a small fraction of the bulk Ar, Kr and Xe found in the inner planets and in bulk meteorites. Isotopic analysis of Xe in the He-rich atmosphere of Jupiter is planned for the Galileo mission, and the results should delineate the spatial distribution of type-X gases in the primitive planetary nebula and provide a clear test of the suggestion that the noble gases in Jupiter are primarily type-X (SABU and MANUEL, 1980a).

In addition to the type-X and type-Y gases that were incorporated into meteoritic grains, many meteorites also contain noble gases that were implanted into the grain surfaces by the solar wind. This third component, type-S noble gases, contains all five noble gases in roughly cosmic proportions. The He and Ne in the type-S component are characterized by values of $^3He/^4He = 4.4 \times 10^{-4}$ and $^{20}Ne/^{22}Ne = 13.5$ (GEISS et al., 1972), whereas in the type-X gases, $^3He/^4He = 1.4 \times 10^{-4}$ and $^{20}Ne/^{22}Ne = 8.2$ (REYNOLDS et al., 1978).

There are considerably more data available on the terrestrial noble gases than on the noble gases in the other inner planets. The latter is limited to remote analysis of gases in the atmosphere of Mars and Venus, and we will discuss the implications of those data after first reviewing the implications of the following well-documented findings in terrestrial noble gases:

(i) The observation of primordial ^3He in samples from the Earth's interior (MAMYRIN et al., 1969; 1972; CLARKE et al., 1969; BENNETT and MANUEL, 1970; CRAIG et al., 1975; CRAIG and LUPTON, 1976; SAITO et al., 1978a; KANEOKA et al., 1978; KANEOKA and TAKAOKA, 1978; 1980; KYSER, 1980; RISON, 1980).

(ii) The occurrence of excess radiogenic ^{129}Xe, the decay product of extinct ^{129}I ($t_{1/2} = 16 \times 10^6$ yr), in samples from the Earth's interior (BUTLER et al., 1963; BOULOS and MANUEL, 1971; HENNECKE and MANUEL, 1975a, b; PHINNEY et al., 1978; KANEOKA and TAKAOKA, 1978, 1980; KYSER, 1980; RISON, 1980).

(iii) The observation of low values of the $^{40}Ar/^{36}Ar$ ratio in many samples from the Earth's mantle (THOMPSON et al., 1978; SAITO et al., 1978a, b; KANEOKA et al., 1978; KANEOKA and TAKAOKA, 1980; KYSER, 1980; RISON, 1980).

(iv) The finding of high values of the $^{20}Ne/^{22}Ne$ ratio in gases from the Earth's mantle (HENNECKE and MANUEL, 1975a; CRAIG and LUPTON, 1976; PHINNEY et al., 1978; DOWNING et al., 1977; KYSER, 1980; RISON, 1980).

(v) The production of ^4He, $^{131-136}Xe$ and ^{40}Ar by the decay of Th, U, (^{244}Pu?), and ^{40}K.

(vi) The observation of a characteristic abundance pattern for terrestrial xenon isotopes which is distinct from that seen in Xe-X, Xe-Y, or Xe-S.

SYSTEMATICS OF TERRESTRIAL NOBLE GAS ABUNDANCES

Elemental abundances of Ne, Ar, Kr, and Xe in terrestrial samples of deep-seated origin (FISHER, 1970; 1973; 1974; DYMOND and HOGAN, 1973; HENNECKE and MANUEL, 1975b; DOWNING et al., 1977; KANEOKA et al., 1977; KANEOKA and TAKAOKA, 1978; 1980; THOMPSON et al., 1978; TAKAOKA and OZIMA, 1978; SAITO et al., 1978a,b; KYSER, 1980; RISON, 1980) are compared with those in sea water at 1°C (KYSER, 1980) and in air (VERNIANI, 1966) in Figs. 1-3. The latter, computed by dividing the total atmospheric content of each noble gas by the mass of the Earth, would represent the concentration of terrestrial noble gases if complete degassing had occurred.

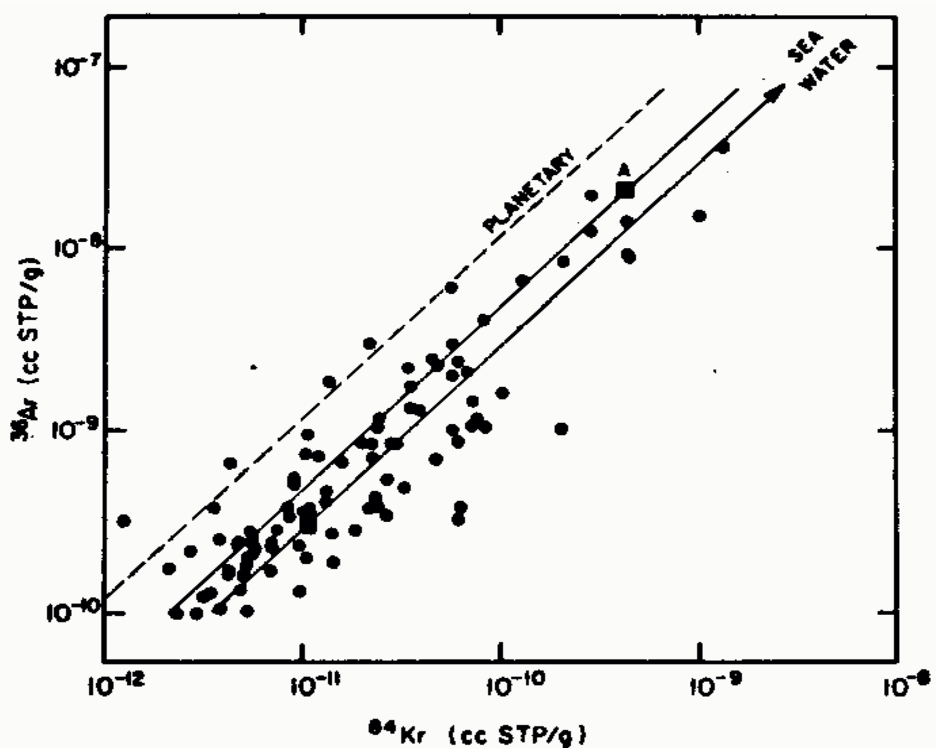

Fig. 1. Concentrations of ^{36}Ar and ^{84}Kr in deep-seated samples (●). Point A identifies the atmospheric abundance divided by the mass of the Earth, and the elemental Ar/Kr ratio in typical chondrites, in air and in sea water are represented by the 45° lines. Concentrations of ^{36}Ar and ^{84}Kr in most deep-seated samples are 10 to 100 times lower than that represented by point A, as expected if the samples were derived from a degassed region.

In this paper we consider the noble gas data for about 120 samples reported by the above authors. The majority of these samples are basalts, kimberlites, or their inclusions that contain noble gases which the original investigators considered to be of deep origin.

As shown in Fig. 1, the concentrations of ^{36}Ar and ^{84}Kr in these samples are generally lower, by a factor of 10 to 100, than the value computed for air. Thus, most of the samples were apparently derived from a part of the Earth's interior that has been extensively degassed.

The concentrations of noble gases in sea water at 1°C are high, and the Ar/Kr ratio is slightly lower than that in air. Noble gases in seawater would lie off the graph in the direction indicated by the arrow in the upper right of Fig. 1. Noble gases in average chondrites display a higher Ar/Kr ratio than in air, but the spread of values for individual meteorites encompasses the value of the Ar/Kr ratio in air.

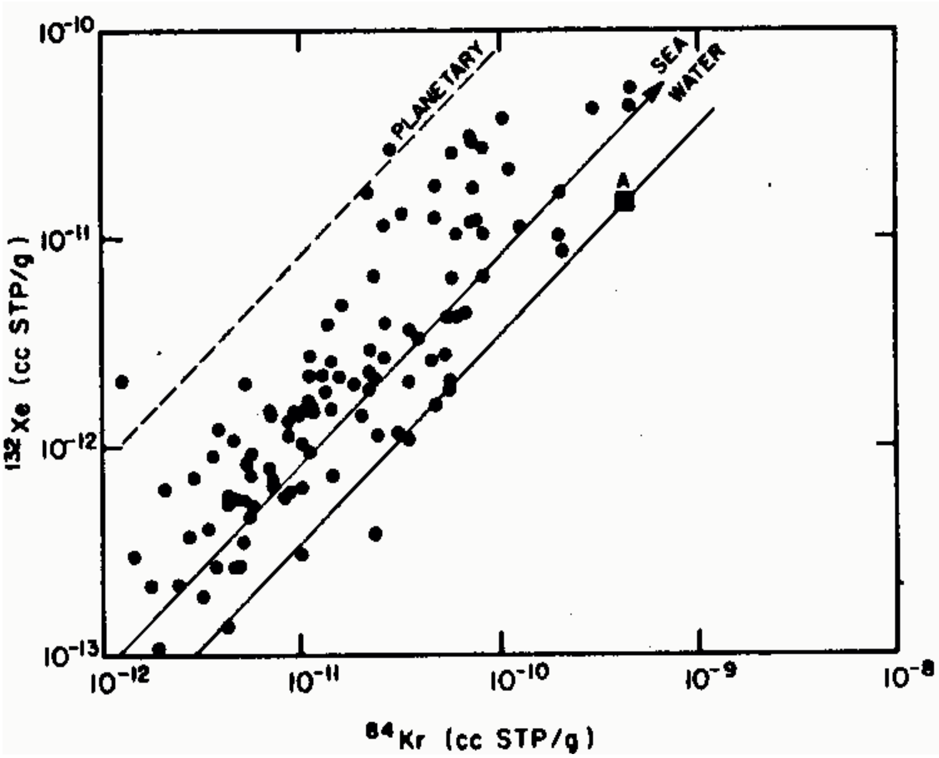

Fig. 2. Concentrations of ^{132}Xe and ^{84}Kr in deep-seated samples (●). Point A and the lines are as defined in Fig. 1. In most of the samples, ^{132}Xe and ^{84}Kr concentrations are lower, by one or two orders of magnitude, than the value computed from air, point A. The Xe/Kr ratios shown here and the Ar/Kr ratios shown in Fig.1 resemble those in sea water, suggesting possible reincorporation of atmospheric gases by dissolution in water.

Although the abundance pattern of noble gases in individual samples from the Earth's interior may be governed by diverse factors, such as solubility in melt, interaction with water, or physical fractionation caused by adsorption, diffusion, etc., the Ar/Kr ratio in the bulk of the samples shown in Fig. 1 is similar to that in sea water.

The concentrations of ^{132}Xe and ^{84}Kr in these deep-seated samples are shown in Fig. 2. The Xe content for the bulk of these samples is also less than that shown for air, by factors of 10 to 100, as expected if these came from a region that was depleted of noble gases. The Xe/Kr ratio in air is, however, lower by a factor of 3 to 4 than that observed in most of these deep-seated samples. It has been shown that physical adsorption on surfaces of carbonaceous or fine-grained sediments may be responsible for the selective depletion of Xe from air (CANALAS et al., 1968; FANALE and CANNON, 1971). The noble gases in these are characterized by high values of Xe/Kr. The data shown in Figs. 1-3 are, however, limited to deep-seated samples and do not include noble gases in sedimentary material.

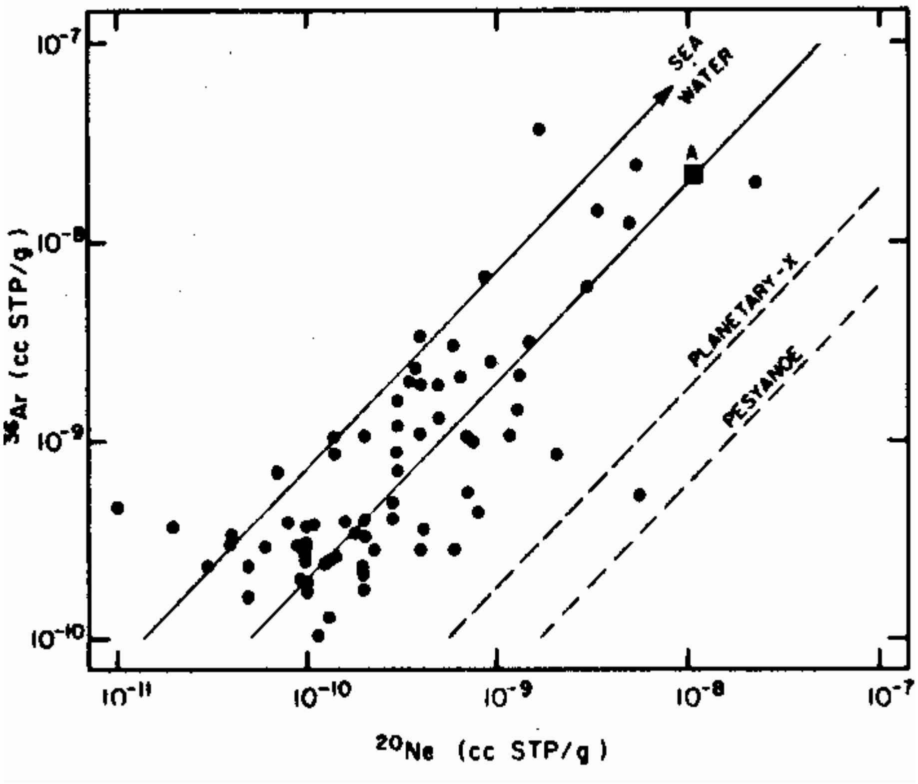

Fig. 3. Concentrations of ^{36}Ar and ^{20}Ne in deep-seated rocks (●). Point A and the line to sea water are as defined in Fig. 1. Values of the ^{36}Ar/ ^{20}Ne ratio in type-X noble gases and in the solar-wind-implanted gases of the Pesyanoe meteorite are shown by the broken lines. In most of the samples, the ^{36}Ar/ ^{20}Ne ratio is similar to that in air although the concentrations of these two gases are less than that computed for point A by factors of 10 to 100.

It should be noted in Fig. 2 that the Xe/Kr ratio in the bulk of the deep-seated samples is much smaller than the Xe/Kr ratio observed in average chondrites but higher than the Xe/Kr ratio in air. The Xe/Kr ratio in these deep-seated samples is, in fact, rather similar to that incorporated into sea water in contact with air. This suggests the possibility that the heavy noble gases in most of these samples were derived from atmospheric gases via dissolution in water. Subduction of crustal material containing water with dissolved noble gases may play an important role in the natural geochemical cycle of the noble gases. The concentrations of heavy noble gases in these rock samples are typically only 0.01-0.10% of their concentration in saturated sea water.

Figure 3 shows the ^{20}Ne and ^{36}Ar concentrations in the deep-seated samples. Fewer data points are shown there because Ne was not analyzed in many of the samples. Although the correlation between these two gases is not so well defined as in the three heavy noble gases, the ^{20}Ne concentration in the bulk of these samples is also depleted by a factor of 10 to l00 relative to the value computed by dividing the ^{20}Ne content of air by the mass of the Earth.

Unlike the correlations shown for the three heavy noble gases in Figs. 1 and 2, the Ar/Ne ratio in the bulk of these deep-seated samples is shifted away from that in sea water toward the Ar/Ne ratio in air. There are several possible reasons for this observation. The solubility of noble gases in silicate melts favors incorporation of the lighter noble gases (KIRSTEN, 1968), and preferential diffusion of light-weight noble gases into samples has generated high Ne/Ar ratios in tektites (HENNECKE et al., 1975) and in lava rocks with low concentrations of indigenous noble gases (HENNECKE and MANUEL, 1975c). In addition to these fractionation processes, it has been noted that contamination problems sometimes generate erroneously high Ne values in measurements of rocks with low Ne contents (CRAIG and LUPTON, 1976; KYSER, 1980).

The Ar/Ne ratios in the type-S gases implanted in the Pesyanoe meteorite (MARTI, 1969) and the type-X noble gases that were trapped in meteorites (SABU and MANUEL, 1980a) are shown in Fig. 3 for comparison. Type-Y noble gases are not shown because these contain no Ne.

Concentrations of ^{3}He and ^{20}Ne in the deep-seated rocks are shown in Fig. 4. Correlation lines expected for noble gases in sea water, air, primordial type-X gases, and solar wind implanted type-S gases are shown in the manner employed in Fig. 3. Although the experimental data provide little evidence that the ^{3}He correlates with ^{20}Ne, it is obvious from Fig. 4 that the ^{3}He/^{20}Ne ratio in these deep-seated samples is higher than that in air by three to five orders of magnitude. This great enrichment of ^{3}He relative to the other noble gases and the occurrence of high ^{3}He/^{4}He ratios in these samples suggest that the source of ^{3}He is different from that of Ne, Ar, Kr and Xe.

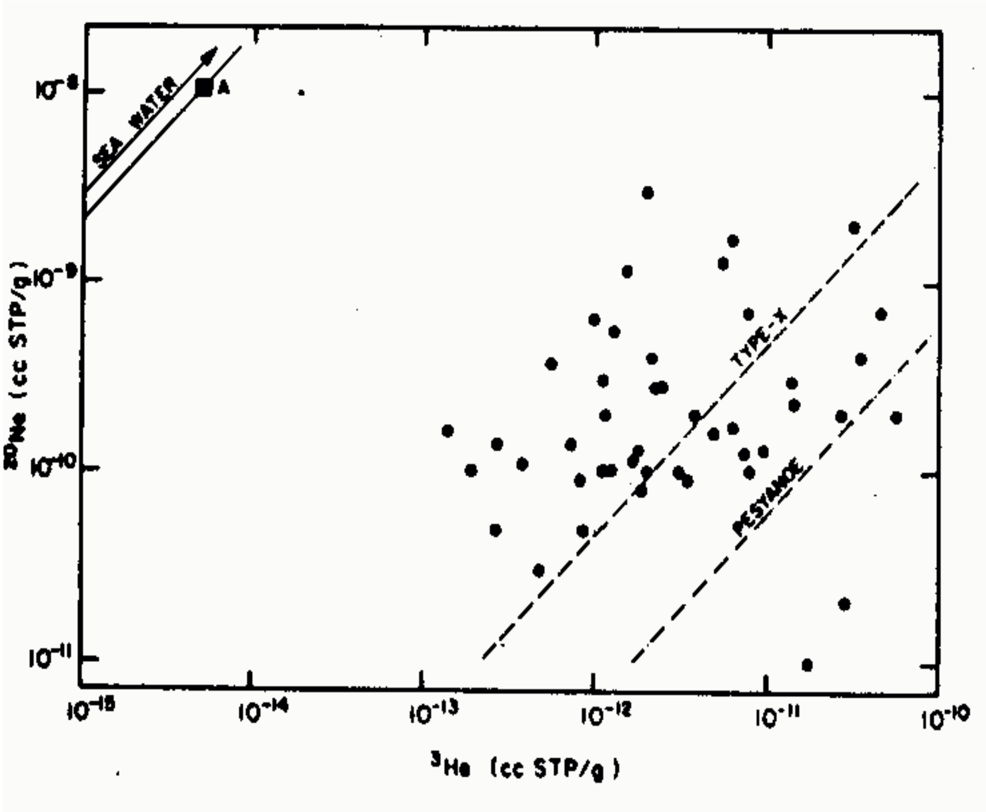

Fig. 4. Concentrations ^{20}Ne and ^{3}He in deep-seated samples (●). The bulk of these samples are enriched in ^{3}He by several orders of magnitude, but depleted in ^{20}Ne, relative to atmospheric gases. There is no apparent correlation of ^{3}He and ^{20}Ne concentrations. Point A and the lines are defined in the earlier figures.

The trends shown in elemental abundances of noble gases in Fig. 1-4 are summarized in Fig. 5, where the noble gas concentrations are shown relative to those in sea water (KYSER, 1980):

$$F^{m} = [^{m}X]_{\text{Sample}} / [^{m}X]_{\text{Sea Water}} \qquad (1)$$

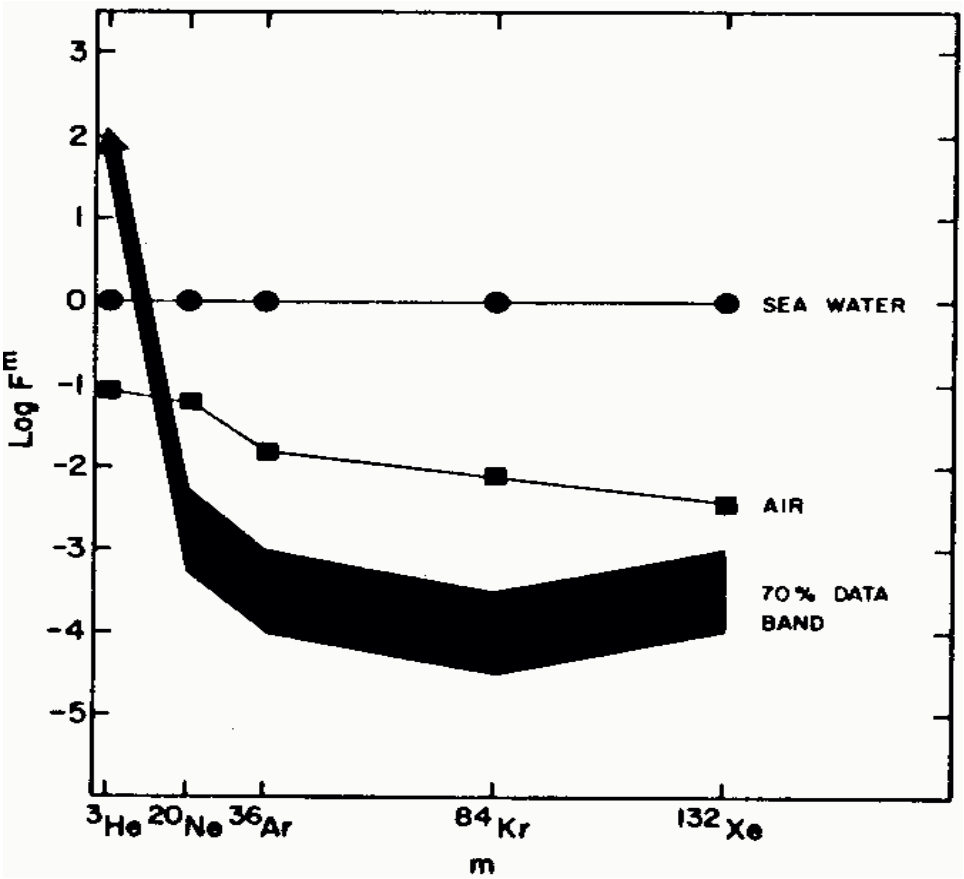

Fig. 5. Concentrations of noble gases in deep-seated samples and in air (■) relative to those in sea water (●). The concentrations of Ne, Ar, Kr and Xe in 70% of the deep-seated samples lie within the dark bank, i.e., they are depleted by 3 to 4 orders of magnitude in the heavy noble gases relative to those in sea water. The ^{3}He in these samples is enriched up to 3 orders of magnitude relative to that in sea water. The source of data and definition of F^m are given in the text.

Here [^{m}X] represents the concentration of the noble gas of atomic mass, m. The dark band in Fig. 5 encompasses 70% of the data for the Ne, Ar, Kr and Xe in these samples. The ^{3}He concentrations in these samples are 1 to 1,000 times the ^{3}He concentration in sea water, but the four heavier noble gases are depleted by 3 to 4 orders of magnitude relative to sea water. For comparison we have also shown, relative to sea water, the total atmospheric content of each noble gas divided by the mass of the Earth. The trends shown in Fig. 5 are important in demonstrating the possible role of sea water in explaining the heavy noble gas contents of samples from the upper mantle or lower crust. Clearly, ^{3}He cannot be accounted for by this mechanism.

To further demonstrate that ^{3}He and ^{20}Ne are of different origins, the correlation of ^{3}He concentrations with values of the ^{3}He/^{20}Ne ratio is shown in Fig. 6. On such a diagram, the data would form a vertical, linear array if ^{3}He correlated with ^{20}Ne. The 45°

correlation displayed by the data in Fig. 6 is further evidence that variations in the ^{3}He content are essentially independent of the ^{20}Ne contents of the rocks. Concentrations of ^{3}He *vs*. ratios of ^{3}He to ^{36}Ar, ^{84}Kr or ^{132}Xe display similar 45° correlations (not shown), as expected if ^{3}He came from a different source than the other noble gases.

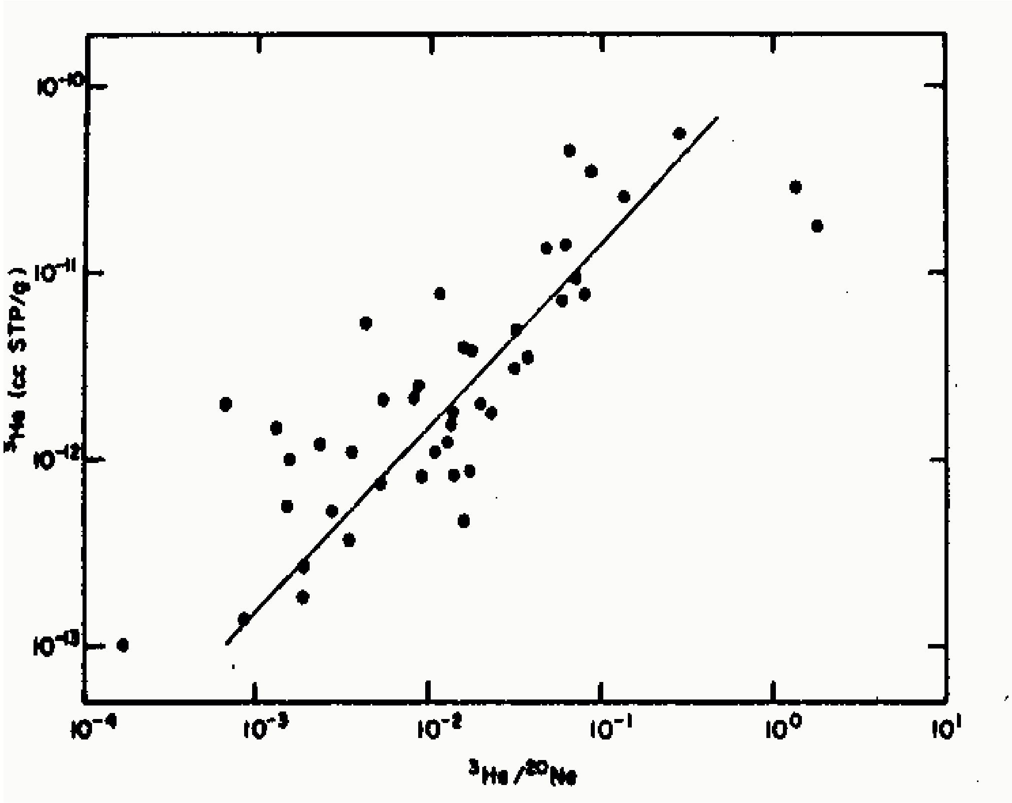

Fig. 6. Concentrations of ^{3}He and values of the ^{3}He/^{20}Ne ratio in deep-seated samples (●). The 45° correlation of the data indicates separate sources for the ^{3}He and ^{20}Ne contents.

In conclusion, the noble gas abundances of deep-seated rocks shown in Figs. 1-5 may indicate that the bulk of the Ne, Ar, Kr and Xe in these samples was derived from air, perhaps *via* water, but ^{3}He is an independent component of primitive gas which is leaking from the deeper interior of the Earth. Based on the high ^{3}He/^{4}He ratio alone, other investigators have concluded earlier that this must represent a primordial gas component (MAMYRIN et al., 1969; CLARKE et al., 1969; CRAIG et al., 1975; CRAIG and LUPTON, 1976; KANEOKA and TAKAOKA, 1978; KYSER, 1980; RISON, 1980). Our interpretation of the elemental abundances of Ne, Ar, Kr and Xe suggests that these samples were derived from a region of the Earth's interior that had once been almost quantitatively degassed. MATSUBAYASHI et al. (1978) have also shown that atmospheric rare gases dissolved in water may explain the abundance pattern of Ne, Ar, Kr and Xe in fumarolic gases of Japanese volcanic areas.

The upper mantle is an obvious source for deep-seated rocks collected at the Earth's surface, and the subduction of sedimentary material is an obvious mechanism for the reincorporation of atmospheric noble gases into this region. According to this view, the independent component of primitive ^{3}He is derived from the lower mantle. The retention of ^{3}He in the lower mantle over the history of the Earth suggests that the less mobile noble gases-Ne, Ar, Kr and Xe-should also have been retained there.

The existence of a primitive lower mantle was indicated by earlier studies of Sm-Nd systematics in kimberlites and their inclusions (BASU and TATSUMOTO, 1978; 1979). A similar model was developed to explain the Sm-Nd systematics of young volcanic rocks from oceanic and continental regions (WASSERBURG and DEPAOLO, 1979; DEPAOLO, 1980). According to WASSERBURG and DEPAOLO (1979) the lower mantle has been undifferentiated except for degassing of volatiles and loss of Fe to the core. However, the presence of primordial ^{3}He and other noble gases in the lower mantle seems difficult to reconcile with WASSERBURG and DEPAOLO'S position. The presence of an iron core inside an undifferentiated lower mantle that has retained primordial ^{3}He is more easily understood in terms of heterogeneous accretion (EUCKEN, 1944; TUREKIAN and CLARK, 1969; VINOGRADOV, 1975; MANUEL and SABU, 1975). According to this view, the iron cores of the terrestrial planets formed first, in an Fe-rich region of the protoplanetary nebula, and subsequently acquired silicates. As noted earlier, recent studies of iron meteorites (WASSON, 1970; BILD, 1977; NIEMEYER, 1979) provide independent evidence that some of these bodies also were formed by nebular processes rather than by the movement of Fe to the core of some parent body.

THE HELIUM AND NEON RECORD

The isotopic compositions of terrestrial Ar, Kr, and Xe are suggestive of type-Y, rather than type-X, noble gases. Since no He or Ne are associated with type-Y noble gases (SABU and MANUEL, 1980a), we assume that the terrestrial abundances of these two light gases were implanted, by the solar wind, on the surfaces of grains prior to accretion of the planet. We have shown earlier that Ar, Kr, and Xe are predominantly type-Y in the inner regions of the solar system (SABU and MANUEL, 1976) where the flux gradient of solar wind (type-S) gases is high. It should be noted that an early solar wind irradiation is possible since our model of condensation from concentric, chemically-zoned supernova debris does not require a high density of material in the inner region of the protoplanetary nebula. If instead the entire protoplanetary nebula initially had a homogeneous, cosmic composition, then an early irradiation by the solar wind would have been inhibited by the high concentrations of other elements that would have initially accompanied elements such as iron in the inner part of the solar system.

Clearly, we do not know the exact physical conditions of the inner protoplanetary nebula. However, it can easily be shown that complete volatilization of all planetary material presently found between the asteroid belt and the surface of the sun would produce a sphere with only 10^{-12} torr pressure at 2000° K. At such low pressures, the present solar wind flux (GEISS, 1973) would generate in preterrestrial grains the entire initial He and

Ne inventory of the Earth in a very short exposure period.

Independent evidence for irradiation of dust grains prior to compaction is provided by the distribution of solar wind implanted gases (WILKENING, 1971) and excess ^{21}Ne (SRINIVASAN et al., 1977; SABU and MANUEL, 1980b) in meteorites. We will show later that solar-wind implanted gases can account for the Earth's inventory of primordial He and Ne without affecting the isotopic compositions of the heavier noble gases.

Seismic measurements show that the Earth's upper mantle extends to a depth of about 700 km, corresponding to a mass of 1×10^{27} g or 25 % of the total mantle, and the lower mantle extends to a depth of about 3,000 km, corresponding to a mass of 3×10^{27} g (e.g., HERNDON, 1980). We assume that these regions correspond to the depleted upper mantle and the primitive lower mantle indicated by the abundances of ^{3}He and other noble gases in deep-seated rock.

In air ^{3}He/^{4}He = 1.4×10^{-6}, and in deep-seated rock samples the highest observed value for this ratio is ^{3}He/^{4}He = 4.5×10^{-5} (SAITO et a/., 1978a; KANEOKA and TAKAOKA, 1980). Intermediate values of ^{3}He/^{4}He have been observed in many other mantle-derived samples. We assume that helium in the lower mantle is characterized by ^{3}He/^{4}He $\geq 4.5 \times 10^{-5}$ because of the likelihood that primitive helium from the lower mantle will have been diluted with radiogenic ^{4}He from the upper mantle or crust.

CRAIG et al. (1975) have shown that ^{3}He is presently leaking into the atmosphere at a rate of 4 atoms cm^{-2}sec^{-1}. This corresponds to 2.4×10^{7} cm^{3} STP yr^{-1} of ^{3}He and 5.3×10^{11} cm^{3} STP yr^{-1} of ^{4}He from the lower mantle. The latter is much smaller than the expected production rate of radiogenic ^{4}He in the lower mantle.

To calculate the minimum production rate of ^{4}He in the lower undepleted mantle, we assume a uranium content of 20 ppb. ANDERS (1977) estimates a uranium content of 18 ppb for the whole earth which, when corrected for the core, corresponds to 27 ppb for the mantle. For a Th/U ratio of 3.7 and a U concentration of 20 ppb, the present production rate of radiogenic ^{4}He in the lower mantle will be 1.3×10^{13} cm^{3} STP yr^{-1}. This is about a factor of 20 higher than the maximum escape rate of ^{4}He from the lower mantle. Thus, the inventory of radiogenic ^{4}He in the lower mantle is still building up.

The annual escape rate of ^{4}He is less than one part in 10 billion parts of the total radiogenic ^{4}He produced in the lower mantle over the last 4.55×10^{9} yr (PATTERSON, 1956), 1.0×10^{23} cm^{3} STP. Since the maximum ^{4}He escape rate is only 5% of the present ^{4}He production rate, i.e., ^{4}He is still accumulating, we assume that a negligible fraction of radiogenic ^{4}He leaked from the lower mantle, except for that lost in an initial catastrophic degassing period to be discussed later.

A current ^{3}He/^{4}He ratio of 4.5×10^{-5} and a radiogenic ^{4}He content of 1.0×10^{23} cm^{3} STP, correspond to a value of 5.1×10^{18} cm^{3} STP of primordial ^{3}He in the present lower mantle. Solar-wind implanted gases are characterized by a ^{3}He/^{4}He ratio of 4.4×10^{-4} and a ^{3}He/^{20}Ne ratio of 0.214 (GEISS et al., 1972). Since ^{3}He would be expected to leak preferentially over ^{20}Ne from the lower mantle, the minimum ^{20}Ne content of the lower mantle is presently 2.4×10^{19} cm^3 STP. It should be stressed that the above calculations do *not* assume quantitative retention of primordial ^{3}He or ^{20}Ne in the lower mantle.

Since the total ^{20}Ne content of the atmosphere is 6.5×10^{19} cm^3 STP, the total ^{3}He which has been released to the atmosphere must be $> 1.4 \times 10^{19}$ cm^3 STP. This minimum value is obtained by assuming that the ^{3}He/^{20}Ne ratio in gases escaping to the atmosphere was the same as that implanted by the solar wind, i.e., assuming that there was no preferential leakage of ^{3}He. The minimum inventory of primordial ^{3}He, ^{4}He, and ^{20}Ne for the total Earth are, respectively, 1.9×10^{19}, 4.3×10^{22} and 8.9×10^{19} cm^3 STP. If the upper and lower mantle initially had the same composition and the core contained negligible amounts of noble gases, then 75% of the above values would be the minimum initial He and Ne inventory of the lower mantle.

If the upper mantle has released essentially its entire inventory of ^{20}Ne to the atmosphere, and if there has been no escape of ^{20}Ne from the atmosphere, then the lower mantle has retained a minimum of $(2.4 \times 10^{19})/(2.4 \times 10^{19} + 6.5 \times 10^{19}) = 27\%$ of the entire mantle’s initial inventory of ^{20}Ne. This corresponds to a minimum value of 36% for the retention of the lower mantle's initial inventory of ^{20}Ne.

Pertinent features of the Earth’s helium record are summarized in Table 1. Temporal variations of the ^{3}He/^{4}He ratio and the ^{4r}He/^{4p}He ratio in the lower mantle are presented in Fig. 7.

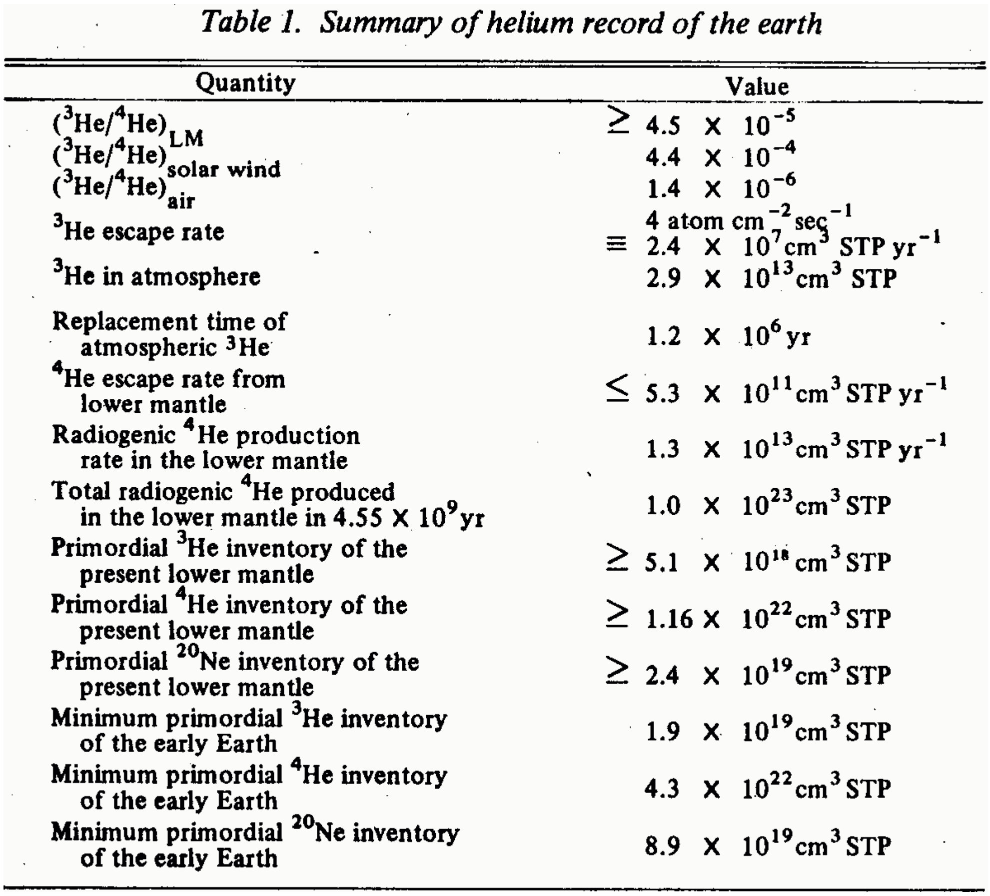

Table 1. Summary of helium record of the earth

Quantity	Value
$(^3He/^4He)_{LM}$	$\geq 4.5 \times 10^{-5}$
$(^3He/^4He)_{solar\ wind}$	4.4×10^{-4}
$(^3He/^4He)_{air}$	1.4×10^{-6}
^3He escape rate	4 atom $cm^{-2} sec^{-1}$ $\equiv 2.4 \times 10^7 cm^3$ STP yr^{-1}
^3He in atmosphere	$2.9 \times 10^{13} cm^3$ STP
Replacement time of atmospheric ^3He	1.2×10^6 yr
^4He escape rate from lower mantle	$\leq 5.3 \times 10^{11} cm^3$ STP yr^{-1}
Radiogenic ^4He production rate in the lower mantle	$1.3 \times 10^{13} cm^3$ STP yr^{-1}
Total radiogenic ^4He produced in the lower mantle in 4.55×10^9 yr	$1.0 \times 10^{23} cm^3$ STP
Primordial ^3He inventory of the present lower mantle	$\geq 5.1 \times 10^{18} cm^3$ STP
Primordial ^4He inventory of the present lower mantle	$\geq 1.16 \times 10^{22} cm^3$ STP
Primordial ^{20}Ne inventory of the present lower mantle	$\geq 2.4 \times 10^{19} cm^3$ STP
Minimum primordial ^3He inventory of the early Earth	$1.9 \times 10^{19} cm^3$ STP
Minimum primordial ^4He inventory of the early Earth	$4.3 \times 10^{22} cm^3$ STP
Minimum primordial ^{20}Ne inventory of the early Earth	$8.9 \times 10^{19} cm^3$ STP

The widespread occurrence of helium with $^3He/^4He = 1.3 \times 10^{-5}$ in submarine basalts (CRAIG and LUPTON, 1976; KANEOKA and TAKAOKA, 1978; KYSER, 1980; RISON, 1980) clearly indicates that radiogenic ^4He and primordial ^3He from the lower mantle are well mixed in large suboceanic regions of the upper mantle. Such mixing is a natural consequence of the dynamic equilibrium that is anticipated from the present model; ^3He is uniformly leaking at a constant rate from the primitive lower mantle, traversing a vertical distance of about 700 km in the upper mantle, being released to the atmosphere where its mean residence time is 1.2 My, and ultimately escaping to space. During its ascent through the upper mantle, mixing produces a $^3He/^4He$ ratio that is unable to record any heterogeneity in the distribution of uranium in the region of the upper mantle that is traversed by the ^3He. Since the 3He is expected to move through a large volume of the upper mantle, it is not surprising that relatively constant $^3He/^4He$ ratios are observed in submarine basalts. More rapid ascent of the helium, e.g., in hot spots, might result in higher $^3He/^4He$ ratios (KANEOKA and TAKAOKA 1978).

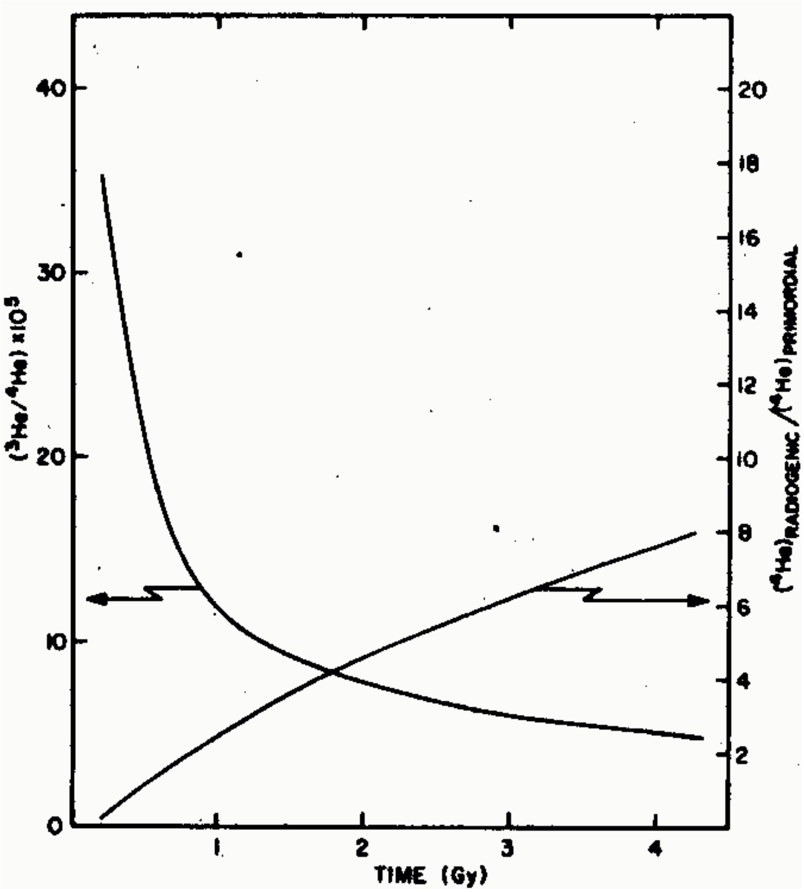

Fig. 7. Values of the ^{3}He/ ^{3}He ratio (left ordinate) and the ratio of radiogenic: primordial ^{4}He (right ordinate) in the lower mantle. The basis of these calculated values is given in the text.

Values of the ^{20}Ne/^{22}Ne ratio in type-X gases, in air, and in the solar wind are 8.2 (REYNOLDS et al., 1978), 9.8 (NIER, 1950) and 13.5 (GEISS et al., 1972), respectively. The solar-wind implanted Ne in lunar soils reveal fractionation effects which cause the ^{20}Ne/^{22}Ne ratio to vary from 8.5 to 14 (HOHENBERG et al., 1970; MEGRUE and STEINBRUNN, 1972; SRINIVASAN, 1973). The value of the ^{20}Ne/^{22}Ne in the lower mantle is not known, but several investigators have reported ^{20}Ne/^{22}Ne ratios in deep-seated samples that are higher than the value in air (HENNECKE and MANUEL, 1975a; CRAIG and LUPTON, 1976; PHINNEY et al., 1978; DOWNING et al., 1977; KYSER, 1980). The highest value, ^{20}Ne/^{22}Ne = 11.6, was observed in CO_2 gas which contained a large excess of radiogenic ^{129}Xe (PHINNEY et al., 1978).

We suspect that fractionation is responsible for the fact that the ^{20}Ne/^{22}Ne ratio in air is lower than that in the solar wind (SABU and MANUEL, 1980b). However, we cannot specify the locale of fractionation from presently available data, whether during implantation of solar wind gases on grain surfaces or later by loss from the Earth's atmosphere. Any loss of neon from the Earth's atmosphere would require a higher original inventory of He and Ne, and a correspondingly lower fractional retention of these elements in the lower mantle. However, the minimum inventories shown above and in Table 1 for He and Ne in the present lower mantle would be unchanged. It should be noted that continuous degassing would tend to produce a higher $^{20}Ne/^{22}Ne$ ratio in air than in the residual neon of the mantle. The available data provide no evidence for the occurrence of this type of fractionation.

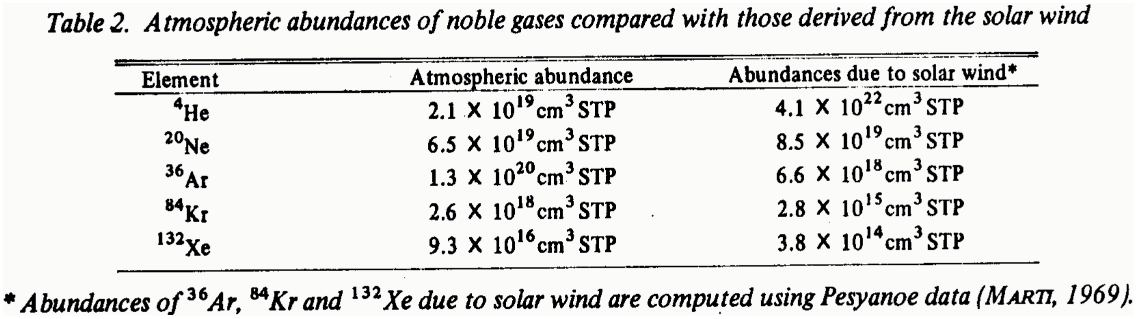

Table 2. Atmospheric abundances of noble gases compared with those derived from the solar wind

Element	Atmospheric abundance	Abundances due to solar wind*
^{4}He	$2.1 \times 10^{19} cm^3$ STP	$4.1 \times 10^{22} cm^3$ STP
^{20}Ne	$6.5 \times 10^{19} cm^3$ STP	$8.5 \times 10^{19} cm^3$ STP
^{36}Ar	$1.3 \times 10^{20} cm^3$ STP	$6.6 \times 10^{18} cm^3$ STP
^{84}Kr	$2.6 \times 10^{18} cm^3$ STP	$2.8 \times 10^{15} cm^3$ STP
^{132}Xe	$9.3 \times 10^{16} cm^3$ STP	$3.8 \times 10^{14} cm^3$ STP

** Abundances of ^{36}Ar, ^{84}Kr and ^{132}Xe due to solar wind are computed using Pesyanoe data (MARTI, 1969).*

In Table 2, the atmospheric abundances of noble gases are compared with those from the solar wind, assuming that the Earth’s initial inventory of He and Ne is of solar wind origin. It can be seen that the amounts of Ar, Kr, and Xe added from the solar wind would constitute only a small fraction of those in air, and it will be shown later that the atmosphere itself represents only a small fraction of the Earth’s total inventory of Ar, Kr, and Xe. Terrestrial Ar, Kr and Xe are the type-Y noble gases that are tenaciously retained in carbon-rich minerals of meteorites (GÖBEL et al., 1978; REYNOLDS et al., 1978) in contrast to the solar-wind implanted He and Ne that reside on grain surfaces (WILKENING, 1971). It would not be surprising if the solar-wind implanted gases preferentially leaked from the lower mantle.

THE ARGON RECORD

There have been many attempts to use the decay of ^{40}K to gaseous ^{40}Ar to obtain information on the evolution of the atmosphere (See OZIMA, 1975; HAMANO and OZIMA, 1978; HART et al., 1979, and references therein). We will forego a review of these because of the large number and wide range of conclusions drawn from the K-Ar chronometer for atmospheric evolution schemes. It should be noted, however, that the value of K = 170 ppm for the entire Earth, as suggested in one report (ANDERS, 1977), would require melting of essentially the entire Earth to account for the ^{40}Ar content of the atmosphere. Such an event is difficult to reconcile with observations of primordial ^{3}He and radiogenic ^{129}Xe in samples from the Earth’s interior. For simplicity, we therefore assume a chondritic Earth rather than an exotic mix of early condensates, remelted and unremelted [sic] metals and silicates, troilites, mysterites, etc., although the latter is certainly a versatile model (ANDERS, 1977).

If the K content of the mantle is about 800 ppm, then the entire atmospheric inventory of ^{40}Ar, 3.7 × 10^{22} cc STP, could be generated within the first 300 My of the Earth's history. However, other features of terrestrial noble gases clearly indicate that the Ar record is not that simple. We have shown earlier that the lower mantle is presently accumulating radiogenic ^{4}He and that it has retained an appreciable fraction of its initial inventory of primordial He and Ne. It is also reasonable to expect that the lower mantle has retained heavy noble gases preferentially over He and Ne. We have shown, however, that the concentrations of Ne, Ar, Kr, and Xe in samples from the upper mantle are appreciably lower than the value obtained by dividing the atmospheric inventory of these gases by the entire mass of the Earth (See Figs. 1-3). These two findings suggest that the bulk of the Ar, Kr, and Xe in air were derived by a thorough degassing of the upper mantle alone. In that case, the present concentrations of Ar, Kr, and Xe in samples from the upper mantle should be compared with the atmospheric inventory of these gases divided by the mass of the upper mantle. The upper mantle constitutes only 1/6 of the Earth's mass; accordingly the gas concentrations labeled A in Figs. 1-3 should be systematically increased by a factor of 6. When corrected thusly, the concentrations of heavy noble gases in the bulk of these deep-seated samples can be shown to comprise only 0.1 to 1.0% of the upper mantle's initial inventory of these elements - in spite of the ongoing introduction of gas-rich sediments into the upper mantle by subduction.

We therefore assume that ^{36}Ar was quantitatively lost from the upper mantle in an early catastrophic event over a time period that will later be shown to be about 200 My. Only a small fraction of the ^{40}K will have decayed during that period, so that the value of the ^{40}Ar/^{36}Ar ratio will be about 56. Temporal changes in the ^{40}Ar/^{36}Ar ratio are shown in Fig. 8 for two plausible scenarios.

Figure 8 was constructed using the chondritic value of 800 ppm for the K content of the primitive upper mantle and assuming that the entire atmospheric inventory of ^{36}Ar was derived from the upper mantle in the first 200My. The values used for other parameters in constructing Fig. 8 are as follows: Mass of upper mantle = 1 × 10^{27} g; ^{36}Ar content of atmosphere = 5.56 × 10^{15} moles (VERNIANI, 1966); Mass of the Earth's crust = 28.5 × 10^{24} g; K content of the crust = 1.9 % (RONOV and YAROSHEVSKI, 1969).

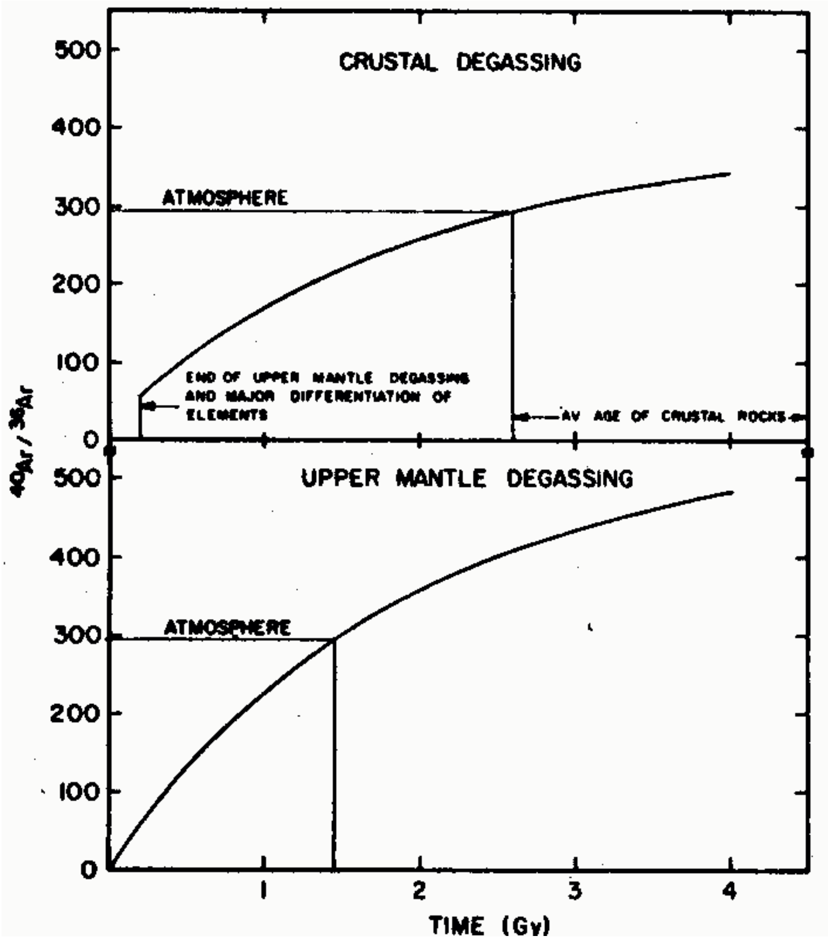

Fig. 8. Evolution of atmospheric ^{40}Ar/^{36}Ar ratios if crustal degassing alone contributed radiogenic ^{40}Ar to the atmosphere after the end of initial 200My period of catastrophic degassing (top section) and if the entire upper mantle continued to release radiogenic ^{40}Ar to the atmosphere (bottom section). The evolution of ^{40}Ar/^{36}Ar ratios in the undifferentiated lower mantle would resemble that shown by the lower section. The model shown in the top section is preferred because this yields an average age of 2Gy for crustal rocks.

The top section of Fig. 8 shows values of ^{40}Ar/^{36}Ar obtained if the bulk of the K in the present lithosphere was transported from the upper mantle during the first 200 My period, and this alone degassed until the present atmospheric value of ^{40}Ar/^{36}Ar = 296 was realized. The curve represents atmospheric values of the ^{40}Ar/^{36}Ar ratio generated by total degassing of Ar from the upper mantle for the first 200 My, followed by degassing of the crust alone. As shown in the top of Fig. 8, crustal degassing would have continued until about 2Gy ago, and this should therefore correspond to the average K-Ar age of crustal rocks. It should be stressed that we have assumed a very simple model of total ^{40}Ar degassing prior to solidification of the crust, rather than the commonly defined “continuous degassing” that is described by a first order rate equation (See HAMANO and OZIMA, 1978 and references therein).

The bottom section of Fig. 8 shows the evolution of the $^{40}Ar/^{36}Ar$ ratio in air by exhaustive degassing of the upper mantle-plus-crust system. If K differentiation had no effect on the degassing of radiogenic ^{40}Ar from the upper mantle, then the present atmospheric value of $^{40}Ar/^{36}Ar = 296$ would have been established 3Gy ago, and this should correspond to the average K-Ar age of the present crust and upper mantle system:

An average age of 3Gy for crustal rocks is inconsistent with other observations (HURLEY and RAND, 1969). We prefer the ^{40}Ar degassing model indicated in the upper section of Fig. 8 because this yields a reasonable value for the average age of crustal rocks. It takes into account the very real possibility of preferential degassing of crustal material, and it is consistent with the ^{129}Xe record to be discussed later. The Ar record indicated by the upper section of Fig. 8 is somewhat like that of HART et al. (1979). On the basis of radiogenic ^{40}Ar alone, HART et al. (1979) concluded that the upper 25 % of the total mantle was preferentially degassed during an unspecified time period.

Subducted sediments are an obvious possible source for the argon with low values of $^{40}Ar/^{36}Ar$ that have been reported in many deep-seated samples (THOMPSON et al., 1978; SAITO et al., 1978a, b; KANEOKA et al., 1978; MELTON and GIARDINI, 1980; KANEOKA and TAKAOKA, 1980; KYSER, 1980). In a few cases the low $^{40}Ar/^{36}Ar$ ratios may indicate the entrapment of Ar from the undepleted lower mantle, e.g., in samples with other indications of great depth (KANEOKA and TAKAOKA, 1978; KYSER, 1980; RISON, 1980). The evolution of the $^{40}Ar/^{36}Ar$ ratio in the lower mantle will be similar to that shown in the bottom section of Fig. 8. Samples containing $^{40}Ar/^{36}Ar < 296$ (MELTON and GIARDINI, 1980) may be understood as Ar released from the lower mantle within the first 1.5Gy, i.e., more than 3Gy ago.

THE KRYPTON RECORD

So far as the noble gas record of the Earth is concerned, the elemental abundance of Kr appears to contain more significant information than does its isotopic composition. The latter is useful in confirming the absence of type-X gases, but the isotopic composition of Kr is not a sensitive monitor of any geological events in evolution of the atmosphere.

In type-Y noble gases the $^{84}Kr/^{132}Ar$ ratio is about 1.4. In air the $^{84}Kr/^{132}Xe$ ratio is 29, although the $^{36}Ar/^{84}Kr$ ratio in air is similar to that seen in meteorites. Thus, Xe appears to be underabundant in air by about a factor of 20.

It has been suggested that Xe was depleted by adsorption on fine grained and carbonaceous sediments or by incomplete degassing from the upper mantle. There is unambiguous evidence for preferential adsorption of Xe on sediments and carbonaceous material, although it should be noted that there may be a serious underestimation of the amount of adsorbed Xe (OLIVER and MANUEL, 1981). In most of the experimental work, the samples are preheated under vacuum to remove adsorbed gases prior to the release of gases for analysis. In one report on Xe in Wausau granite (HENNECKE et al., 1978), a sample that had been preheated for 1 hour at 100°C under vacuum was found to contain 6 times the Xe concentration of another sample that had been preheated with an IR lamp for 30 minutes. The excess Xe was released from the first sample at low extraction temperatures, as expected for an adsorbed component. In another study (KURODA et al., 1977), it was reported that over 80% of the total xenon in Red Rock granite was released at extraction temperatures of 200°C and 400°C, although this sample had also been preheated under vacuum and those gases were pumped away prior to gas analysis.

Until experiments are designed and employed to measure the total amount of Xe adsorbed on terrestrial samples, the role of adsorption in producing the high Kr/Xe ratio of air cannot be fairly evaluated. There is, however, already overwhelming evidence that the ^{84}Kr/^{132}Xe ratio in carbonaceous and sedimentary material is much lower than the atmospheric value of 29 (CANALAS et al., 1968; FANALE and CANNON, 1971; PHINNEY, 1972; BOGARD et al., 1965; KURODA and SHERRILL, 1977; FRICK and CHANG, 1977; PODOSEK et al., 1980), and in several of these samples the ^{84}Kr/^{132}Xe ratio is even less than the chondritic value of ^{84}Kr/^{132}Xe = 1.4. We will therefore assume that the total Xe in the upper-mantle-plus-crust system is 20 times the Xe content of air.

THE XENON RECORD

Unlike Kr, Xe is blessed with an overabundance of isotopic ratios which play a major role in our understanding of the noble gas record of terrestrial and meteoritic samples. Of particular significance to the time frame for evolution of the atmosphere is the occurrence of large enrichment of ^{129}Xe, the decay product of extinct 16 My ^{129}I, in the Earth's interior (BUTLER et al., 1963; BOULOS and MANUEL, 1971; HENNECKE and MANUEL, 1975a, b; PHINNEY et al., 1978; KANEOKA and TAKAOKA, 1978, 1980; KYSER, 1980; RISON, 1980).

Xenon is composed of nine stable isotopes, and the isotopic compositions of chondritic and terrestrial Xe differ across the entire spectrum-from ^{124}Xe to ^{136}Xe (REYNOLDS, 1960b). The features of this general isotopic anomaly pattern are suggestive of fractionation (KRUMMENACHER et al., 1962; OZIMA and NAKAZAWA, 1980), although fractionation fails to account for details of the anomaly pattern at several isotopes. Solar-wind implanted Xe is isotopically unlike terrestrial or chondritic Xe, and the general features of the anomaly pattern for type-S Xe are also suggestive of fractionation.

The origin of differences between the general isotopic patterns of chondritic and terrestrial Xe was partially resolved with the realization that chondritic Xe is a mixture of type-X and type-Y components with different nucleogenetic origins (MANUEL et al., 1972; SABU and MANUEL, 1976, 1980a). Type-X Xe is enriched in the r- and p-products of nucleosynthesis, and recently a complementary Xe component enriched in $^{128-132}$Xe isotopes from the s-process of nucleosynthesis has also been reported in chondrites (SRINIVASAN and ANDERS, 1978; BALLAD et al., 1979). After subtraction of these nucleogenetic components, differences in the isotopic compositions of terrestrial, chondritic and solar-wind implanted Xe provide evidence of mass dependent fractionation.

The resolution of different nucleogenetic components in terrestrial Xe is not a primary concern of this paper on the Earth's noble gas record, except in establishing the initial values of specific isotopic ratios that may have subsequently been altered by radioactive decay. This subject is treated in the Appendix, where it is shown that the ^{136}Xe/^{130}Xe ratio in air is essentially the same as that which was present in the Earth initially, i.e., fission products from ^{244}Pu and ^{238}U have not altered this ratio appreciably. Radiogenic ^{129}Xe from the decay of extinct ^{129}I has, however, increased the ^{129}Xe/^{130}Xe ratio in air by about 5 % from an initial value of 6.19 to its present value, 6.48.

Even larger enrichments of radiogenic ^{129}Xe have been observed in a few terrestrial samples. In all cases where the enrichment is large, the radiogenic ^{129}Xe is accompanied by CO_2 (BOULOS and MANUEL, 1971; HENNECKE and MANUEL, 1975a, b; PHINNEY et al., 1978; KYSER, 1980; RISON, 1980). These observations suggest that radiogenic 129Xe may also have been transported to the atmosphere in a CO_2 carrier.

Differences between the present and the initial ^{129}Xe/^{130}Xe ratio of atmospheric Xe, 6.480- 6.195 (See Appendix) and the ^{130}Xe content of air yield a value of 4.0×10^{15} cc STP for the present abundance of radiogenic ^{129}Xe in air. The total radiogenic ^{129}Xe content of the upper-mantle-plus-crust system, 20 times the atmospheric inventory, is 8×10^{16} cc STP. There are 39.9×10^{22} g of CO_2 in the crust (RONOV and YAROSHEVSKI, 1969), so that the volume ratio of radiogenic ^{129}Xe to CO_2 is 3.9×10^{-10}.

In a sample of CO_2 well gas the volume ratio of radiogenic ^{129}Xe to CO_2 is 4.5×10^{-13} (PHINNEY et al., 1978). If CO_2 was the carrier gas in both cases, then difference between these two volume ratios may reflect a temporal change in the ^{129}I/^{127}I ratio. Hence the site represented by the CO_2 well gas sample may have started to retain the decay product of ^{129}I about 200 My after degassing started.

It should be stressed that large enrichments of radiogenic ^{129}Xe have only been observed in samples rich in CO_2, and the Ar in these samples consistently displays high values of ^{40}Ar/^{36}Ar (HENNECKE and MANUEL, 1975a, b; PHINNEY et al., 1978; KYSER, 1980; RISON, 1980). KANEOKA and TAKAOKA (1980) also report definite excesses of ^{129}Xe only in Hawaiian samples with ^{40}Ar/^{36}Ar >~ 4,000, although they earlier reported a small enrichment of ^{129}Xe in one olivine phenocryst with ^{40}Ar/^{36}Ar $\approx$ 700 (KANEOKA and TAKAOKA, 1978). Since the lower mantle has retained most of its heavy noble gases, the high ^{40}Ar/^{36}Ar ratios are, in our view, evidence that the CO_2 carries gases from the depleted upper mantle. Thus, excess ^{129}Xe occurs in the upper mantle, and this observation limits the time period for exhaustive degassing of xenon to a few half-lives of ^{129}I.

SUMMARY OF EARTH'S NOBLE GAS RECORD

Before discussing the noble gas record of the other inner planets, it seems appropriate to compare the conclusions from our consideration of the five terrestrial noble gases with those of others who have sought to understand the manner by which the terrestrial atmosphere was degassed from the interior of the Earth. Although our conclusions differ in many important aspects from those of earlier studies, the similarities are also noteworthy.

We agree, for example, with the earlier suggestions that the terrestrial inventory of argon isotopes indicates an early catastrophic degassing (DAMON and KULP, 1958; FANALE, 1971; SCHWARTZMAN, 1973; OZIMA, 1975; HAMANO and OZIMA, 1978; HART et al., 1979). We also agree with previous suggestions that the presence of radiogenic ^{129}Xe in the mantle indicates a very short time period for any exhaustive release of volatiles to the atmosphere (BOULOS and MANUEL, 1971; BERNATOWICZ and PODOSEK, 1978; THOMSEN, 1980). Yet, we concur with TOLSTIKHIN (1975) in concluding that the helium isotopes indicate continuous degassing of the Earth. We have shown that atmospheric contamination can account for the Ne, Ar, Kr and Xe observed in most deep-seated samples, and we agree with the suggestion (TOLSTIKHIN, 1978) that the escape of helium into space from the Earth's atmosphere maintains the low atmospheric level of helium that permits us to observe primitive helium in these samples in spite of a major noble gas component from the atmosphere.

The undepleted lower mantle suggested by the terrestrial noble gas data has been proposed earlier to explain the distribution of other terrestrial elements (BASU and TATSUMOTO, 1978; 1979; WASSERBURG and DEPAOLO, 1979; DEPAOLO, 1980). Noble gas studies by KYSER (1980) and RISON (1980) support the concept of an undepleted lower mantle, but we disagree with the suggestion that xenon with a high ^{129}Xe/^{132}Xe ratio came from this undepleted lower mantle (RISON, 1980). BERNATOWICZ and PODOSEK (1978) suggested earlier that the atmosphere may have been formed by rapid degassing of only a small part of the Earth, but concluded that any definite statement of the Earth's degassing history would be premature.

Although the constant ^{3}He/^{4}He ratio in submarine tholeiites from mid-ocean ridge basalts and in some mantle xenoliths suggest that the suboceanic mantle is homogeneous on a large scale, the noble gas data do not rule out lateral heterogeneities of the upper mantle. In fact, high values of the ^{3}He/^{4}He ratio in an olivine phenocryst (KANEOKA and TAKAOKA, 1978) and submarine tholeiites (KYSER, 1980) from Kilauea suggest heterogeneities in the chemical composition of the upper mantle or in the transport process of He from the lower mantle. Isotopic compositions of Pb, Sr and Nd in tholeiites from mid-ocean ridge basalts also differ from those in alkalic basalts of ocean islands, and Nd-isotopic data in xenoliths of continental kimberlites suggest that the subcontinental and the suboceanic mantle differ above 200 km (BASU and TATSUMOTO, 1980). In our opinion, the presently available noble gas data provide strong support for early catastrophic degassing of Ne, Ar, Kr and Xe from the upper mantle and for continuous degassing of He from the lower mantle. Further studies of terrestrial noble gases may reveal additional fine structure in the noble gas record of the early history of the Earth and the volution of its atmosphere.

The existence of a primitive lower mantle suggested by this and other studies cited above seems to be compatible with the suggestion that the solar system formed from the chemically heterogeneous debris of a single supernova (MANUEL and SABU, 1975), but an undepleted lower mantle is difficult to reconcile with the model of homogeneous accretion of the Earth in a gas of solar composition. HAYASHI et al. (1979) note that the blanketing effect of a dense primordial atmosphere of solar chemical composition would maintain the surface temperature of the proto-Earth high enough to melt most of the materials. They suggest that the mass of this primitive atmosphere (mostly H and He) was as large as 10^{26} g, but it was blown away between the time of the Earth's formation and the formation of the present atmosphere.

We do not assume that an envelope of H and He was blown away from the inner planets. We assume instead that the primitive protoplanetary nebula was chemically zoned in the manner of elements in an evolved star, with Fe concentrated in the central region and the light elements, H, He and type-X noble gases concentrated in the outer region. <u>As noted earlier, isotopic analysis of Xe in Jupiter will provide an unambiguous test of this model</u>.

THE NOBLE GAS RECORD OF VENUS AND MARS

For Earth, we have shown that the noble gas record suggests that the atmosphere and crust were produced by differentiation of the upper mantle, i.e., the upper one-sixth of the Earth. The model developed to explain terrestrial noble gases may also be useful in understanding the noble gas abundances in the atmospheres of Mars and Venus.

The puzzling high abundances of noble gases in the atmosphere of Venus (POLLACK and BLACK, 1979) and low abundances of these elements in the atmosphere of Mars (OWEN, 1978) may also be understood in terms of different degrees of degassing. Venus is closer to the Sun than is Earth, and it would therefore tend to collect more radiant energy from the Sun. It is approximately the same size as the Earth, and both would be expected to generate heat from sources such as radioactive decay and the release of gravitational energy during accretion. However, more extensive degassing is expected for Venus because of its higher ambient temperature, at present (POLLACK and YUNG, 1980) and in its protoplanetary stage.

Likewise, Mars collects less radiant energy than Earth because it is both farther from the Sun and smaller in size. It is therefore expected to degas to a lesser extent than Earth.

The extent of degassing of Mars can be approximated in the following manner. The radiogenic ^{129}Xe in its atmosphere is equivalent to 1.1×10^{-12} cc STP per g for the entire planet (OWEN, 1978). Based on 50 ppb I and an initial ^{129}I/^{127}I ratio of 1×10^{-5}, the total amount of radiogenic ^{129}Xe expected is 8.7×10^{-11} cc STP per g. Thus only 1-2% of the radiogenic ^{129}Xe has been released into the Martian atmosphere.

In a similar fashion, in the Martian atmosphere the presence of 4.8×10^{-7} cc STP of radiogenic ^{40}Ar per g of the planet (OWEN, 1978) and a K content of 800 ppm indicate that degassing of the upper 1.6% of the planet for one half-life of ^{40}K (1.28Gy) can account for the Martian inventory of atmospheric ^{40}Ar.

Thus, chondritic abundances and extensive degassing of the upper 1-2% layer of Mars can account for its atmospheric inventory of radiogenic ^{129}Xe and ^{40}Ar. The total noble gas content of Mars is therefore expected to be about 100 times that observed in its atmosphere.

Isotopic data for the noble gases in the atmosphere of Venus are not well known, although preliminary data indicates a surprisingly low value for the ^{40}Ar/^{36}Ar ratio (POLLACK and BLACK, 1979). This might suggest an early degassing of a large fraction of its primordial noble gases, followed by the release of only a small fraction of its radiogenic ^{40}Ar. In comparing the abundance patterns of noble gases in the terrestrial planets, we will assume that the primordial noble gases were completely degassed from Venus.

Figure 9 compares the noble gases in Venus, Earth and Mars with those in two meteorite samples rich in type-Y noble gases, Allende's mineral "Q" (LEWIS et al., 1975) and the Kenna ureilite (WILKENING and MARTI, 1976). In each case, the gas contents are shown relative to the solar-wind implanted noble gases (type-S) in the Pesyanoe achondrite (MARTI, 1969).

The atmosphere of Mars shows the lowest noble gas content, but we have shown that both ^{40}Ar and ^{129}Xe suggest that the total inventory of Martian noble gases is higher, by about 2 orders of magnitude, than the values plotted in Fig. 9. When thus corrected for the limited extent of Martian degassing, the noble gas abundance pattern would plot near that shown for the Earth's upper-mantle-plus-crust system.

The noble gas abundance pattern in air shows a depletion of Xe. The dashed line shows the value when corrected for adsorbed Xe. Also shown is the Earth's total noble gas inventory, calculated on the basis of formation of the atmosphere by extensive degassing of the upper 1/6 of the entire Earth.

The atmospheric inventory of Venusian Xe and He has not been reported (POLLACK and BLACK, 1979). The dashed line represents an estimate of its Xe, assuming that the Xe/Kr ratio is terrestrial. The values represent complete degassing of Venus. The reasons given earlier for this assumption would also suggest complete degassing of Mercury.

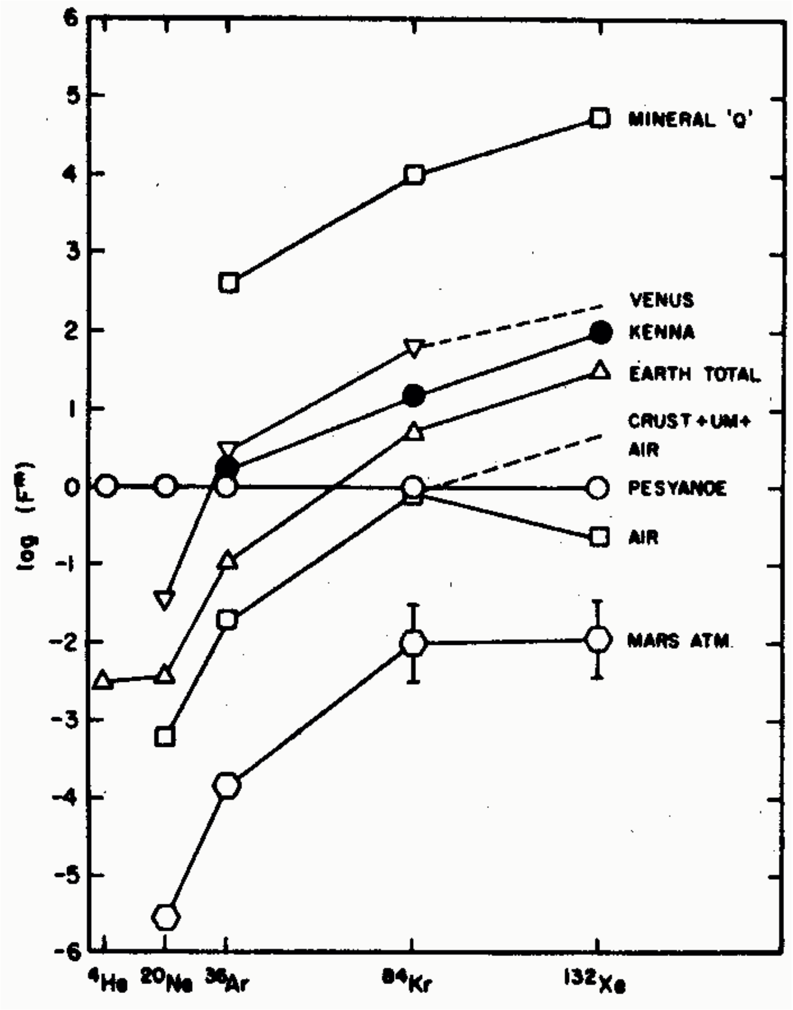

Fig. 9. The abundance patterns of noble gases in select meteorites and in the terrestrial planets relative to those implanted in the Pesyanoe meteorite by the solar wind. Values of F^m are calculated by dividing the concentration of any noble gas isotope of mass, m, by the concentration of that isotope in Pesyanoe. Similarities of the abundance patterns of noble gases in meteorites and in the terrestrial planets suggest that their atmospheres were produced by quantitative degassing of specific regions, rather than by partial degassing of an entire planet in fractionating mode.

The heavy noble gas content of the Kenna ureilite is intermediate to the total noble gas contents of Venus and Earth. A similar abundance pattern is displayed by the heavy noble gases in Allende’s mineral “Q”, although the concentrations of Ar, Kr, and Xe in “Q” are about three orders of magnitude higher than those of the Earth.

Thus, the abundance patterns of the heavy noble gases for the terrestrial planets are remarkably similar to each other and to that of type-Y noble gases in meteorites. Partial degassing of an entire planet, in contrast to the proposed model of exhaustive degassing of a well-defined upper layer, would be expected to fractionate the elemental abundances of noble gases in the planet's atmosphere. Similarities in the atmospheric abundance patterns of noble gases for the terrestrial planets, and their agreement with the abundance pattern of meteoritic noble gases, suggest that the atmospheres were produced by exhaustive degassing of specific layers. Since carbonaceous matter is the carrier phase of these gases in meteorites (FRICK and CHANG, 1978), differences in the amounts of noble gases in the terrestrial planets may be related to their carbon or CO_2 contents.

CONCLUSIONS

Presently available data on the terrestrial noble gases suggest that the atmosphere was produced by an early, extensive degassing of the upper mantle within the first 200My of the Earth's history. This early period of extensive degassing of the upper mantle is indicated both by the presence of radiogenic ^{129}Xe in the upper mantle and by the present low escape rate of ^{3}He from the lower mantle. Presumably the bulk of oceanic water was also degassed at this time.

The lower mantle has retained its primitive character, and this is the source of the primordial ^{3}He observed in deep-seated samples. The primitive nature of the lower mantle rules out the formation of the iron core by partial melting and geochemical differentiation. The internal structure of the inner planets was produced by heterogeneous accretion in the central iron-rich region of the primitive nebula (MANUEL and SABU, 1975). In addition to the role played by chemical heterogeneities in generating the iron cores prior to layering by silicates, it should be noted that rotational motion of protoplanetary matter may act as a centrifuge, collecting the dense Fe-Ni toward the center.

The atmospheric inventory of ^{36}Ar was released from the upper mantle during the initial 200My period of thorough degassing. Lithophile elements were concentrated into a top layer and most of the atmospheric ^{40}Ar was subsequently generated by degassing of this material. The atmospheric content of radiogenic ^{40}Ar indicates that the average age of this lithospheric material is 2Gy.

Both subduction of crustal material and leakage of Ar from the undepleted lower mantle may play a role in explaining the low ^{40}Ar/^{36}Ar ratios observed in many mantle-derived rocks.

Atmospheric Xe constitutes only about 5% of that in the upper-mantle-plus-crust system. Adsorption is probably responsible for the retrapping of atmospheric xenon. The Xe deficiency cannot be explained by partial degassing of the upper mantle, because this would inhibit production of the high ^{129}Xe/^{130}Xe ratios that are observed in residual Xe of the upper mantle.

Spontaneous fission of ^{244}Pu is responsible for less than 1 % of the atmospheric abundance of ^{136}Xe. Radiogenic ^{129}Xe comprises about 5% of the total ^{129}Xe in air.

Terrestrial-like Xe may not be unique to Earth as observations indicate its presence in blocky sulfides of Allende, in meteoritic troilite, and perhaps in other meteoritic and lunar samples. The nonradiogenic isotopes of terrestrial Xe may be understood in terms of mass fractionation of type-Y Xe. The Ar and Kr in air are also type-Y, but the Earth's inventory of He and Ne was derived from the solar wind.

The abundance pattern of noble gases in the terrestrial planets are similar to each other and to those observed in meteorites.

Parts of the conclusions of this study have been reached independently by other investigators (EUCKEN, 1944; DAMON and KULP, 1958; TUREKIAN and CLARK, 1969; FANALE, 1971; OZIMA, 1975; VINOGRADOV, 1975; TOLSTIKHIN, 1975; 1978; BERNATOWICZ and PODOSEK, 1978; BASU and TATSUMOTO, 1978; MANUEL, 1978; WASSERBURG and DEPAOLO, 1979; HART et al., 1979; KYSER, 1980; RISON, 1980; THOMSEN, 1980).

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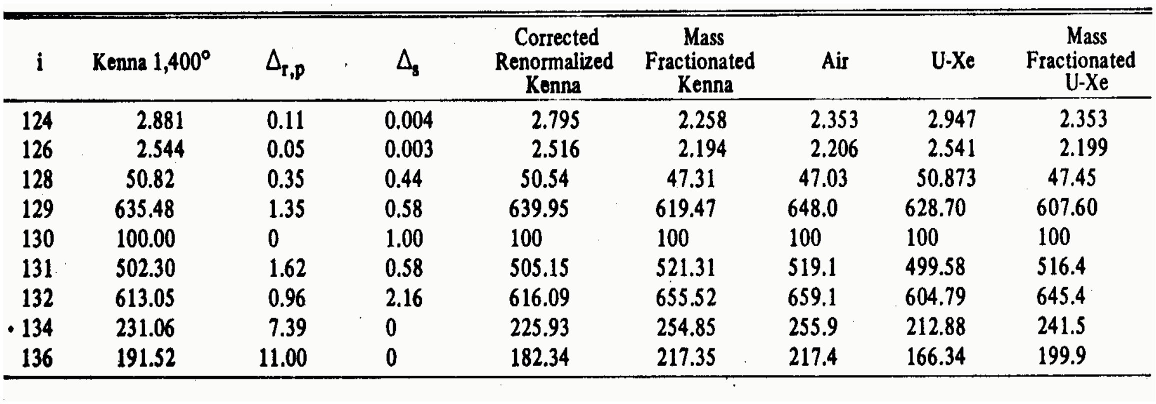
APPENDIX

THE RELATIONSHIP BETWEEN TERRESTIAL AND METEORITIC XENON

Type-X Xe comprises a smaller fraction of the Xe in ureilites than in chondrites, but terrestrial Xe appears to contain the smallest fraction of Xe-X. This is illustrated in Table 3, where one possible relationship between the isotopic composition of atmospheric and ureilite Xe is outlined. The first column shows the mass number, i, of each stable isotope, ^{i}Xe. The isotopic composition of Xe released from the Kenna ureilite at 1,400°C (WILKENING and MARTI, 1976), as shown in the second column, represents the bulk of Kenna's Xe. The next two columns show isotopic abundances of two different nucleogenetic components that have been identified in meteoritic Xe. The first, $\Delta_{r,p}$, represents a component that consists of a mixture of r- and p-products of nucleosynthesis (MANUEL et al., 1972). The values shown there were computed from the isotopic correlation lines given by ALAERTS et al. (1980), with $\Delta_{r,p} \equiv 11.00$ at $i = 136$. The next, Δ_s, represents a component of s-products (SRINIVASAN and ANDERS, 1978), and the values shown there were computed from an average of the yields reported by ALAERTS et al. (1980) with $\Delta_s \equiv 1.00$ at $i = 130$.

Table 3. A Comparison of atmospheric Xe with mass fractionated meteoritic Xe corrected for nucleogenetic components.



i	Kenna 1,400°	$\Delta_{r,p}$	Δ_s	Corrected Renormalized Kenna	Mass Fractionated Kenna	Air	U-Xe	Mass Fractionated U-Xe
124	2.881	0.11	0.004	2.795	2.258	2.353	2.947	2.353
126	2.544	0.05	0.003	2.516	2.194	2.206	2.541	2.199
128	50.82	0.35	0.44	50.54	47.31	47.03	50.873	47.45
129	635.48	1.35	0.58	639.95	619.47	648.0	628.70	607.60
130	100.00	0	1.00	100	100	100	100	100
131	502.30	1.62	0.58	505.15	521.31	519.1	499.58	516.4
132	613.05	0.96	2.16	616.09	655.52	659.1	604.79	645.4
134	231.06	7.39	0	225.93	254.85	255.9	212.88	241.5
136	191.52	11.00	0	182.34	217.35	217.4	166.34	199.9

After subtracting these two components and renormalizing the corrected Kenna spectrum to ^{130}Xe, one obtains the values shown in the fifth column of Table 3. Fractionation of the corrected Kenna Xe yields the values shown in the sixth column. The latter are within ±1 % of the isotopic composition of atmospheric Xe at all values of i, except at i = 124 and 129. The discrepancy at mass 129 can be attributed to the presence of radiogenic ^{129}Xe in air (BOULOUS and MANUEL, 1971), and the discrepancy at mass 124 could be eliminated by subtraction of a ^{124}Xe-enriched component from atmospheric Xe. Such a component was recently reported in sulfides of the Allende meteorite (LEWIS et al., 1979), but the component is poorly characterized and has not been confirmed by other studies.

Thus, the isotopic composition of atmospheric Xe can be related to that in the Kenna ureilite by mass dependent fractionation, after subtraction of two well characterized nucleogenetic components from the ureilite Xe and the subtraction of radiogenic ^{129}Xe and a poorly characterized component of ^{124}Xe from air. To a first approximation, fractionation alone can account for differences in the isotopic compositions of atmospheric, bulk meteoritic (type-Y) and solar-wind-implanted Xe (KRUMMENACHER et al., 1962; KAISER, 1972; OZIMA and NAKAZAWA, 1980). However, most investigators now recognize that nucleogenetic effects must also be considered in seeking a quantitative explanation for differences in the isotopic composition of Xe in these reservoirs (SABU and MANUEL, 1980a; PEPIN and PHINNEY, 1980; HEYMANN and DZICZKANIEC, 1980).

It is not yet known if the isotopic composition of terrestrial Xe represents a mix of nucleogenetic components and mass dependent fractionation that is unique in the solar system. A distinctive isotopic composition for terrestrial Xe is an implicit assumption of arguments which attribute all observations of terrestrial-like Xe in meteorites to contamination. A terrestrial-like isotopic composition has been reported for Xe in the moon (LIGHTNER and MARTI, 1974), in achondrites (ROWE and BOGARD, 1966; MUNK, 1967a), in iron meteorites (MUNK, 1967b: HENNECKE and MANUEL, 1977),

and in blocky sulfides of the Allende chondrite (LEWIS et al., 1979).
Contamination may be a viable explanation for some of these observations. LEWIS et al. (1979) suggest that atmospheric contamination can explain the occurrence of terrestrial-like Xe in the 900°C fraction of Allende's blocky sulfides and troilite-rimmed chondrules, but this interpretation is difficult to reconcile with the release of type-X Xe from these same sulfides at lower extraction temperatures. Terrestrial-like Xe has also been reported in troilite from the Bruderheim chondrite (MERRIHUE, 1966) and in troilite inclusions from the Mundrabilla (NIEMEYER, 1979), Odessa and Toluca (HWAUNG et al., 1981) iron meteorites. Thus, it appears that terrestrial-type Xe may be a common component of meteoritic sulfides, and hence have existed as the dominant from of Xe in the inner part of the early solar system (MANUEL and SABU, 1975).

The relationship shown in Table 3 between the isotopic compositions of atmospheric and meteorite Xe is not a unique solution, but the results compare favorably with other suggested relationships. For example, PEPIN and PHINNEY (1980) have extrapolated isotopic trends in meteoritic Xe to obtain the composition of a hypothetical component which they label U-Xe. This, and a mass fractionated form of U-Xe, are shown in the last two columns of Table 3. Although mass fractionated U-Xe is similar to that in air for the light isotopes, the agreement at i = 131-136 is poor.

Both methods of computing the Earth's initial abundance of ^{129}Xe indicate that the ^{129}Xe/^{130}Xe ratio in the present atmosphere has been augmented by the decay of extinct ^{129}I. The percentage increase calculated in this ratio, 5 to 7%, is similar to the value obtained independently by comparing the isotopic compositions of atmospheric and solar-wind implanted Xe (BOULOS and MANUEL, 1971).

It should be noted that independent evidence for the occurrence of radiogenic ^{129}Xe in air is provided by several observations of excess ^{129}Xe in deep seated terrestrial samples (BUTLER et al., 1963; BOULOS and MANUEL, 1971; HENNECKE and MANUEL, 1975a, b; PHINNEY et al., 1978; KANEOKA and TAKAOKA, 1978; KYSER, 1980).

PEPIN and PHINNEY (1980) suggest that the occurrence of ^{244}Pu fission products in air can account for the discrepancy between the values that they calculate for mass fractionated U-Xe and the value of ^{i}Xe/^{130}Xe at i = 131-136 (See Table 3). The amount of fissiogenic ^{136}Xe which must exist in the atmosphere to explain the 8.8% discrepancy in the calculated and observed ^{136}Xe/^{130}Xe ratios is 2.5×10^{15} cc STP. If one considers that adsorption has depleted the atmospheric inventory of Xe by a factor of 20, then the total amount of ^{244}Pu-produced ^{136}Xe present in the upper mantle and crust by PEPIN and PHINNEY's model is 5.0×10^{16} cc STP. This amount of fission-produced ^{136}Xe is appreciably higher than that expected from the U content of this system, unless the Earth trapped actinides with a much higher ^{244}Pu/^{238}U ratio than did the chondrites.

It can be shown that fission-produced ^{136}Xe instead comprises less than 1 % of the ^{136}Xe in air. For a chondritic Earth, the upper-mantle-plus-crust system might be expected to contain about 20ppb U. Fission of ^{238}U in the upper mantle and crust would have produced a total of 6.3×10^{13} cc STP of ^{136}Xe in this 1×10^{27} g system. If the Earth initially trapped actinides with $^{244}Pu/^{238}U = 1.6 \times 10^{-2}$, the ratio observed in the high temperature, gas-retentive sites of the St. Severin chondrite (PODOSEK, 1970), then fission of ^{244}Pu would have produced 4.5×10^{15} cc STP of ^{136}Xe in the upper-mantle-plus-crust system.

When the factor of 20 depletion of atmospheric Xe is taken into account, the ^{244}Pu-produced ^{136}Xe can be shown to comprise only 0.74% of the total ^{136}Xe in the upper-mantle-plus-crust system.

We believe that 0.74% is an upper limit on the $^{136f}Xe/^{136}Xe$ ratio in air because the $^{244}Pu/^{238}U$ ratio in bulk meteorites is lower, by as much as a factor of 10 (SABU and KURODA, 1967; PODOSEK, 1970; 1972) than the value of 1.6×10^{-2}. This suggests that the material which accreted to form meteorites and the Earth might have lost fission-produced ^{136}Xe from their less retentive sites prior to accretion.

Failure to observe either an excess of ^{244}Pu-produced ^{136}Xe, or a deficiency of ^{136}Xe, in any of the deep-seated terrestrial rocks analyzed to date also suggest that fission-produced ^{136}Xe comprises a small fraction of that in air.

Finally, it should be noted that the amount of radiogenic ^{129}Xe in the upper mantle and crust correspond to an initial value of $^{129}I/^{127}I$ and a ^{129r}Xe content that are similar to those in chondrites. If the Earth's nonradiogenic Xe was characterized by $^{129}Xe/^{130}Xe = 6.195$, as shown in Table 3, then the upper mantle and crust contains a total of 8.0×10^{16} cc STP of radiogenic ^{129}Xe. This corresponds to 8.0×10^{-11} cc STP ^{129r}Xe per g, not unlike the value in chondrites (SABU and KURODA, 1968).

If the upper-mantle-plus-crust system contains an average of 50ppb I, then the above amount of ^{129r}Xe corresponds to an initial value of $^{129}I/^{127}I = 9 \times 10^{-6}$. Although the gas-retentive, high-temperature sites of chondrites yield a value of $^{129}I/^{127}I = 1 \times 10^{-4}$ (HOHENBERG et al., 1967), the $^{129r}Xe/^{127}I$ ratio of bulk chondrites is about a factor of 10 lower (REYNOLDS, 1960c).

ADDENDUM: An earlier suggestion by ANUFRIEV and coworkers that the Earth contains solar-type He and Ne should have been cited in our paper. Please see ANUFRIEF, G. S. (1979) Isotopic ratios and abundances of the light inert gases in the geosphere. *Dokl. Akad. Nauk SSSR 241*, 1202-1206 and references therein.