

Noble Gas Constraints on the Evolution of the Earth's Atmosphere

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A model for the degassing of Xe, Ar, and He from the Earth has been constructed. The Earth is divided into three idealized reservoirs in terms of their noble gas inventories: undegassed mantle, degassed mantle or mid-ocean ridge basalt (MORB) mantle, and atmosphere plus continental crust. Degassing is assumed to occur via the partitioning of gases between a vapor phase and basaltic melt, in accord with He-Ar isotope systematics which require that ^3He be degassed at a slower rate than ^{36}Ar on average. A total inversion technique is used to handle the large uncertainties associated with the input parameters. The model successfully reconciles presently available isotope ratios of $^{129}\text{Xe}/^{130}\text{Xe}$, $^{40}\text{Ar}/^{36}\text{Ar}$, and $^4\text{He}/^3\text{He}$ in the different Earth reservoirs, and accurately predicts the present degassing rates of He and Ar. This is the first time that noble gas isotope data have been shown to be consistent with a single degassing model. The success of this model demonstrates the feasibility of a solubility-controlled degassing mechanism, and shows that there is a relationship between noble gas isotope ratios and the melt-vapor partition coefficients for those gases, which has been obscured by the complicated radiogenic growth and degassing equations. The high $^{129}\text{Xe}/^{130}\text{Xe}$ ratios in MORB are shown to be consistent with the low solubility of Xe in silicate melts, which resulted in a faster degassing rate for Xe than for other gases in the context of this model. Therefore, the mean degassing time derived from Xe is not directly applicable to other gases. The degassed mantle, our end-member degassed mantle reservoir, is found to be almost completely degassed for the noble gases, while the exact degree of degassing depends on the species under consideration, as well as the choice of isotope ratios to characterize this mantle segment. If extreme isotope ratios are used, the degree of degassing for the degassed mantle is: 99.92% for ^{130}Xe , 99.7% for ^{36}Ar , 97.5% for ^3He , 82% for ^{40}Ar and 88% for ^4He . The mean time of degassing, measured from the formation of Earth, is 21 ± 7 Ma for ^{130}Xe , 56 ± 19 Ma for ^{36}Ar , 310 ± 120 Ma for ^3He , ~ 1.5 Ga for ^{40}Ar , and ~ 0.8 Ga for ^4He . Because the degassing is likely to be solubility controlled at some level, study of noble gases alone does not fully constrain the evolution of the atmosphere. However, the model can be extended to major gaseous species in the Earth's primary atmosphere if the relevant solubilities are known. Similarities between the solubilities of CO_2 , CO, and He, and between N_2 and Ar, suggest a mean age for the total atmosphere on the order of 4.4 to 4.3 Ga. The formation of the oceans was a much later event because of the much higher solubility of H_2O in silicate melt. If H_2O has been the primary outgassing species for ocean water, the oceans have a mean age on the order of 2.7 Ga, suggesting that the volume ratio of continental crust to the oceans might have remained relatively constant during Earth history.

INTRODUCTION

Recent work has established that basalts from ocean islands and mid-ocean ridges are characterized by distinct noble gas isotope ratios and abundance patterns [e.g., *Kyser and Rison*, 1982; *Staudacher and Allegre*, 1982; *Allegre et al.*, 1983a; *Marty et al.*, 1983; *Ozima and Zashu*, 1983a, b; *Hart et al.*, 1983, 1985; *Kurz and Jenkins*, 1981; *Kurz et al.*, 1982; *Sarda et al.*, 1985; *Allegre et al.* 1986/87]. The documentation of these systematics has reinforced the suggestion that the Earth's mantle may be described as consisting of more degassed and less degassed (or undegassed) components [e.g., *Bernatowicz and Podosek*, 1978; *Manuel and Sabu*, 1981; *Staudacher and Allegre*, 1982; *Allegre et al.*, 1983a; *Ozima and Podosek*, 1983; *Sarda et al.*, 1985; *Hart et al.*, 1985; *Allegre et al.* 1986/87]. In this context, noble gas isotope ratios in the mantle and atmosphere may be used to constrain the outgassing history of the Earth.

For nearly three decades, there has been considerable interest in using noble gas isotope ratios to describe the evolution

history of Earth's atmosphere (see *Ozima and Podosek* [1983] for a review). Early quantitative models usually considered only one of the noble gases and did not result in predictions which permit independent evaluation. The recent discovery of the high $^{129}\text{Xe}/^{130}\text{Xe}$ isotope ratios in mid-ocean ridge basalts (MORB) demands very early degassing of Xe with a mean degassing time of 10 to 25 m.y., which may be adequately modeled by a simple exponential function as shown by *Staudacher and Allegre* [1982]. However, *Staudacher et al.* [1986] noted that "several authors called the reliability of this data in question" primarily because the data do not seem to fit with other noble gas isotope systems (i.e., Ar). *Sarda et al.* [1985] added Ar to the model of *Staudacher and Allegre* [1982], and noted that either ^{130}Xe outgassed more rapidly than ^{36}Ar , or that a more complex two-stage degassing function was needed. They contended, however, that ^{130}Xe did not outgas more rapidly than ^{36}Ar and adopted a two-stage degassing function which could not be solved uniquely given the many unconstrained parameters. A likely solution gave ~ 100 my for the mean degassing time which was interpreted as that of the atmosphere. *Allegre et al.* [1986/87] included He in the modeling and found again that He system cannot be reconciled with the model of *Sarda et al.* [1985]. They therefore proposed a ^4He flux from the lower mantle to the upper mantle (effectively, from the undegassed mantle to the degassed

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mantle) because ^4He flux from the MORB mantle suggests an even longer degassing history. Such a ^4He flux from the lower mantle to the upper mantle not only is highly speculative but also created a problem for ^3He , as will be later discussed. *Hart et al.* [1985] modeled the outgassing of Ar and He and their isotopic evolution in the mantle using a qualitative approach and mass balance constraints, and concluded that the "mean cessation time" of Ar outgassing is 1.2 to 1.8 Ga ago and that the difference in $^3\text{He}/^{36}\text{Ar}$ in different mantle reservoirs derives from the different solubilities of Ar and He in basaltic magma.

This paper considers the coupled evolution of Xe, Ar and He in the mantle, crust and atmosphere. Given the coherence of U, Th and K, we will show that Ar-He isotope systematics require that He be degassed more slowly than Ar, which supports the contention of *Hart et al.* [1985] that the degassing is via melt-vapor equilibrium. Using solubility [*Jambon et al.*, 1986; *Lux*, 1985; *Hayatsu and Waboso*, 1985; *Ozima and Podosek*, 1983] and isotopic constraints, we can describe the degassing history of the three noble gases by a set of coupled degassing equations. Because of large uncertainties associated with the isotope ratios and other input parameters (which should be improved by further measurements), we used a total inversion technique [*Tarantola and Valette*, 1982; *Wunsch and Minster*, 1982; *Allegre et al.*, 1983b, c; *Menke*, 1984] to constrain the input parameters and to see which parameters are more important in constraining the problem. We will show that all presently available data can be cast in terms of a well-constrained, self-consistent degassing model, except for the high $^{130}\text{Xe}/^{36}\text{Ar}$ ratios observed in MORB glass. Therefore the measured high $^{129}\text{Xe}/^{130}\text{Xe}$ in MORB can be related to the $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^3\text{He}$ in the various reservoirs by the lower solubility of Xe in silicate melts, and they together tell a consistent story: Xe is degassed faster than other gases due to its low solubility in silicate melt and therefore Xe in MORB is "more radiogenic" than Ar, which is "more radiogenic" than He. Other gases may have a different degassing history because of their distinct solubilities. Put in another way, our treatment shows that there is a relationship between the isotope ratios of the noble gases in the various Earth reservoirs, and the solubilities of the gases in basaltic melt.

THE DEGASSING MODEL

Definition of Reservoirs

Following *Staudacher and Allegre* [1982] and *Sarda et al.* [1985], our model is a simple box model with three noble gas reservoirs: (1) the undegassed mantle; (2) the degassed mantle; and (3) the atmosphere plus continental crust. The undegassed mantle (UM) is considered to be mantle material which remains relatively undifferentiated subsequent to accretion. The compositional characteristics of UM are derived from estimates for the composition of the bulk silicate Earth. As we will discuss later, UM, as conceived here, need not comprise the entire lower mantle, nor must UM material reside entirely within the lower mantle [see, e.g., *Zindler and Hart*, 1986]. The degassed mantle (DM) is taken to be the source of MORB because of the high $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios measured in MORBs by *Allegre et al.* [1983a], *Sarda et al.* [1985] and *Staudacher et al.* [1986]. MORBs themselves are considered to be mixed back into DM on a relatively short time scale. Although DM is known to be heterogeneous in terms of various chemical parameters (e.g., Pb, Nd, and Sr isotope

ratios), the relative constancy of $^4\text{He}/^3\text{He}$ in MORB, and the fact that He is the only noble gas which cannot be easily contaminated by interaction with seawater, suggest that the noble gas isotopic heterogeneity in DM may be relatively minor. Even if they are variable, however, the extreme isotope ratios we will use may be viewed as characterizing extensively degassed end-member DM. The atmosphere plus continental crust (AC) is taken as the noble gas component which escaped from the mantle through time as well as all of the radiogenic noble gases that were produced in the continental crust. That is, we assume that AC is complementary to DM, (except, of course, for He) and if the present AC were mixed back into the present DM, the mixture would be equivalent to UM. This assumption, referred to as the closed-system assumption, is essential to the development of the model presented here. This three-box model is undoubtedly an oversimplification of the real Earth, given the chemical and isotopic complexities known to characterize the mantle; the reservoirs we have defined are little more than idealized, hypothetical end-members. We believe, however, that some of the global features of the mantle degassing process can be informatively addressed in this context.

How Good Is the Closed System Assumption?

In view of the fact that there has been considerable discussion regarding the early accretion of an atmosphere by the release of volatiles during meteorite bombardment [e.g., *Lange and Ahrens*, 1988; *Melosh and Vickery*, 1988] and about early loss of an atmosphere [*Horedt*, 1982; *Harris*, 1978] during a highly active phase of the Sun, it is important to examine the closed system assumption carefully.

We can consider two possible effects that would invalidate the closed system assumption. One is the extraterrestrial flux of noble gases directly to the atmosphere, and the other would be the early loss of an atmospheric component that had been outgassed from the mantle. The extraterrestrial influx includes the gas that was released directly from incoming planetesimals during accretion and solar wind additions throughout the Earth's history. If initially the whole mantle of the Earth was outgassing uniformly without fractionation of relative gas abundances, gases released during such a stage would also be included in the extraterrestrial influx because it is equivalent to the release of volatiles from meteorites during meteorite bombardment. This extraterrestrial gas component may also have been greatly depleted during the loss of an early atmosphere.

The loss of such an atmosphere could not be much later than several half lives of ^{129}I ; otherwise the degassed mantle and present atmosphere would have nearly identical $^{129}\text{Xe}/^{130}\text{Xe}$ ratios. Accordingly, the loss of ^{40}Ar would be negligible. Any extraterrestrial source for ^{40}Ar is also negligible due to the very small $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in gas-rich meteorites, and in the solar wind [*Anders and Ebihara*, 1982]. Therefore the closed system assumption for ^{40}Ar is well-founded.

Now for ^{36}Ar , we have:

$$^{36}\text{Ar}_{\text{BSE}}^0 = ^{36}\text{Ar}_{\text{AC}}^T + ^{36}\text{Ar}_{\text{DM}}^T + ^{36}\text{Ar}_{\text{UM}}^T + ^{36}\text{Ar}_{\text{Loss}}^T - ^{36}\text{Ar}_{\text{ET}}^T \quad (1)$$

where $^{36}\text{Ar}_{\text{BSE}}^0$ refers to the amount of ^{36}Ar in the original bulk silicate earth, and does not include ^{36}Ar outgassed initially and uniformly from the whole mantle. "ET" is extraterrestrial source, "Loss" represents the lost atmosphere, and the "T"

refers to present. The AC, DM and UM are atmosphere plus continental crust, degassed mantle, and undegassed mantle, respectively. To cast the present-day AC reservoir as the outgassed complement of the degassed mantle, DM, the lost atmosphere should be added back to AC and the extraterrestrial component should be subtracted from it. Because the lost atmosphere and extraterrestrial gain represent opposing effects, only the difference, $^{36}\text{Ar}_{\text{Loss}} - ^{36}\text{Ar}_{\text{ET}}$, can be resolved and it is the magnitude of this difference, or net loss, which affects the closed-system assumption.

We can, therefore, define

$$^{36}\text{Ar}_{\text{Loss}} - ^{36}\text{Ar}_{\text{ET}} = f^{36}\text{Ar}_{\text{AC}}^T \quad (2)$$

where the parameter f quantifies the closeness of approach to true closed system behavior. If f is small, then the closed system assumption is good for ^{36}Ar . We also have

$$^{36}\text{Ar}_{\text{UM}}^T = (^{36}\text{Ar}/^{40}\text{Ar})_{\text{UM}}^T \cdot ^{40}\text{Ar}_{\text{UM}}^T = (^{36}\text{Ar}/^{40}\text{Ar})_{\text{UM}}^T \cdot ^{40}\text{Ar}_{\text{BSE}}^T (M_{\text{UM}}^T/M_{\text{BSE}}) \quad (3)$$

where M_{UM}^T and M_{BSE} are the masses of UM at present, and of BSE, respectively. After algebraic manipulation of (1), (2) and (3), ignoring $^{36}\text{Ar}_{\text{DM}}$ and recognizing that $^{40}\text{Ar}_{\text{BSE}}^T/^{36}\text{Ar}_{\text{BSE}}^T = (^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$ by definition (note that $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{BSE}}^T \neq (^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$ due to the possible net loss of ^{36}Ar), we have:

$$[1+f] (^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T = [^{40}\text{Ar}_{\text{BSE}}^T/^{36}\text{Ar}_{\text{AC}}^T] [M_{\text{DM}}^T/M_{\text{BSE}}] \quad (4)$$

If we can evaluate this expression, then we can arrive at an estimate for f and assess the reliability of the closed-system assumption for ^{36}Ar .

Among the parameters involved, $^{36}\text{Ar}_{\text{AC}}^T$ is well-known since ^{36}Ar in the continental crust can be ignored compared to ^{36}Ar in the atmosphere [Ozima and Podosek, 1983]. The value of $^{40}\text{Ar}_{\text{BSE}}^T$ can be estimated with good precision from K concentration in UM: taking the U concentration in UM (and the bulk silicate Earth) as 20.8 ppb (as derived by Hart and Zindler, 1986, for "primitive upper mantle" or PUM, which is essentially the bulk silicate Earth) and the K/U ratio as 1.27×10^4 [Jochum et al., 1983], the K concentration in UM is 264 ppm; taking the age of the Earth as ~ 4.5 Ga, this corresponds to $\sim 3.8 \times 10^{18}$ moles of ^{40}Ar for the present-day Earth. $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$ is very difficult to estimate. We would expect this parameter to be greater than 296, the atmospheric ratio, because otherwise we should have observed $^{40}\text{Ar}/^{36}\text{Ar}$ ratios less than 296 in modern volcanic rocks with low $^4\text{He}/^3\text{He}$ ratios. We therefore use $^{40}\text{Ar}/^{36}\text{Ar}$ ratios measured in two Loihi basalts (350 ± 50 [Allegre et al., 1983a]) as an estimate for $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$. This estimate is considered to be a minimum because of the possibility of atmospheric contamination of the Loihi samples. The parameter $M_{\text{DM}}^T/M_{\text{BSE}}$ can be estimated from ^{40}Ar and the closed system assumption for ^{40}Ar :

$$(1-x) ^{40}\text{Ar}_{\text{BSE}}^T M_{\text{DM}}^T/M_{\text{BSE}} = ^{40}\text{Ar}_{\text{AC}}^T = ^{40}\text{Ar}_{\text{Atm}}^T + ^{40}\text{Ar}_{\text{CC}}^T \quad (5)$$

where CC = continental crust; $1-x$ is the present degree of degassing of DM for ^{40}Ar (x is the fraction of ^{40}Ar in DM that is not outgassed). If $^{40}\text{Ar}_{\text{CC}}^T$ is about 30% of $^{40}\text{Ar}_{\text{Atm}}^T$ (equivalent to $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{AC}}^T = 385$; see Hart et al. [1985]), and if $x = 0.1$ (see Appendix B), then $M_{\text{DM}}^T/M_{\text{BSE}} = 0.63$. Using (4) and the above estimates for the involved parameters, f equals 0.2 if $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T = 350$ and -0.1 if $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T = 500$. Considering

large errors associated with the estimate of f , we conclude that f cannot be distinguished from zero and the closed system assumption is fairly good for ^{36}Ar . The accuracy of this assumption can be assessed in the future with better knowledge of $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$, the degree of degassing of ^{40}Ar from DM, $^{40}\text{Ar}_{\text{CC}}$, and the K concentration in the bulk Earth.

For Xe, similar conclusions cannot be reached because there is no analog for ^{40}Ar . However, by analogy to ^{36}Ar , the closed system assumption is probably not too bad for ^{130}Xe , and it is very unlikely that the mass of lost ^{130}Xe is comparable to that of the present ^{130}Xe , even if the outgassing of ^{130}Xe was 3 times as fast as ^{36}Ar , as suggested by solubility constraints (see later sections).

Isotopic Ratios in the Undegassed Mantle

Before proceeding with the model, we need to estimate $^{129}\text{Xe}/^{130}\text{Xe}$, $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^3\text{He}$ in UM, as they define our starting condition. We can constrain $^{40}\text{Ar}/^{36}\text{Ar}$ in UM based on an estimate for K in UM and ^{36}Ar in AC without assuming that any particular group of basalts is derived from this type of the mantle. The total amount of ^{40}Ar in the bulk silicate Earth (including UM, DM, and AC) at present was estimated in the previous section to be 3.8×10^{18} moles. An absolute minimum estimate for the amount of ^{36}Ar in the bulk silicate Earth is 5.6×10^{15} moles (atmospheric ^{36}Ar [Ozima and Podosek, 1983]). Thus, the maximum possible $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in UM is 680. Because even the MORB mantle still contains some ^{36}Ar (as shown by measurements of MORBs made by, e.g., Kyser and Rison, [1982]; Hart et al., [1983], Allegre et al. [1983a] and Sarda et al. [1985]) and because some mantle-derived rocks contain less radiogenic Ar which suggests a source with higher ^{36}Ar contents (e.g., Hawaiian volcanics; [Kyser and Rison, 1982; Allegre et al., 1983a]), we adopt a maximum of 600 for $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$. Using the closed-system assumption, a minimum $^{40}\text{Ar}/^{36}\text{Ar}$ ratio can be estimated from $^{40}\text{Ar}/^{36}\text{Ar}$ in AC. This minimum is greater than 300 and likely greater than or equal to 350, considering the total ^{40}Ar in continental crust [Hart et al., 1985]. Therefore, $^{40}\text{Ar}/^{36}\text{Ar}$ in UM most likely lies between 350 and 600 (475 ± 125) and we will use this range as input for our calculations. This estimate of $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}^T$ is in good agreement with Hart et al. [1985] and also with $^{40}\text{Ar}/^{36}\text{Ar}$ ratios measured at two Hawaiian volcanoes [Allegre et al., 1983a].

Again using the closed-system assumption, we know that the $^{129}\text{Xe}/^{130}\text{Xe}$ ratio in UM must lie between that of AC and DM. However, we also know that Xe in DM probably does not constitute a significant fraction of either ^{130}Xe (based both on measured abundances in MORBs [Allegre et al., 1983a; Staudacher et al., 1986] and solubility-based arguments discussed in Appendix B) or ^{129}Xe (because $^{129}\text{Xe}/^{130}\text{Xe}$ ratios in MORB are not very different from those in the atmosphere). Therefore, $^{129}\text{Xe}/^{130}\text{Xe}$ in UM is taken as 6.48, the ratio in the atmosphere.

Due to the escape of He from the atmosphere and the consequent fractionation of $^4\text{He}/^3\text{He}$, the closed-system assumption is clearly not appropriate for He. Values of $^4\text{He}/^3\text{He}$ in UM must be as low as or lower than the lowest $^4\text{He}/^3\text{He}$ measured in young basalts, unless some region of the mantle became enriched in He relative to U early in Earth history. The lowest $^4\text{He}/^3\text{He}$ value measured in a submarine basaltic glass (which we can confidently say is not contaminated by cosmogenic He [Kurz, 1986]) is ~ 22500 ($^3\text{He}/^4\text{He} \sim 32$ Ra) for a

basalt from Loihi seamount [Kurz *et al.*, 1983] and much lower ratios are possible. We will, therefore, adopt a value of 19000 ± 7000 for $({}^4\text{He}/{}^3\text{He})_{\text{UM}}$ (27-60 Ra).

Based on the discussion of Ar systematics in this and the previous section, it can be shown that the degassed mantle must comprise a minimum of 43% of the total mantle (essentially, this follows directly from a comparison of ${}^{40}\text{Ar}$ in the atmosphere to ${}^{40}\text{Ar}$ in the entire Earth). This is a minimum value both because ${}^{40}\text{Ar}$ in the atmosphere, being almost entirely radiogenic, was not markedly affected by rapid early degassing, and because we know that there remains ${}^{40}\text{Ar}$ trapped in the continental crust today. In the previous section, we allowed for some ${}^{40}\text{Ar}$ trapped in the continental crust and still residing in DM, and arrived at an estimate of 63% for the fraction of DM, and our "preferred" value for $({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{UM}}^T$ of 475 ± 125 suggests that DM comprises $70 \pm 18\%$ of the whole mantle. Therefore, the "lower mantle", or that portion of the mantle which lies below 670 km, must be at least partially degassed, and DM, even as cast using extreme isotope ratios, is larger than the "upper mantle". We remind the reader that our reservoirs are idealized end-members, and the mantle may actually consist of heterogeneous zones which are intermediate in composition between the end-members. It is clear, however, that simple convective isolation of UM from DM across the 670-km seismic discontinuity is not consistent with noble gas systematics as discussed here.

Basic Evolution Equations

Using ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ as an example, we can write equations for the isotopic evolution of the various reservoirs. Throughout this paper, t refers to time elapsed since the formation of the Earth, $t = T = 4.5$ Ga refers to the present, and $t = 0$ refers to the initial time.

The ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ evolution in UM may be simply described by a growth equation:

$$\left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^t = \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^0 + \frac{\lambda_e}{\lambda_{40}} \left[\frac{{}^{40}\text{K}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^0 (1 - e^{-\lambda_{40}t}) \quad (6)$$

where λ_{40} is the total decay constant of ${}^{40}\text{K}$, and λ_e is the decay constant of ${}^{40}\text{K}$ to ${}^{40}\text{Ar}$. The superscript on the right-hand side of each term refers to time passed since the formation of the Earth and the subscript refers to the reservoir (see Table 1 for explanations of notation). If we assume that degassing does not fractionate isotope ratios, then ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in DM can be described by the following equation:

$$\begin{aligned} \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^t &= \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^0 + \int_0^t \lambda_e \left[\frac{{}^{40}\text{K}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^{\tau} d\tau \\ &= \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^0 + \int_0^t \left[\frac{{}^{39}\text{K}}{{}^{36}\text{Ar}}\right]_{\text{DM}} \left[\frac{{}^{40}\text{K}}{{}^{39}\text{K}}\right]_{\text{DM}}^0 \lambda_e e^{-\lambda_{40}\tau} d\tau \end{aligned} \quad (7)$$

Using the closed system assumption, it follows that the total number of moles of ${}^{40}\text{Ar}$ are conserved:

$${}^{36}\text{Ar}_{\text{DM}}^t \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^t + {}^{36}\text{Ar}_{\text{AC}}^t \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{AC}}^t = {}^{40}\text{Ar}_{\text{UM}}^t \frac{M_{\text{DM}}}{M_{\text{UM}}} \quad (8)$$

which can be rewritten as

$$\left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{AC}}^t = \frac{\left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^t \frac{M_{\text{DM}}}{M_{\text{UM}}} - {}^{36}\text{Ar}_{\text{DM}}^t \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^t}{{}^{36}\text{Ar}_{\text{AC}}^t} \quad (9)$$

We now define S_{Ar} and R_{Ar} such that

$$S_{\text{Ar}} = \frac{\left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^T - \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{DM}}^0}{\left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^T - \left[\frac{{}^{40}\text{Ar}}{{}^{36}\text{Ar}}\right]_{\text{UM}}^0} \quad (10)$$

TABLE 1. Notations

Symbol	Definition
AC	atmosphere plus continental crust, used in text and as subscript in equations
$M_{\text{DM}}, M_{\text{UM}}$	mass of DM and UM
DM	mantle reservoir of the degassed mantle, taken as the MORB source, used in text and as subscript in equations
Ra	${}^3\text{He}/{}^4\text{He}$ ratio divided by atmospheric ratio
R_{Ar}	change in ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ over Earth history in DM relative to AC
$R_{\text{He}}, R_{\text{Xe}}$	similar to R_{Ar}
Q_i	$Q_i = 1/K_i \rho_m R T_m$ where K_i is partition coefficient of volatile i between melt and vapor, ρ_m and T_m are density and temperature of melt, R is gas constant
S_{Ar}	change in ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ over Earth history in DM relative to UM
$S_{\text{He}}, S_{\text{Xe}}$	similar to S_{Ar}
t	time passed since the formation of the earth
t_i	mean time of degassing of species i
T	age of the Earth (4.5 Ga)
UM	undegassed mantle, used in text and as subscript in equations
$({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{UM}}^T$	ratio in UM at elapsed time t since the formation of the Earth; similar forms are used for other isotope ratios
$\alpha(i)$	the concentration of i in present DM divided by that in present UM
β	the degassing constant
μ	the mantle depletion constant
ν	the time constant to account for depletion of Th relative to U

$$R_{Ar} = \frac{\left[\frac{^{40}Ar}{^{36}Ar} \right]_{DM}^T - \left[\frac{^{40}Ar}{^{36}Ar} \right]_{DM}^0}{\left[\frac{^{40}Ar}{^{36}Ar} \right]_{AC}^T - \left[\frac{^{40}Ar}{^{36}Ar} \right]_{AC}^0} \quad (11)$$

where the definition of R_{Ar} is similar to that used by *Staudacher and Allegre* [1982] and *Sarda et al.* [1985]. These definitions allow us to eliminate the unknown $(^{39}K/^{36}Ar)_{DM}^0$ which is required to evaluate the integral in (7). We can therefore deal exclusively with isotope ratios and evolution equations for $^{39}K_{DM}^t$, $^{39}K_{DM}^0$ and $^{36}Ar_{DM}^t/^{36}Ar_{DM}^0$.

After algebraic manipulation of equations (6), (7), (9), (10) and (11), we get

$$S_{Ar} = \frac{1}{1 - e^{-\lambda_{40}T}} \int_0^T \frac{^{39}K_{DM}^t}{^{39}K_{DM}^0} \frac{^{36}Ar_{DM}^0}{^{36}Ar_{DM}^t} \lambda_{40} e^{-\lambda_{40}t} dt \quad (12)$$

$$R_{Ar} = \frac{\frac{^{36}Ar_{AC}^T}{^{36}Ar_{UM}^T} S_{Ar} \frac{M_{UM}}{M_{DM}}}{1 - \frac{^{36}Ar_{DM}^T}{^{36}Ar_{UM}^T} S_{Ar} \frac{M_{UM}}{M_{DM}}} \quad (13)$$

By again invoking the closed-system assumption (i.e., no initial atmospheric ^{36}Ar), we can write that $^{36}Ar_{AC} + ^{36}Ar_{DM} = ^{36}Ar_{UM} = M_{DM}/M_{UM}$, and (13) can be rewritten as

$$\frac{R_{Ar}}{S_{Ar}} = \frac{1 - \frac{^{36}Ar_{DM}^T}{^{36}Ar_{DM}^0}}{1 - \frac{^{36}Ar_{DM}^T}{^{36}Ar_{UM}^T} S_{Ar}} = 1 + \frac{^{36}Ar_{DM}^T}{^{36}Ar_{DM}^0} (R_{Ar} - 1) \quad (14)$$

The above equation is preferable to expression (13) or (9) because there is no requirement of knowing M_{DM}/M_{UM} .

Similarly for Xe and He we have

$$S_{Xe} = \frac{1}{1 - e^{-\lambda_{129}T}} \int_0^T \frac{^{127}I_{DM}^t}{^{127}I_{DM}^0} \frac{^{130}Xe_{DM}^0}{^{130}Xe_{DM}^t} \lambda_{129} e^{-\lambda_{129}t} dt \quad (15)$$

$$\frac{R_{Xe}}{S_{Xe}} = \frac{1 - \frac{^{130}Xe_{DM}^T}{^{130}Xe_{DM}^0}}{1 - \frac{^{130}Xe_{DM}^T}{^{130}Xe_{UM}^T} S_{Xe}} = 1 + \frac{^{130}Xe_{DM}^T}{^{130}Xe_{DM}^0} (R_{Xe} - 1) \quad (16)$$

$$S_{He} = \frac{\int_0^T \left(8 \frac{^{238}U_{DM}^t}{^{238}U_{DM}^0} \lambda_{238} + 7 \frac{^{235}U_{DM}^t}{^{235}U_{DM}^0} \lambda_{235} + 6 \frac{^{232}Th_{DM}^t}{^{238}U_{DM}^0} \lambda_{232} \right) ^3He_{DM}^0 dt}{8 (1 - e^{-\lambda_{238}T}) + 7 \left(\frac{^{235}U}{^{238}U} \right)^0 (1 - e^{-\lambda_{235}T}) + 6 \left(\frac{^{232}Th}{^{238}U} \right)^0 (1 - e^{-\lambda_{232}T})} \quad (17)$$

$$\frac{R_{He}^*}{S_{He}} = \frac{1 - \frac{^3He_{DM}^T}{^3He_{DM}^0}}{1 - \frac{^3He_{DM}^T}{^3He_{UM}^T} S_{He}} = 1 + \frac{^3He_{DM}^T}{^3He_{DM}^0} (R_{He}^* - 1) \quad (18)$$

where R_{He}^* is the predicted ratio if no escape of He from the atmosphere had occurred.

Equations (15), and (17) involve the parental nuclides I, U and Th. By invoking known similarities in geochemical behavior of U, Th, and K, and making a justifiable approximation regarding the chemical behavior of I, these parameters can be eliminated. K, U and Th all behave incompatibly during melting and their concentrations in the DM are related. K/U in MORBs is relatively constant and similar to that predicted for the bulk Earth (1.127×10^4), while Th/U in MORBs is somewhat more variable [e.g., *Jochum et al.*, 1983]. We can therefore write that

$$\left(\frac{^{238}U}{^{39}K} \right)_{DM}^t = \left(\frac{^{238}U}{^{39}K} \right)_{DM}^0 e^{-\lambda_{238}t} \quad (19)$$

$$\left(\frac{^{235}U}{^{39}K} \right)_{DM}^t = \left(\frac{^{235}U}{^{39}K} \right)_{DM}^0 e^{-\lambda_{235}t} \quad (20)$$

$$\left(\frac{^{232}Th}{^{39}K} \right)_{DM}^t = \left(\frac{^{232}Th}{^{39}K} \right)_{DM}^0 e^{-\lambda_{232}t} e^{-\nu t} \quad (21)$$

where $e^{-\nu t}$ in (21) accounts for the relative depletion of Th in the present-day DM with respect to K. Because Th/U in present UM is about 3.8, and Th/U in present DM is probably 2.5 [*Jochum et al.*, 1983; *Condomines et al.*, 1981; *Newman et al.*, 1983], ν can be taken as $(\ln 1.52)/T$ and it can be shown that the variation of ν from 0 to $(\ln 1.52)/T$ does not significantly influence the main result (compare run 1 and run 1" in Table 3). The behavior of iodine during melting is not well-known, but due to the short half life of ^{129}I the influence of $^{127}I_{DM}^t/^{127}I_{DM}^0$ on S_{Xe} is not significant and we therefore use the following:

$$\left[\frac{^{127}I}{^{39}K} \right]_{DM}^t = \left[\frac{^{127}I}{^{39}K} \right]_{DM}^0 \quad (22)$$

Using the above results, equation (15) and (17) can be rewritten as follows:

$$S_{Xe} = \frac{1}{1 - e^{-\lambda_{129}T}} \int_0^T \frac{^{39}K_{DM}^t}{^{39}K_{DM}^0} \frac{^{130}Xe_{DM}^0}{^{130}Xe_{DM}^t} \lambda_{129} e^{-\lambda_{129}t} dt \quad (23)$$

$$S_{He} = \frac{1}{8.9475} \int_0^T \frac{^{39}K_{DM}^t}{^{39}K_{DM}^0} \left(8 \lambda_{238} e^{-\lambda_{238}t} + 7 \lambda_{235} \left(\frac{^{235}U}{^{238}U} \right)^0 e^{-\lambda_{235}t} + 6 \lambda_{232} \left(\frac{^{232}Th}{^{238}U} \right)^0 e^{-(\lambda_{232} + \nu)t} \right) \frac{^3He_{DM}^0}{^3He_{DM}^t} dt \quad (24)$$

To evaluate these expressions, we must find an appropriate functional form for $^{39}K_{DM}^t/^{39}K_{DM}^0$. We first investigated the function $1 - P_K + P_K e^{-\mu t}$ to allow for recycling of continental crust (see Appendix A). However, a few trial calculations showed P_K to be ~ 1 with a large uncertainty. We have therefore taken $^{39}K_{DM}^t/^{39}K_{DM}^0$ to be equal to $e^{-\mu t}$. This implies that a significant fraction of the continental crust (>16%) had been produced by 3.8 Ga, and that significant depletion of incompatible elements in the MORB mantle had occurred by this time, in accord with evidence from pre-3.8 Ga zircon ages [e.g., *Froude et al.*, 1983].

Relationships between the Degassing Rates of Different Noble Gases

Equations (12), (23) and (24) contain the ratios $(^{36}\text{Ar}^f/\beta^{36}\text{Ar}^0)_{\text{DM}}$, $(^{130}\text{Xe}^f/\beta^{130}\text{Xe}^0)_{\text{DM}}$, and $(^3\text{He}^f/\beta^3\text{He}^0)_{\text{DM}}$ which can be related to one another depending on the model one chooses to describe the degassing process. Previous quantitative models considering two or more noble gases simultaneously [Sarda *et al.*, 1985, Allegre *et al.* 1986/87] assumed that all the noble gases have the same degassing function. Although Sarda *et al.* [1985] found a discrepancy between the mean ages of degassing of ^{130}Xe and of ^{36}Ar when a simple exponential degassing function was used, they used a degassing function with two exponential terms to reconcile the discrepancy based on their belief that the two mean ages should be the same. In this section, we will first demonstrate that this reconciliation is almost impossible for ^3He and ^{36}Ar given the isotope constraints and the geochemical coherence of K, U and Th. We will then discuss the potential for solubility-controlled degassing and the resulting relationships between the different noble gases.

Our estimates for S_{Ar} and S_{He} are 59 ± 16 and 7 ± 3 , respectively (see Appendix B). Rewriting equations (12) and (24), we have

$$S_{\text{Ar}} = \int_0^T F(t) dt$$

$$S_{\text{He}} = \int_0^T F(t) G(t) \frac{^3\text{He}_{\text{DM}}^0/\beta^3\text{He}_{\text{DM}}^f}{^{36}\text{Ar}_{\text{DM}}^0/\beta^{36}\text{Ar}_{\text{DM}}^f} dt$$

where,

$$F(t) = \frac{1}{1 - e^{-\lambda_{40}t}} \frac{^{39}\text{K}_{\text{DM}}^f}{^{39}\text{K}_{\text{DM}}^0} \frac{^{36}\text{Ar}_{\text{DM}}^0}{^{36}\text{Ar}_{\text{DM}}^f} \lambda_{40} e^{-\lambda_{40}t}$$

and,

$$G(t) = \frac{1 - e^{-\lambda_{40}t}}{8.9475} \left(8 \frac{\lambda_{238}}{\lambda_{40}} e^{(\lambda_{40} - \lambda_{238})t} + 7 \frac{\lambda_{235}}{\lambda_{40}} \left(\frac{^{235}\text{U}}{^{238}\text{U}} \right)^0 e^{(\lambda_{40} - \lambda_{235})t} + 6 \frac{\lambda_{232}}{\lambda_{40}} \left(\frac{^{232}\text{Th}}{^{238}\text{U}} \right)^0 e^{(\lambda_{40} - \lambda_{232} - \nu)t} \right) \quad (25)$$

$G(t)$ is plotted against t in Figure 1 and its upper limit and lower limit are 2.7 and 0.74, respectively. Therefore, if ^3He and ^{36}Ar had the same degassing function, that is,

$$\frac{^3\text{He}_{\text{DM}}^0/\beta^3\text{He}_{\text{DM}}^f}{^{36}\text{Ar}_{\text{DM}}^0/\beta^{36}\text{Ar}_{\text{DM}}^f} = 1$$

then $S_{\text{He}}/S_{\text{Ar}}$ would lie between 0.74 and 2.7. However, our estimate for $S_{\text{He}}/S_{\text{Ar}}$ is 0.12 ± 0.07 , implying that ^3He and ^{36}Ar do not have the same degassing function. Hence $^3\text{He}_{\text{DM}}^0/\beta^3\text{He}_{\text{DM}}^f$ must be smaller than $^{36}\text{Ar}_{\text{DM}}^0/\beta^{36}\text{Ar}_{\text{DM}}^f$ by at least a factor of 6 on average, and the relative degassing rate of ^3He must be slower than ^{36}Ar . By analogy then, the degassing functions for Xe, Ar and He are all likely to be different from one another, and the single function used by Sarda *et al.* [1985] to describe the degassing of Ar and Xe cannot be correct. This conclusion is

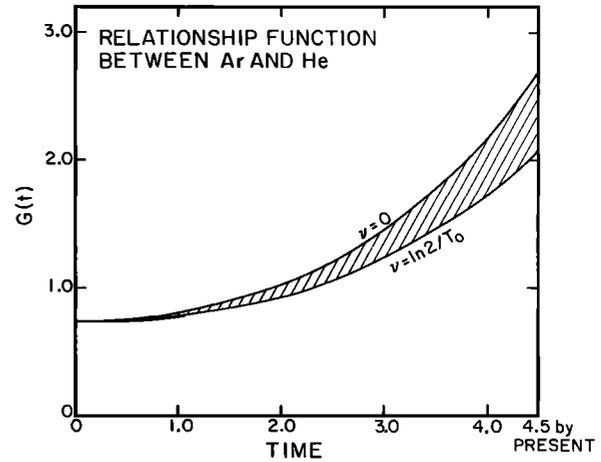


Fig. 1. Plot of the function $G(t)$ (see equation 25) versus time. For this calculation $(^{232}\text{Th}/^{238}\text{U})^0$ was taken as 3.8. See text for discussion.

relatively independent of our choice of input values. Our initial $(^4\text{He}/\beta^3\text{He})$ of 7000 (~ 100 Ra) is clearly an upper limit for this parameter [Ozima and Podosek, 1983]; taking a lower initial $(^4\text{He}/\beta^3\text{He})$ (e.g., 2500; $^3\text{He}/^4\text{He} \sim 290$ Ra) leads to a lower value of S_{He} (~ 5) and hence a slower degassing rate of ^3He . There is no constraint on the minimum possible $(^4\text{He}/\beta^3\text{He})_{\text{UM}}$ except that it should be lower than or equal to the measured minimum 22500 (32 Ra), unless there is an old gas-enriched part in the mantle (i.e., with low $[\text{U}+\text{Th}]/\text{He}$). Given our assumptions about input parameters, 0.74 is the minimum value for $S_{\text{He}}/S_{\text{Ar}}$ which can reconcile the degassing rates of ^{36}Ar and ^3He . If we use $(^{40}\text{Ar}/\beta^{36}\text{Ar})_{\text{DM}} = 28,000$, $(^{40}\text{Ar}/\beta^{36}\text{Ar})_{\text{UM}} = 475$, and $(^4\text{He}/\beta^3\text{He})_{\text{DM}} = 88,000$ (~ 8 Ra), then $(^4\text{He}^*/\beta^3\text{He})_{\text{UM}}$ (where the asterisk signifies radiogenic ^4He integrated over the age of the Earth) must be less than or equal to 1860 to make $S_{\text{He}}/S_{\text{Ar}} \geq 0.74$. This would require that $(^4\text{He}/\beta^3\text{He})_{\text{UM}} \leq 8860$ (≥ 81 Ra), and that about 79% of ^4He is original if $(^4\text{He}/\beta^3\text{He})^0 = 7000$ (~ 100 Ra), or that $(^4\text{He}/\beta^3\text{He})_{\text{UM}} \leq 4360$ (≥ 164 Ra) if $(^4\text{He}/\beta^3\text{He})^0 = 2500$ (~ 290 Ra). Even if we take $(^{40}\text{Ar}/\beta^{36}\text{Ar})_{\text{DM}}$ to be 18,000, as suggested by Fisher [1986], $(^4\text{He}^*/\beta^3\text{He})_{\text{UM}}$ must be less than or equal to 2900 to make $S_{\text{He}}/S_{\text{Ar}} \geq 0.74$. This requires that $(^4\text{He}/\beta^3\text{He})_{\text{UM}} \leq 9900$ (≥ 72 Ra), and that about 71% of present ^4He is original [for $(^4\text{He}/\beta^3\text{He})^0 = 7000$ (~ 100 Ra)]. It further implies that $(^3\text{He})_{\text{UM}} \geq 1.15 \times 10^{-8}$ cm³ STP/g and $(^3\text{He}/\beta^{36}\text{Ar})_{\text{UM}} \geq 0.192$, if the U concentration in UM is taken as 20.8 ppb.

None of these possibilities can be absolutely eliminated because of the unconstrained nature of the He problem. However, available data are much more compatible with a model where ^3He outgasses more slowly than ^{36}Ar . Therefore, we need to find a means to account for ^{36}Ar degassing faster than ^3He . Diffusion can be ruled out because it would require that He be outgassed faster than ^{36}Ar , and it is also too slow to account for large scale degassing. Differential solubility has been suggested by Hart *et al.* [1985] to explain the higher $^3\text{He}/\beta^{36}\text{Ar}$ in DM than PUM, and the arguments put forth here support this suggestion.

The above discussion shows that with present data, the $^4\text{He}/\beta^3\text{He}$ ratio in DM cannot be reconciled with $^{40}\text{Ar}/\beta^{36}\text{Ar}$ in DM if we use the same degassing function for both, because the $^4\text{He}/\beta^3\text{He}$ in DM is not "radiogenic" enough, and/or ^3He is too high in DM. Allegre *et al.* [1986/87] also noticed the inconsistency but discussed it from a different point of view.

They argued that the production rate of ^4He in the depleted mantle is only 43% of the degassing rate of ^4He at mid-ocean ridges using the parameters they derived. They then proposed a ^4He flux from the lower mantle to the upper mantle to account for the observed degassing rate of ^4He . This created a ^3He flux from the lower mantle to the upper mantle of 2200 mol/yr, twice the ^3He degassing rate. We think there are a few shortcomings in their proposal. First, the solution to the ^4He abundance problem created a ^3He problem of similar magnitude (within a factor of two) although they argue that the latter is more acceptable. Secondly, the steady-state degassing requirement used to identify the ^4He problem may not be valid because they also showed that for ^{40}Ar , the degassing rate is slower than the production rate. Furthermore, the parameters they used to calculate the production rate (U concentration 3.3 ppb; proportion of the depleted mantle 0.35) lie at the lower side of our estimates (U concentration 2 to 8 ppb with a mean of 4.5 ppb; proportion of the degassed mantle 0.70 ± 0.18). If our preferred values are used, the production rate of ^4He in DM is almost identical to the degassing rate, and thus, ^4He systematics support our earlier contention based on ^{40}Ar that the DM is on the order of twice the mass of the upper mantle. Thirdly, *Allegre et al.* [1986/87] did not discuss the mechanism for the He flux, which seems to us somewhat arbitrary.

Sarda et al. [1985] rejected solubility as the controlling mechanism for degassing based on their belief that thermodynamic equilibrium is unlikely to be reached during degassing associated with volcanic activity. Local equilibrium, however, between vapor and melt will always be reached during separation of a vapor phase. Therefore solubility will always play a role, although the process may be diffusion-limited at some level. However, measurements of noble gas concentrations in volcanic glass and associated vesicles have documented the existence of bulk equilibrium between vesicles and glass or melt (for He, *Kurz and Jenkins* [1981]; and for Ar, *Marty and Ozima* [1986]). In view of recent results by *Stolper and Holloway* [1988] which show that CO_2 in MORB glass may be oversaturated with respect to seafloor pressures, it may be that this vesicle-glass equilibrium is one attained in a subsurface magma chamber. For the purposes of our model, it does not matter whether the melt-vapor distribution reflects seafloor or sub-seafloor pressures, only that equilibrium solubility does play an important role in determining the volatile distribution. We therefore consider it justified to assume that equilibrium between melt and vapor phases is attained, and go on to model the process based on this assumption.

A Model for the Degassing Process

Using the experimentally determined solubility relationships in basaltic magma (see Appendix B), we can relate the degassing functions of the nonradiogenic noble gas isotopes. The exact relationships depend on the form of the degassing models. Here we will consider two end-member models and refer to them as equilibrium and fractional degassing. The equilibrium degassing model implies that the entire "vapor phase" (including the atmosphere and volatiles stored in ocean and in sediments) is in equilibrium with the bulk degassed mantle for the non-radiogenic noble gas nuclides. Because degassing is a gradual process and an evolved vapor phase will separate from the melt and residual mantle, it seems intuitively unlikely that an equilibrium degassing model would be viable.

In the fractional degassing model, only the infinitesimal fraction of vapor separating at a given instant is assumed to be in equilibrium with the melt.

The solubility relationships for the equilibrium and fractional degassing models are derived in Appendix C. The concentrations of different gases in DM during equilibrium degassing are related by equation (C6) derived in Appendix C, which is rewritten here:

$$\frac{\frac{^{130}\text{Xe}_{\text{DM}}^0}{^{130}\text{Xe}'_{\text{DM}}} - 1}{Q_{\text{Xe}}} = \frac{\frac{^{36}\text{Ar}_{\text{DM}}^0}{^{36}\text{Ar}'_{\text{DM}}} - 1}{Q_{\text{Ar}}} = \frac{\frac{^3\text{He}_{\text{DM}}^0}{^3\text{He}'_{\text{DM}}} - 1}{Q_{\text{He}}} = \frac{V_g}{V_m} \quad (26)$$

where $Q_i = 1/K_i RT_m \rho_m$ (K_i is the solubility of gas i expressed as moles of gas per gram of melt per bar; R is the universal gas constant; T_m is the temperature of the melt; and ρ_m is the density of the melt). The term V_g/V_m is the "time-integrated vesicularity". Essentially, this is the volume ratio of gas (i.e., bubbles) to melt at the time of separation, integrated over Earth history; it changes only as a function of time. The concentrations of different gases in DM during fractional degassing are given by equation (C7) derived in Appendix C:

$$\frac{1}{Q_{\text{Xe}}} \ln \frac{^{130}\text{Xe}_{\text{DM}}^0}{^{130}\text{Xe}'_{\text{DM}}} = \frac{1}{Q_{\text{Ar}}} \ln \frac{^{36}\text{Ar}_{\text{DM}}^0}{^{36}\text{Ar}'_{\text{DM}}} = \frac{1}{Q_{\text{He}}} \ln \frac{^3\text{He}_{\text{DM}}^0}{^3\text{He}'_{\text{DM}}} = \frac{V_g}{V_m} \quad (27)$$

Selection of a degassing function depends on the degassing model we adopt. For the fractional degassing case, V_g/V_m was initially selected as βt , and therefore

$$\frac{X_i'}{X_i^0} = e^{-Q_i \beta t} \quad (28)$$

where $X_i = ^{130}\text{Xe}_{\text{DM}}$, $^{36}\text{Ar}_{\text{DM}}$ or $^3\text{He}_{\text{DM}}$. Using this formulation, the "mean time" for degassing a given species is approximately $1/(Q_i \beta)$ and is directly proportional to the solubility. Trial calculations, however, demonstrated that this form for the degassing equation is not consistent with observed values for S_{Xe} , S_{Ar} and S_{He} .

If V_g/V_m is represented by a function of the form $A(1 - e^{-\beta t})$, then the calculation of the total inversion is much less straightforward. We nevertheless carried out the calculation and found again that the solution is not consistent with even a liberal set of the input constraints. In particular, S_{He} was shown to be less than 1 in the total inversion runs, which means the depletion of U and Th in DM is faster than that of ^3He . For example, values for $^{36}\text{Ar}_{\text{DM}}/^{36}\text{Ar}_{\text{DM}}^0$ in the range 0.001-0.003 lead to $^3\text{He}_{\text{DM}}/^3\text{He}_{\text{DM}}^0$ of 0.48-0.54, given $(Q_{\text{He}}/Q_{\text{Ar}}) = 0.105$. This value of 0.51 ± 0.03 is higher than $^{39}\text{K}_{\text{DM}}/^{39}\text{K}_{\text{DM}}^0$ which means that ^3He was depleted more slowly than K (and, therefore, U and Th), which is not consistent with He isotope systematics. Therefore, we conclude that the fractional degassing model, as formulated here, cannot accurately describe the degassing history of the Earth.

For the equilibrium degassing case, V_g/V_m was approximated as $A(1 - e^{-\beta t})$, which means that the overall degassing rate decreases exponentially ($dV_g/dt = A\beta V_m e^{-\beta t}$). This function is also well-suited to our needs as integrations which involve it

can be carried out formally. This formulation for degassing leads to

$$\frac{X_i^0}{X_i^t} = 1 + Q_i A (1 - e^{-\beta t}) = 1 + B_i (1 - e^{-\beta t}) \quad (29)$$

where X_i may be ^{130}Xe , ^{36}Ar or ^3He in DM, and B_i for the different species is related to the solubility.

Using (29), we can write (23), (12) and (24) as:

$$\begin{aligned} S_{\text{Xe}} &= \int_0^T e^{-\mu t} (1 + B_{\text{Xe}} - B_{\text{Xe}} e^{-\beta t}) \lambda_{129} e^{-\lambda_{129} t} dt \\ &= (1 + B_{\text{Xe}}) \frac{\lambda_{129}}{\mu + \lambda_{129}} - B_{\text{Xe}} \frac{\lambda_{129}}{\mu + \beta + \lambda_{129}} \end{aligned} \quad (30)$$

$$\begin{aligned} S_{\text{Ar}} &= \frac{1}{1 - e^{-\lambda_{40} T}} \int_0^T e^{-\mu t} (1 + B_{\text{Ar}} - B_{\text{Ar}} e^{-\beta t}) \lambda_{40} e^{-\lambda_{40} t} dt \\ &= \frac{1}{1 - e^{-\lambda_{40} T}} \left[(1 + B_{\text{Ar}}) \frac{\lambda_{40}}{\mu + \lambda_{40}} (1 - e^{-(\mu + \lambda_{40}) T}) \right. \\ &\quad \left. - B_{\text{Ar}} \frac{\lambda_{40}}{\mu + \beta + \lambda_{40}} (1 - e^{-(\mu + \beta + \lambda_{40}) T}) \right] \end{aligned} \quad (31)$$

$$\begin{aligned} S_{\text{He}} &= \frac{1}{8.9475} \int_0^T e^{-\mu t} (1 + B_{\text{He}} - B_{\text{He}} e^{-\beta t}) [8\lambda_{238} e^{-\lambda_{238} t} \\ &\quad + 7\lambda_{235} \left(\frac{^{235}\text{U}}{^{238}\text{U}}\right)^0 e^{-\lambda_{235} t} + 6\lambda_{232} \left(\frac{^{232}\text{Th}}{^{238}\text{U}}\right)^0 e^{-(\nu + \lambda_{232}) t}] dt \\ &= 0.8941 \left[(1 + B_{\text{He}}) \frac{\lambda_{238}}{\mu + \lambda_{238}} (1 - e^{-(\mu + \lambda_{238}) T}) \right. \\ &\quad \left. - B_{\text{He}} \frac{\lambda_{238}}{\mu + \beta + \lambda_{238}} (1 - e^{-(\mu + \beta + \lambda_{238}) T}) \right] \\ &\quad + 0.23738 \left[(1 + B_{\text{He}}) \frac{\lambda_{235}}{\mu + \lambda_{235}} (1 - e^{-(\mu + \lambda_{235}) T}) \right. \\ &\quad \left. - B_{\text{He}} \frac{\lambda_{235}}{\mu + \beta + \lambda_{235}} (1 - e^{-(\mu + \beta + \lambda_{235}) T}) \right] \\ &\quad + 1.584 \left[(1 + B_{\text{He}}) \frac{\lambda_{232}}{\mu + \nu + \lambda_{232}} (1 - e^{-(\mu + \nu + \lambda_{232}) T}) \right. \\ &\quad \left. - B_{\text{He}} \frac{\lambda_{232}}{\mu + \beta + \nu + \lambda_{232}} (1 - e^{-(\mu + \beta + \nu + \lambda_{232}) T}) \right] \end{aligned} \quad (32)$$

where we assume that $(^{232}\text{Th}/^{238}\text{U})_{\text{UM}}^T = 3.8$. Unlike the case for fractional degassing, trial calculations using these equations show that they do constitute a viable model for degassing the Earth, in the context of the constraints invoked here. The results of the inversion calculations are discussed in the section on results for the noble gases.

Physical Consideration of the Degassing Process

Although the "fractional" degassing model is intuitively much more reasonable, only the equilibrium model formulated here can satisfy the constraints we invoke. In this section we will demonstrate that the average fractionations among different gases produced during "fractional degassing" are similar to those produced by our "equilibrium degassing" model.

Let us consider the following process as representative of a large number of degassing events which together produce the Earth's atmosphere. When a batch of mantle is brought near to the surface, it will be partially melted. We assume that, during melting, essentially all of the gas partitions into the melt phase. This is probably a defensible position even in view of the relatively high Xe solid/liquid partition coefficient of 0.2 measured by *Hiyagon and Ozima* [1986], given that degrees and rates of melting were high early in Earth history. In this system we will consider a column of melt which is just saturated with volatiles (primarily CO_2) at the bottom ($P = P_{\text{sat}}$) and is losing volatiles from the top ($P = P_{\text{top}}$; this pressure may be approximately that at the ocean floor). This melt column will be variably outgassed with the degree of outgassing at each level depending on the ambient pressure. The soluble fraction of the volatiles is assumed to return to the mantle via subduction of the oceanic lithosphere. At each depth corresponding to a surrounding pressure P inside the degassing column, the following is true at saturation:

$$P = \sum P_i = \sum \frac{C_i}{K_i} \quad (33)$$

where C_i is the in situ concentration of volatile i in the melt and K_i is the melt/vapor partition coefficient for species i (expressed in terms of mol/g-atm). Suppose at each depth, the degassing is "fractional"; then from (C5),

$$\frac{C_i}{C_i^0} = e^{-Q_i x} \quad (34)$$

where $x = V_g/V_m$ at the given depth. Then

$$P = \sum \frac{C_i^0}{K_i} e^{-Q_i x} = \sum P_i^0 e^{-Q_i x} \quad (35)$$

where P_i^0 is the partial pressure of species i in the vapor coexisting with the initial melt. The average concentration of species j in the degassing layer, \bar{C}_j , can be found by

$$\frac{\bar{C}_j}{C_j^0} = \frac{1}{P_{\text{sat}} - P_{\text{top}}} \int_{P_{\text{top}}}^{P_{\text{sat}}} \frac{C_j}{C_j^0} dP \quad (36)$$

where the integration is made with respect to P (instead of z) because P is nearly linear to depth z . From (35), we have

$$dP = -\sum Q_i P_i^0 e^{-Q_i x} dx \quad (37)$$

Combining (34), (36), and (37), and performing the integration, we get

$$\frac{\bar{C}_j}{C_j^0} = \frac{1}{P_{sat} - P_{top}} \sum_i \frac{Q_i P_i^0}{Q_i + Q_j} (1 - e^{-(Q_i + Q_j)x_0}) \quad (38)$$

where x_0 is V_g/V_m at the top of the degassing layer. Usually only one major gas (e.g., CO_2) dominates the sum in (38), and the exponential term is small when degassing at the top is extensive. Therefore

$$\frac{\bar{C}_j}{C_j^0} \approx \frac{1}{P_{sat} - P_{top}} \frac{Q_{major} P_{major}^0}{Q_{major} + Q_j} = \frac{A}{1 + \frac{Q_j}{Q_{major}}} \quad (39)$$

where

$$A = \frac{P_{major}^0}{P_{sat} - P_{top}} \approx \frac{P_{major}^0}{P_{sat}} \approx 1$$

A strong similarity between (39) and the equilibrium degassing equation (C4) in Appendix C is evident. In Table 2, we report the results of a sample calculation comparing these two equations using a basalt melt with volatile concentrations similar to those reported by *Javoy and Pineau* [1986]; for the calculation we actually used equation (38), the unabbreviated form of (39). For simplicity, constant partition coefficients have been used for all the gases. P_{sat} is calculated using the solubility data in Table B1 and P_{top} is taken as 300 bars (the approximate pressure at a mid-ocean ridge). As seen by comparing the data in the last two rows of Table 2, the intergas fractionation calculated using (38) is nearly indistinguishable from that produced during "equilibrium degassing" as formulated here. Therefore, if the atmosphere is produced by a large number of degassing events of the type described here, then these results would imply that at each stage of Earth

history, the entire atmosphere (plus the volatile component stored in the crust) was nearly in equilibrium with the degassed mantle (given that recycling of volatiles into the degassed mantle is not important). Therefore, our equilibrium degassing formulation may, in fact, constitute a reasonable model for the Earth.

Xe/Ar Problem

A potential problem for the model presented here is the observation of very high $^{130}\text{Xe}/^{36}\text{Ar}$ ratios in MORB glasses when compared to the atmosphere and seawater (10^{-4} to 10^{-2} in MORB glasses as compared to 10^{-4} for the atmosphere and $3\text{-}5 \times 10^{-4}$ in seawater [*Sarda*, 1985; *Allegre et al.*, 1983a; *Ozima and Podosek*, 1983; *Broecker and Peng*, 1982]). Furthermore, the average MORB ratio must be considered a minimum, as Xe outgasses more readily than Ar in the context of the solubility model. So, why is the atmospheric $^{130}\text{Xe}/^{36}\text{Ar}$ ratio lower than that in the depleted mantle? This is simply another statement of the notorious "missing Xe problem" [see, e.g., *Ozima and Podosek*, 1983]. There are several ways to get around the problem, which are discussed below, but none is truly satisfactory.

One possibility is that the true MORB $^{130}\text{Xe}/^{36}\text{Ar}$ ratio is smaller than the atmospheric ratio, and that contamination of MORB magmas causes the high observed ratios. Seawater $^{130}\text{Xe}/^{36}\text{Ar}$ is 3-5 times higher than the atmospheric ratio, and the differential solubilities of Xe and Ar in water [*Ozima and Podosek*, 1983] could conceivably result in even higher $^{130}\text{Xe}/^{36}\text{Ar}$ in hydrothermal solutions. Alteration of MORB glass by such solutions could conceivably cause the high $^{130}\text{Xe}/^{36}\text{Ar}$ ratios. However, the care with which glass samples are typically prepared (to exclude all visible signs of alteration) argues against the viability of this hypothesis. Another potential mechanism for contamination is via adsorption of gases to the glass or rocks, as suggested by *Marty et al.* [1983]. If either of these possible contamination mechanisms explains the disparity of $^{130}\text{Xe}/^{36}\text{Ar}$ ratios observed in MORBs and the atmosphere, true MORB mantle $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios would have to be higher than the ratios assumed here (because even samples with the highest $^{129}\text{Xe}/^{130}\text{Xe}$ and $^{40}\text{Ar}/^{36}\text{Ar}$ ratios have $^{130}\text{Xe}/^{36}\text{Ar}$ of about 10^{-3}). In this context, the results of our modeling would have to be reevaluated, the effect being to push degassing to even earlier

TABLE 2. Calculation for Average Fractionation During Fractional Degassing

	H ₂ O	CO ₂	N ₂	Ar	He	Xe
C_i^a , (10^6 mol/g^{-1})	300	65.4	0.067	0.00125	0.0026	1.2×10^{-8}
P_i^b , (bar)	267.9	3651.7	18.8	0.56	0.10	1.6×10^{-5}
Q_i^c	2.42	151	755	1209	110	3555
$C_j C_i^d$	0.9851	0.5076	0.1703	0.1137	0.5874	0.0419
$C_j C_i^e$	0.9849	0.5089	0.1717	0.1146	0.5872	0.0422

^a C_i^0 , the initial concentration of species i in MORB calculated from the data of *Javoy and Pineau* [1986].

^b P_i^0 , the initial partial pressure when the vapor starts to saturate.

^c $Q_i = 1/(K_i \rho_m RT_m)$, see Appendix C for explanation.

^d C_j , average concentration of vapor species j in melt after fractional degassing calculated using (38) and $x_0 = 0.028$, where $x = V_g/V_m$. Here, \bar{x} is 0.00631.

^e C_j , concentration of vapor species j in melt after equilibrium degassing calculated using (A-34) where $V_g/V_m = 0.00639$.

TABLE 3. Modeling

Parameters	Run 1		Run 1'		Run 1''	
	Input ^a	Output ^a	Input	Output	Input	Output
$\ln(\beta T)$	0±10	-1.9±3.2	0±10	-2.4±4.4	0±10	-1.8±3.2
$\ln(\mu T)$	-0.3±1.2	0.42±0.51	-0.3±1.2	0.440±0.489	-0.3±1.2	0.429±0.508
Q_{Xe}/Q_{Ar}	3.3±1.0	3.36±0.92	3.3±1.0	3.35±0.87	3.3±1.0	3.36±0.92
Q_{He}/Q_{Ar}	0.105±0.050	0.105±0.040	0.105±0.05	0.108±0.040	0.105±0.05	0.102±0.04
S_{Xe}	8±3	7.7±2.6	8±3	7.9±2.4	8±3	7.7±2.6
S_{Ar}	59±20	60±14	59±20	58±13	59±20	59±14
$R_{Ar}-S_{Ar}$	11±6	11.3±4.9	11±6	11.5±4.6	11±6	11.2±4.9
S_{He}	7±4	7.0±2.6	7±4	6.9±2.5	7±4	7.3±2.7
$\ln \alpha(^{40}Ar)^b$	-2.3±1	-1.83±0.33	-2.3±1	-1.80±0.34	-2.3±1	-1.82±0.33
$\ln \alpha(^{36}Ar)$	X±5 ^c	-5.92±0.42	X±5	-5.86±0.45	X±5	-5.91±0.43
$\ln \alpha(^{130}Xe)$	X±5	-7.13±0.41	X±5	-7.05±0.48	X±5	-7.12±0.42
$\ln \alpha(^3He)$	X±5	-3.69±0.53	X±5	-3.64±0.53	X±5	-3.65±0.53
$\ln t(^{130}Xe)^d$	X±5	3.03±0.33	X±5	3.02±0.32	X±5	3.04±0.33
$\ln t(^{36}Ar)$	X±5	4.03±0.34	X±5	4.01±0.35	X±5	4.03±0.34
$\ln t(^3He)$	X±5	5.72±0.38	X±5	5.69±0.37	X±5	5.74±0.38

For run 1'' $vT=0$ and for all others $vT=\ln(1.52)$; Run 1' is a Monte Carlo Run.

^a Input and output errors are 2σ .

^b Here, $\alpha(x) = x_{DM}^T/x_{UM}^T$.

^c X±5 means the input average is calculated from the output of the first 9 parameters, and the input error (2σ) is arbitrarily chosen to be 5.

^d Here, t is mean time of degassing in millions of years.

stages of Earth history. Post-eruptive, diffusive degassing would also result in $^{130}Xe/^{36}Ar$ ratios in MORB glasses which are higher than mantle source values. If this effect is sufficiently dramatic, then the $^{130}Xe/^{36}Ar$ ratio in the MORB source region may be lower than the atmospheric value. In this case, there is no real problem for our model.

A second possibility is that the true MORB ratio is higher than the present atmospheric ratio, and that the atmosphere has lost a major fraction of its Xe. This hypothetical reservoir of missing Xe has often been discussed in the context of planetary noble gases because, compared to CI chondrites, the Earth's atmosphere is depleted in ^{130}Xe relative to ^{36}Ar . However, attempts to identify such a reservoir remain unsuccessful [e.g., Bernatowicz *et al.*, 1984, 1985]. If the missing Xe has been subducted into the mantle via adsorption on shales, our numerical results would remain unchanged given that this recycled Xe did not mix with the depleted mantle Xe reservoir uniformly.

Finally, the $^{130}Xe/^{36}Ar$ problem might also be solved if the controlling mechanism for degassing were something other than solubility. Such a mechanism would have to outgas Xe and He more slowly than Ar and the high $^{129}Xe/^{130}Xe$ ratios in MORBs would be difficult to explain in this context.

In conclusion, we must admit that the Xe/Ar problem has potentially serious ramifications for our model; although one can construct arguments to circumvent the apparent inconsistency, none of them is truly satisfactory. However, the existence of this problem does not diminish the compelling fact that noble gas isotope systematics are consistent with a solubility-controlled degassing mechanism.

RESULTS FOR THE NOBLE GASES

Equations (30) and (31) and (32) coupled with (14), are the four main equations used in the total inversion. Equation (16) was not used because it was already used implicitly to derive the conclusion that $(^{129}Xe/^{130}Xe)_{UM}$ is not different from 6.48,

the atmospheric ratio. Equation (18) was not used because we do not have any independent constraint on R_{He} . In total, then, nine parameters are involved in the four equations: β , μ , $^{40}Ar_{DM}^T/^{40}Ar_{UM}^T$, Q_{Xe}/Q_{Ar} , Q_{He}/Q_{Ar} , S_{Xe} , S_{Ar} , $R_{Ar}-S_{Ar}$ and S_{He} . The choice of input ranges for these parameters is discussed in Appendix B. C_{DM}^T/C_{DM}^0 for ^{130}Xe , ^{36}Ar and 3He , and their mean degassing ages are derived from the above parameters. When uncertainties on the derived parameters are needed, as for the degassing rates shown in Figure 2, the derived parameters and the equations used to calculate them are included in the total inversion. Output errors are calculated using the method of Wunsch and Minster [1982] and cross checked using a Monte Carlo method.

Table 3 lists input and output values for the parameters used in the model for several representative runs. Uncertainties reported for the outputs (at the 2σ level) are derived from consideration of the computed covariance matrix. Clearly, the output values from the inversion are consistent with observations, because they are within the range of the input. In other words, the model we have constructed can reconcile the following observations (which was our initial impetus for constructing the model): (1) best estimates of present-day noble gas isotope ratios in the various Earth reservoirs; (2) initial isotope ratios from meteorite studies; (3) ^{39}K and ^{40}Ar content in DM and in UM; and (4) the solubility measurements for noble gases in silicate melt.

Tarantola and Valette [1982] pointed out that for a strongly nonlinear problem, the covariance matrix, even if it could be computed, would not be of great interest. Our problem is strongly nonlinear, and therefore we used a Monte Carlo calculation to cross check the validity of the computed covariance matrix (see run 1', Table 3). We found that the computed variance (i.e., output error) is well correlated to the statistical error, σ_{n-1} , for the Monte Carlo runs. Therefore, we think that for our case, the computed covariance is relevant to the problem.

Results

Run 2		Run 3		Run 4	
Input	Output	Input	Output	Input	Output
0±10	-2.5±3.0	0±10	-2.4±3.0	0±10	-0.17±1.31
-0.3±1.2	-0.35±0.50	-0.3±1.2	0.26±0.66	-0.3±1.2	0.63±0.34
3.3±1.0	3.27±0.92	3.3±1.0	3.40±0.60	3.3±1.0	3.1±0.9
0.105±0.05	0.116±0.044	0.105±0.05	0.106±0.041	0.105±0.05	0.113±0.04
5±2	5.1±1.5	4±10	6.5±3.3	8±3	8.7±2.3
40±10	40±8	59±20	57±16	59±20	57±16
7±4	7.8±3.1	11±6	11.7±4.9	11±6	11.3±5.7
7±4	5.3±2.0	7±4	6.9±2.6	7±4	6.8±2.8
-2.3±1	-1.79±0.30	-2.3±1	-1.75±0.36	-2.3±1.0	-1.78±0.46
X±5	-5.48±0.38	X±5	-5.78±0.54	X±5	-5.82±0.63
X±5	-6.67±0.38	X±5	-6.96±0.60	X±5	-6.95±0.60
X±5	-3.36±0.52	X±5	-3.57±0.60	X±5	-3.66±0.70
X±5	3.45±0.31	X±5	3.20±0.51	X±5	2.91±0.25
X±5	4.41±0.31	X±5	4.16±0.45	X±5	3.85±0.25
X±5	5.97±0.35	X±5	5.83±0.42	X±5	5.51±0.27

TABLE 4. Correlation Matrix of Run 1

	ln(βT)	ln(μT)	$\ln \frac{{}^{40}\text{Ar}_{\text{DM}}^T}{{}^{40}\text{Ar}_{\text{UM}}^T}$	$\frac{Q_{\text{Xe}}}{Q_{\text{Ar}}}$	$\frac{Q_{\text{He}}}{Q_{\text{Ar}}}$	S _{Xe}	S _{Ar}	R _{Ar-S_{Ar}}	S _{He}	ln $\bar{t}_{(130\text{Xe})}$	ln $\bar{t}_{(36\text{Ar})}$	ln $\bar{t}_{(3\text{He})}$
ln(βT)	1.000	0.164	0.277	-0.083	0.072	0.226	-0.196	0.140	-0.115	-0.235	-0.268	-0.263
ln(μT)		1.000	-0.903	-0.267	0.065	0.698	-0.003	-0.801	-0.123	-0.709	-0.812	-0.653
ln(${}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T$)			1.000	0.225	-0.031	-0.585	-0.087	0.838	0.068	0.591	0.677	0.523
Q _{Xe} /Q _{Ar}				1.000	0.023	0.182	-0.179	0.101	-0.031	-0.172	0.331	0.231
Q _{He} /Q _{Ar}					1.000	-0.059	-0.231	-0.154	0.803	0.056	0.065	-0.664
S _{Xe}						1.000	0.469	-0.261	-0.081	-1.000	-0.868	-0.607
S _{Ar}							1.000	0.471	0.366	-0.459	-0.528	-0.227
R _{Ar-S_{Ar}}								1.000	0.260	0.272	0.310	0.339
S _{He}									1.000	-0.075	-0.087	-0.635
ln $\bar{t}_{(130\text{Xe})}$										1.000	0.873	0.613
ln $\bar{t}_{(36\text{Ar})}$											1.000	0.702
ln $\bar{t}_{(3\text{He})}$												1.000

See Table 3 for symbols.

From output of the correlation coefficient matrix (Table 4), we see that μT and ${}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T$ are the two parameters which have the greatest number of correlation coefficients greater than 0.5, and the two of them are highly correlated. Therefore, better understanding of either of these will act to better constrain many of the other parameters. S_{Xe} and R_{Ar-S_{Ar}} are also important in this context. The output uncertainties of S_{He} and Q_{He}/Q_{Ar} are highly correlated to each other but not to other parameters. The mean time of degassing for ¹³⁰Xe is almost entirely dependent on S_{Xe} (which is not true for ³⁶Ar and ³He) as expected from the short half life of ¹²⁹I.

Although the error on the degassing constant β is very large and does not strongly correlate to any other parameter (which means that we cannot further constrain it by better measurements of noble gas isotopic ratios), the resultant uncertainties in the mean time of degassing of the different species are not very large. This counterintuitive result is due to

the correlation of error on B_i [see (29)] with β, which cancels the large error on β in calculating the mean times for degassing. This implies that the mean degassing times and rates for the noble gases are largely determined by the isotope ratios. Note that β is related to the mean time of degassing of the entire atmosphere plus volatiles stored in oceans and continental crust. Thus, the large error on β means that it is difficult to accurately predict the mean age of the entire atmosphere using only noble gas isotope data. This is because the solubility constraint we have adopted dictates that gases with different solubilities have different mean ages. The solubilities of the major gas species in the atmosphere are therefore required to better constrain the mean age of the total atmosphere.

Table 3 contains four different sets of input and output parameters. Runs 1 and 3 used extreme isotopic compositions for DM. Run 2 used a set of "intermediate" or "average" values

for DM, as evidenced by lower values of S_{Ar} and S_{Xe} . (Run 4 will be discussed later.) In both of these cases, we are describing a complex Earth with a simple three-box model. The difference between the two cases relates primarily to the nature and size of the reservoir we choose to represent the "degassed mantle" (see Appendix B). In the following discussions, we will refer primarily to the numerical results for runs 1 and 3.

The numerical results in Table 3 show that the mean degassing times for ^{130}Xe , ^{36}Ar and 3He are 21 ± 7 Ma, 56 ± 19 Ma, and 310 ± 140 Ma, respectively. The mean degassing times for ^{40}Ar and 4He are 1.5 ± 0.5 Ga and 0.8 ± 0.3 Ga, respectively. The mean age for ^{40}Ar in the atmosphere is 3.0 ± 0.5 Ga. These results strongly support the contention that degassing of noble gases was a very early event in Earth's history (a contention made by *Damon and Kulp* [1958] and *Fanale* [1971] and reiterated by many others since then). The mean degassing time for ^{130}Xe derived here is similar to that of *Staudacher and Allegre* [1982]. However, our mean degassing times for the range of noble gases differ from *Sarda et al.* [1985] and *Allegre et al.* [1986/87] because they assumed that all of the noble gases have the same mean degassing time. The mean degassing time of ^{40}Ar (1.5 Ga) differs from the mean cessation time (1.2 to 1.8 Ga ago; read as 3.3 to 2.7 Ga) of *Hart et al.* [1985] because the mean degassing time and the mean cessation time are two different concepts.

Our results also show that DM is $(99.92 \pm 0.04)\%$ degassed for ^{130}Xe , $(99.73 \pm 0.13)\%$ for ^{36}Ar and $(97.5 \pm 1.5)\%$ for 3He . That is, the end-member degassed MORB mantle is almost completely devoid of primordial noble gases. The high degree of degassing of ^{36}Ar can be appreciated from simple comparison of $^{40}Ar/^{36}Ar$ in UM and in DM, with the latter being ~ 60 times higher than the former. Therefore, even if ^{40}Ar concentration in DM were the same as that in UM (no degassing for ^{40}Ar), the DM must still be more than 98% ($=1 - \frac{1}{60}$) degassed. If we use "average" rather than "extreme" MORB isotope ratios for the calculations (as in run 2, Table 3), the extent of outgassing will decrease somewhat and the mass fraction of DM (the degassed reservoir) will become greater than our estimate of $(70 \pm 10)\%$ (the smaller error here is estimated from model output) discussed earlier in the section on the closed system assumption. These estimates suggest greater extents of degassing than those proposed by *Sarda et al.* [1985], and *Staudacher et al.* [1982], but are similar to those proposed by *Allegre et al.* [1986/87]. The DM is $(82 \pm 8)\%$ and $(88 \pm 8)\%$ degassed for ^{40}Ar and 4He , which leads to ^{40}Ar and 4He in present DM to be $3 \pm 1 \times 10^{-6}$ and $(8 \pm 3) \times 10^{-6}$ cm³ STP/g, respectively. This value for 4He is in good agreement with maximum measured He concentrations in MORBs ($\sim 3 \times 10^{-5}$ cm³ STP/g), given both that MORBs represent ~ 5 to 20% melting [*Klein and Langmuir*, 1987] and that even these high measured He concentrations are minima for given magmas.

The output for $\ln(\mu T)$ is 0.42 ± 0.51 . This leads to: (1) $^{39}K_{DM}/^{39}K_{DM} = 0.08$ to 0.40 (with a mean of 0.22), and, therefore, the present K concentration in DM is 20 to 100 ppm; (2) a mean age for ^{39}K in continental crust of 2.8 ± 0.3 Ga; and (3) a mean concentration of K in continental crust of $2.2 \pm 0.6\%$. The mean age of ^{39}K in continental crust is similar to the mean age of continental crust (2.4 Ga) estimated by *Allegre et al.* [1983c].

From the output, we calculated the relative degassing rate for different species as a function of time (Figure 2). The errors for ^{36}Ar and ^{130}Xe are calculated with the total inversion program.

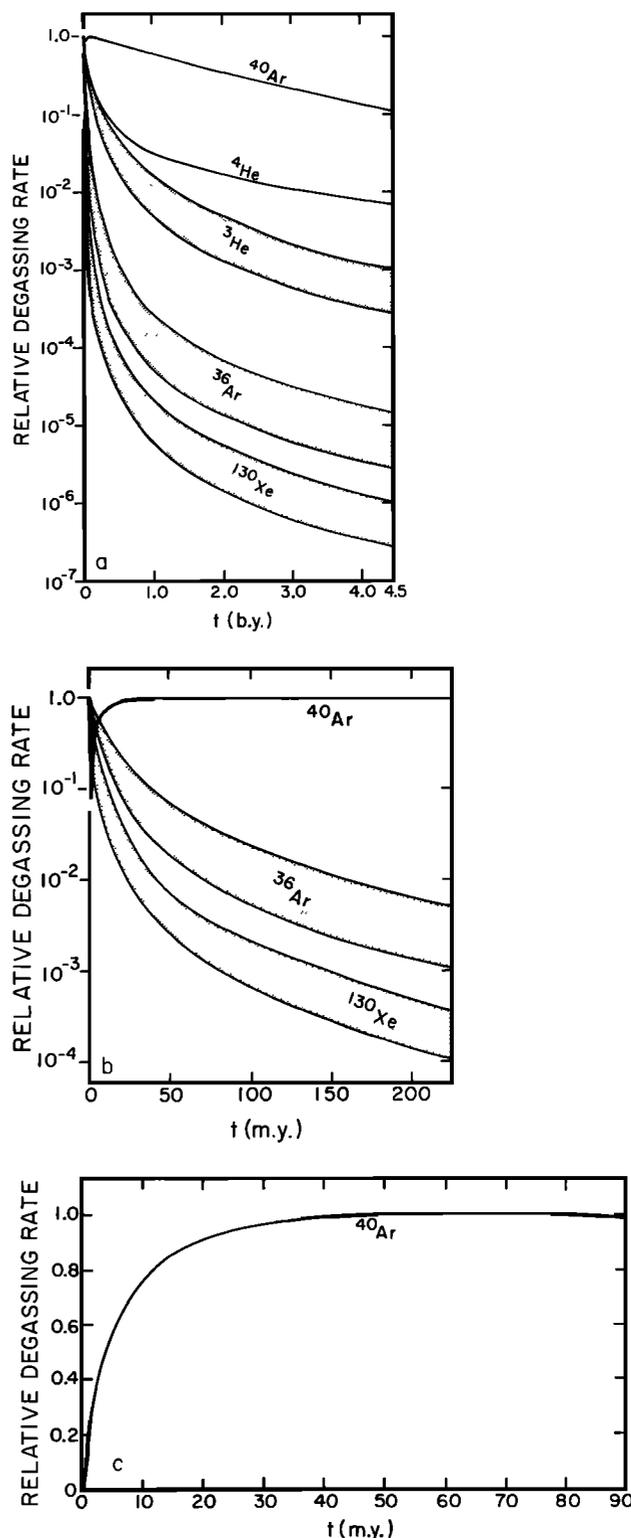


Fig. 2. Relative degassing rates for different noble gas species. For ^{130}Xe , ^{36}Ar , 3He and 4He , the initial degassing rate is taken as 1, while for ^{40}Ar , the maximum degassing rate is set as 1. Error bounds represent 2σ uncertainties derived from the model output. (a) All of Earth history. (b) The first 250 m.y. only. (c) The first 90 m.y. only.

It is seen that the relative degassing rate of ^{130}Xe and ^{36}Ar are distinct even when the large errors are considered. The degassing rate of ^{40}Ar reached a maximum at ~ 70 Ma after the formation of the Earth and has declined ever since. The present

degassing rate of ^{40}Ar is about 10% of its maximum rate, while for every other species, the present degassing rate is less than 1% of the maximum rate.

We can estimate $(^3\text{He}/^{36}\text{Ar})_{\text{UM}}$ from $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}}(^4\text{He}/^{40}\text{Ar})_{\text{UM}}(^4\text{He}/^3\text{He})_{\text{UM}}$, where: $(^{40}\text{Ar}/^{36}\text{Ar})_{\text{UM}} = 475 \pm 90$ (the output error is estimated from the output uncertainty for S_{Ar}); $(^4\text{He}/^3\text{He})_{\text{UM}} = 19,000 \pm 5,000$; and $(^4\text{He}/^{40}\text{Ar})_{\text{UM}}$ can be calculated using $(^4\text{He}/^{40}\text{Ar})_{\text{UM}} = (^4\text{He}^0/{}^4\text{He}^* + 1) {}^4\text{He}^*/{}^{40}\text{Ar}^*$, where ${}^4\text{He}^*/{}^{40}\text{Ar}^* = 1.6 \pm 0.1$ from Hart *et al.* [1985] with the asterisk signifying the radiogenic isotope integrated over the age of the Earth, and ${}^4\text{He}^0/{}^4\text{He}^*$ is $7,000/(19,000 - 7,000) = 0.58$. The resulting value for $(^3\text{He}/^{36}\text{Ar})_{\text{UM}}$ is 0.062 ± 0.020 and is slightly higher than the estimate of 0.03-0.06 of Hart *et al.* [1985]. The discrepancy is largely due to the neglect of ${}^4\text{He}^0$ (initial ${}^4\text{He}$) by Hart *et al.* [1985]. Our estimated $(^3\text{He}/^{36}\text{Ar})_{\text{UM}}$ is higher by a factor of 7 than the planetary ratio of 0.009 [Ozima and Podosek, 1983]. We see no way to reconcile the two ratios in the context of closed system assumption. Thus the Earth must have had a higher ${}^3\text{He}/^{36}\text{Ar}$ than CI chondrites when it was formed. The calculated ${}^3\text{He}/^{36}\text{Ar}$ ratio would imply $(3.3 \pm 1.1) \times 10^{14}$ mol of ${}^3\text{He}$ in the present atmosphere if it had not been lost to outer space. The average escape rate for ${}^3\text{He}$ is 70,000 mol/yr which is about 40 times the present escape rate (taken as 1800 mol/yr [Lupton, 1983]).

Our model used a simple function to describe the evolution of noble gases in the degassed mantle. The real physical meaning of this exercise is like the fitting of a prescribed functional form (similar to straight line or polynomial fitting) to the actual evolution of the noble gases. Because isotopic constraints are the main constraints, the best fit of the curve tends to reproduce the isotope ratios. Because the degassing is an early event and early degassing contributes the most to the observed isotope ratios, the best fit function is biased toward early Earth history (i.e., it describes early history better than more recent time). Therefore, we do not necessarily expect to find agreement between presently observed degassing rates and estimates based on the model, especially since the degassing rate is the slope of the best-fit curve. Nevertheless we have calculated the present-day absolute degassing rates as a cross check. By equating the total initial amount of ^{36}Ar in DM to the present-day atmospheric ^{36}Ar and using the calculated ${}^3\text{He}/^{36}\text{Ar}$ ratio in initial mantle, we get the total initial amount of ^{36}Ar and ${}^3\text{He}$ in the DM. We can then use the model output to estimate present degassing rates of 3-12 (with a mean of 6) atoms $\text{s}^{-1}\text{cm}^{-2}$ for ${}^3\text{He}$ and 6-23 (with a mean of 11) atoms $\text{s}^{-1}\text{cm}^{-2}$ for ^{36}Ar (these rates are shown as a function of time in Figure 3). This yields a present degassing ratio for ${}^3\text{He}/^{36}\text{Ar}$ of about 0.5 ± 0.2 . The calculated rate for ${}^3\text{He}$ agrees surprisingly well with the observed rate of 4-5 atoms $\text{s}^{-1}\text{cm}^{-2}$ [Lupton, 1983], while the degassing ratio of ${}^3\text{He}/^{36}\text{Ar}$ is more controversial. Sarda *et al.* [1985] adopted a value of 2 for the ratio, but recent results from Javoy and Pineau [1986] and Javoy *et al.* [1986], show this value to be ~ 0.5 in popping rocks. They obtained He/Ar ratio of about 1.6; this is essentially a ${}^4\text{He}/^{40}\text{Ar}$ ratio. Assuming no contamination for ${}^4\text{He}$ and ${}^{40}\text{Ar}$ (while contamination for ^{36}Ar may be significant) and taking the mantle ${}^4\text{He}/^3\text{He}$ and ${}^{40}\text{Ar}/^{36}\text{Ar}$ ratios to be 88,000 and 28,000 respectively, the ${}^3\text{He}/^{36}\text{Ar}$ degassing ratio is ~ 0.5 . The apparent success of this model in reproducing observed present-day degassing rates, despite the lack of any input concerning these parameters, is strong support for the general validity of the model. In trial run 4 (Table 3), the present-day

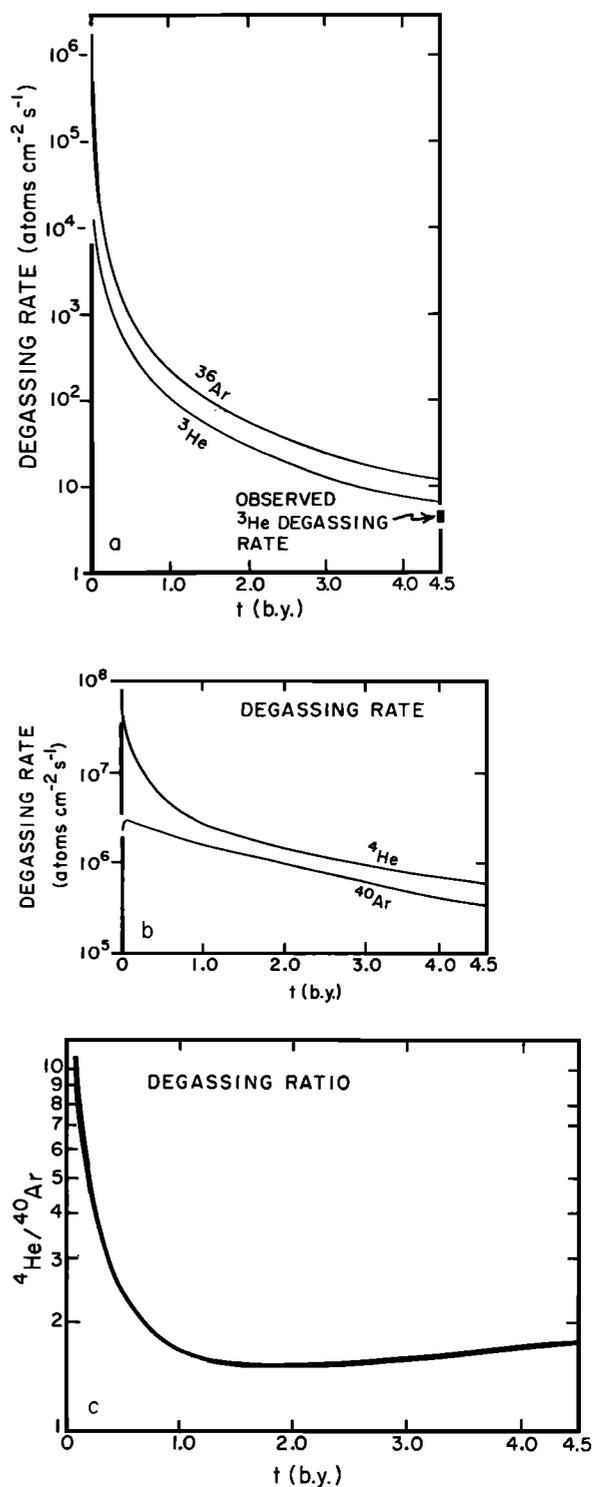


Fig. 3. Absolute degassing rates (in atoms $\text{cm}^{-2}\text{s}^{-1}$) for He and Ar. (a) ${}^3\text{He}$ and ^{36}Ar . (b) ${}^4\text{He}$ and ${}^{40}\text{Ar}$. (c) The ${}^4\text{He}/{}^{40}\text{Ar}$ degassing ratio.

outgassing rate of ${}^3\text{He}$ was used as an additional input parameter; the output of run 4 is very similar to that of run 1, except for a better constrained βT .

The evolution of ${}^{40}\text{Ar}/^{36}\text{Ar}$ and ${}^4\text{He}/^3\text{He}$ in the different reservoirs can also be calculated from the model output (Figure 4). The predicted present-day ${}^4\text{He}/^3\text{He}$, ${}^3\text{He}$ and ${}^4\text{He}$ in AC (if there had been no He exchange with outer space) are $17,000 \pm 6000$, 7.3×10^{18} cm^3 (STP) and 1.24×10^{23} cm^3 (STP).

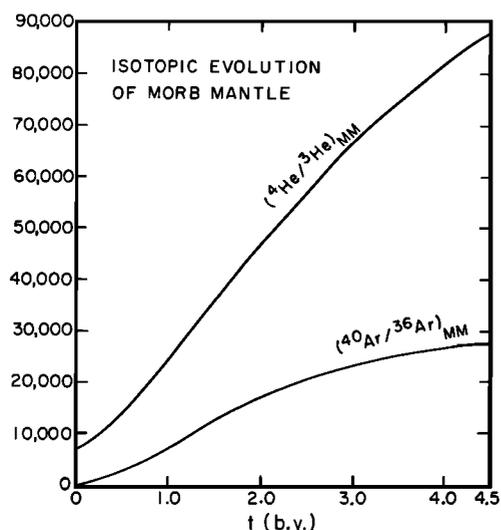


Fig. 4. Evolution of $^{40}\text{Ar}/^{36}\text{Ar}$ and $^4\text{He}/^3\text{He}$ in DM.

The calculated $^{40}\text{Ar}/^{36}\text{Ar}$ in the atmosphere, given no contribution from continental crust, is ~ 240 with an uncertainty too large to permit evaluation of continental crust degassing.

IMPLICATIONS FOR OTHER GASES

One feature of this model which distinguishes it from previous models is that the various gases are assumed to behave differently according to their partitioning behavior in a melt-vapor system. Therefore, we cannot use the mean age of any single gas as the mean age of the atmosphere, and study of the noble gases alone cannot provide a complete history of atmospheric evolution (no more than the evolution history of continents can be accurately evaluated on the basis of the behavior of a single element). However, the model can be used as a new framework to understand evolution of the early atmosphere, and can be extended to the degassing histories of other gaseous components, provided their speciation and solubilities are known. Because the speciation of many components may change through geologic history, extra caution must be exercised in any interpretation.

The solubility of CO_2 in basaltic magma varies with CO_2 concentration, pressure and temperature. Typical values are $0.00022 \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ at 1000 bars [Stolper and Holloway, 1988], $0.0015 \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ at $P_{\text{CO}_2} = 1000 \text{ atm}$, and $0.0009 \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ at $P_{\text{CO}_2} = 3000 \text{ atm}$ [Khitarov and Kadik, 1973]. Values for MORBs obtained by measuring the partitioning between vesicle and glass are 3 to $5 \times 10^{-4} \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ [Javoy and Pineau, 1986], and are of the same order of magnitude as solubilities measured for He (5 to 6×10^{-4} , by Javoy and Pineau [1986] and $5.65 \pm 1.1 \times 10^{-4}$ by Jambon *et al.* [1986]). The solubility of CO is similar to that of CO_2 in diopside melt [Eggler *et al.*, 1979]. The inferred solubility of N_2 in MORB magma is $\sim 8 \times 10^{-5} \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ [Javoy and Pineau, 1986] which is of the same order of magnitude as that of Ar ($5 \times 10^{-5} \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$, by Javoy and Pineau [1986] and $6.5 \pm 0.8 \times 10^{-5}$ by Jambon *et al.* [1986]). The solubility of H_2O is variable but undoubtedly much higher than that of CO_2 or N_2 ; 0.02 to $0.04 \text{ cm}^3 \text{ STP g}^{-1} \text{ atm}^{-1}$ is typical of basaltic magma at $P_{\text{H}_2\text{O}} = 1000$ to 5000 atm [Khitarov and Kadik,

1973]. Therefore if $\text{CO}_2 + \text{CO}$, N_2 and H_2O are the main species for carbon, nitrogen and ocean water over geologic history (see Holland [1984] for a review), we would expect the degassing rate of nitrogen to be similar to Ar and carbon to be similar to He (see Figure 5), and the degassing of water to be much slower. Possible recycling of volatiles via subduction (of, e.g., CO_2 [Javoy *et al.*, 1986]) complicates the picture. Figure 5 diagrams the evolution of various gas species in the atmosphere without consideration of recycling or time-dependent speciation. Although we reiterate that there is no simple "mean age" for the atmosphere, the development of a "mature" atmosphere was still a much earlier event (about 4.3 Ga) than that of the total oceans, because of the high solubility of water in magmas. The mean age and the evolution of the ocean can be estimated if H_2O was the primary species for degassing H. This mean age is ~ 2.7 Ga and is similar to the mean age of continental crust suggesting that the relative volumes of ocean and crust may have remained approximately constant through time. A constant $V_{\text{ocean}}/V_{\text{crust}}$ is supported by the freeboard argument summarized by Taylor and McLennan [1985]. The evolution of the ocean is plotted in Figure 5 by assuming $Q_{\text{H}_2\text{O}}/Q_{\text{Ar}} = 0.002$, and that degassed H_2O condensed into the oceans "immediately" in a geologic sense. The predicted present outgassing rate for H_2O is $7 \times 10^{12} \text{ mol/yr}$, similar to that estimated by Jambon *et al.* [1988]. All the above considerations for nitrogen, carbon and ocean water are preliminary because possible recycling via subduction of continental material (particularly sediments) and different speciation during early degassing can greatly influence the results. A more detailed model for carbon and nitrogen evolution considering recycling via subduction will be presented in a future publication (A preliminary report can be found in Zhang and Zindler, 1988).

Other potentially important gas species in the evolution of the atmosphere include CH_4 , NH_3 , H_2 , SO_2 and H_2S . Unfortunately, the lack of solubility data and constraints on speciation precludes quantitative consideration of these species. Much work is needed on understanding the early speciation and on solubility measurement. Further work is also needed on the distribution of gases in MORB vesicles and

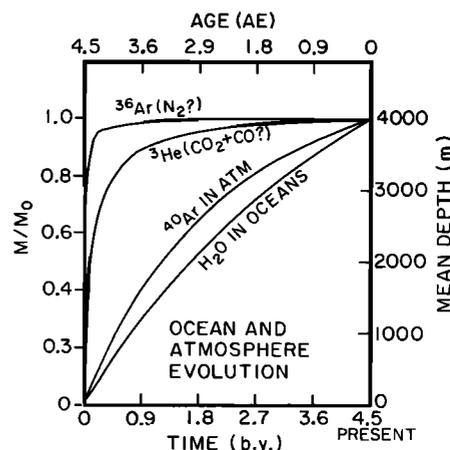


Fig. 5. Accumulation of various gas species in the Earth's atmosphere. The present-day mass of each species is taken as 1.0 for this diagram. Interpretation of results on CO_2 , N_2 and ocean water is limited by our poor understanding of speciation during outgassing and the importance of recycling (see text).

glass. Such results could be compared to ratios in AC, and might lead to constraints on the nature of early speciation and atmospheric evolution if the role of subduction can be accurately assessed.

SUMMARY AND CONCLUSIONS

Ar and He isotopic systematics demonstrate that the relative degassing rate of ³He must be slower than that of ³⁶Ar on the average, which suggests that the degassing history of the Earth might have been controlled by melt-vapor partitioning. A solubility controlled, equilibrium outgassing model for the Earth has been constructed using noble gas isotope ratios and measured solubilities in basaltic magma. Successful reconciliation of the various input constraints (including the apparently inconsistent isotopic ratios of the various noble gases) demonstrates the viability of a solubility controlled degassing mechanism. Accurate prediction of present-day degassing rates for ³He and ³⁶Ar strongly supports the validity of the model.

Early versions of this paper created some confusion among readers as to what was assumption and what was conclusion, particularly with reference to the solubility model. Were the coupling of radiogenic growth with planetary degassing a mathematically simpler matter, we might have been able to assess the viability of a solubility-controlled degassing mechanism by, for example, looking for a linear correlation on a two-dimensional variation diagram. This would be analogous to demonstrating that an igneous rock may have crystallized at a particular time in the past, based on the observation that its constituent minerals define a linear array on an isochron diagram; the observed relationship is necessary, but not sufficient to prove the hypothesis. In this example, the hypothesis that the minerals in question crystallized at a single time from a common magma, and that they have existed as closed systems since that time, can be tested by plotting the data on an isochron diagram. In the context of Earth degassing, the solubility hypothesis, suggested by the requirement of different outgassing rates for Ar and He, has been tested with a mathematical model, and shown to be consistent with observations concerning noble gas isotope ratios in the present-day Earth. The success of this model was necessary, therefore, to demonstrate the feasibility of the solubility hypothesis, as it is developed here, but is not sufficient to prove it.

The results of the modeling suggest that the mean degassing times (in Ma) for ¹³⁰Xe, ³⁶Ar, ³He, ⁴⁰Ar and ⁴He are 21 ±7, 56 ±19, 310 ±120, ~1500 and ~800 respectively. The mean degassing time for ¹³⁰Xe agrees very well with that proposed by *Staudacher and Allegre* [1982]. However, these mean degassing times differ significantly from those of *Allegre et al* [1986/87], and *Sarda et al.* [1985] because those authors assumed that all of the noble gases outgassed at the same rate. The mean degassing time of ~1.5 Ga for ⁴⁰Ar also differs from the "mean cessation time" of 1.2 to 1.8 Ga ago (read as 3.3 to 2.7 Ga) for ⁴⁰Ar as derived by *Hart et al.* [1985], because the mean degassing time and the "mean cessation time" are two different concepts. The mean age of ³⁹K in continental crust is 2.8±0.2 Ga and the average concentration of K in continental crust is 2.2±0.6%.

The degrees of outgassing of the MORB mantle (i.e., our end-member "degassed mantle") for ¹³⁰Xe, ³⁶Ar, ⁴⁰Ar, ³He and ⁴He are (99.92±0.03)%, (99.73±0.10)%, (82±8)%, (97.5±1.5)%, and

(88±8)%, respectively. A minimum of 50% of the whole mantle has been outgassed to these levels. Therefore, given the simplest two-box layered mantle scenario, the upper degassed or depleted layer (although depleted mantle, as used in reference to trace elements, need not be equivalent to degassed mantle) would have to extend to depths considerably in excess of 650 km. Because there is no seismically defined boundary at depths of 1200 to 1800 km, it seems likely that degassed and undegassed mantle segments are not simply layered, as has sometimes been assumed. This does not preclude the upper mantle having a fairly uniform rare gas distribution (as is suggested, for example, by the uniformity of He isotope ratios in MORBs), but if this is the case, then the lower mantle must comprise a mixture of more and less degassed (or even undegassed) zones. This result contravenes the conventional wisdom that convective isolation is required to sustain noble gas isotopic variations over long periods of time in the mantle.

The development and evolution of the oceans and atmosphere can be discussed in the context of our model if the speciation of carbon, nitrogen, hydrogen and sulfur and the solubilities for those species are known. The simplest assumptions regarding these parameters suggest that the development of the atmosphere was a much earlier event than the development of the oceans, and that the mean ages of the oceans and continents are similar. If substantiated, this result would ease somewhat the problem of reconciling a constant freeboard model for the Earth with popular models for crustal growth and structure [see, e.g., *Taylor and McLennan*, 1985].

APPENDIX A: SELECTION OF A POTASSIUM EVOLUTION FUNCTION FOR THE MANTLE

To derive a functional form for K evolution of the MORB mantle, we considered a model with both extraction from and recycling into the MORB mantle.

Let x = total mass of ³⁹K in DM, y = total mass of ³⁹K in crust, then

$$\begin{aligned} x+y &= x_0 \\ \frac{dx}{dt} &= -ax + by \\ \frac{dy}{dt} &= ax - by = -\frac{dx}{dt} \end{aligned} \tag{A1}$$

where ax is the extraction term and by is the subduction term. If a and b are constant (this is surely an oversimplification), then

$$\frac{d^2x}{dt^2} = -a\frac{dx}{dt} + b\frac{dy}{dt} = -(a+b)\frac{dx}{dt} \tag{A2}$$

The solution to the above equation is:

$$\begin{aligned} \frac{{}^{39}\text{K}_{\text{DM}}(t)}{{}^{39}\text{K}_{\text{DM}}(0)} &= 1 - P_K + P_K e^{-\mu t} \\ \frac{{}^{39}\text{K}_{\text{CC}}(t)}{{}^{39}\text{K}_{\text{DM}}(0)} &= P_K (1 - e^{-\mu t}) \end{aligned} \tag{A3}$$

where $\mu = a+b$, $P_K = \frac{{}^{39}\text{K}_{\text{CC}}^\infty}{{}^{39}\text{K}_{\text{DM}}^0}$ and is to be determined. Based on a series of trial runs, we determined that the value of P_K is ~1 (the trial runs had a range of 0.79 to 1 with an average of 0.95).

It follows then that $(1-P_K) \ll 1$, and

$$\frac{{}^{39}\text{K}_{\text{DM}}(t)}{{}^{39}\text{K}_{\text{DM}}(0)} \approx e^{-\mu t} \quad (\text{A4})$$

The mean age of ${}^{39}\text{K}$ in continental crust, \bar{t}_{CC} , is given by

$$\bar{t}_{\text{CC}} = T - \frac{\int_0^T t dy}{\int_0^T dy} = \frac{T}{1-e^{-\mu T}} - \frac{1}{\mu} \quad (\text{A5})$$

APPENDIX B: SELECTION OF PARAMETERS USED IN TOTAL INVERSION

There are four primary equations relating solubility, isotope ratios, and the rate constants (β and μ) for degassing and continental formation. In total, there are nine parameters when P_K is set to 1, and B_{Xe} and B_{He} are replaced by $B_{\text{Ar}}(Q_{\text{Xe}}/Q_{\text{Ar}})$ and $B_{\text{Ar}}(Q_{\text{He}}/Q_{\text{Ar}})$. The nine parameters are: β , μ , B_{Ar} , $Q_{\text{Xe}}/Q_{\text{Ar}}$, $Q_{\text{He}}/Q_{\text{Ar}}$, S_{Xe} , S_{Ar} , R_{Ar} and S_{He} . Because we know nothing about B_{Ar} , which is a model parameter, we can replace it with a parameter about which we know more, so that the input parameters and resulting solution are better constrained. From (29), we have,

$$B_{\text{Ar}} = \frac{\frac{{}^{36}\text{Ar}_{\text{DM}}^0}{T} - 1}{1 - e^{-\beta T}}$$

$$\frac{{}^{36}\text{Ar}_{\text{DM}}^T}{T} = \frac{({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{DM}}^T}{({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{DM}}^0} \frac{{}^{40}\text{Ar}_{\text{DM}}^T}{T} \approx \frac{{}^{40}\text{Ar}_{\text{DM}}^T}{T} / S_{\text{Ar}}$$

where $({}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{DM}}^0)$ is a concentration (not mass) ratio which depends on the degree of degassing of ${}^{40}\text{Ar}$, and can be estimated (see below). Therefore we can replace B_{Ar} by

$$S_{\text{Ar}} = \frac{\frac{{}^{40}\text{Ar}_{\text{DM}}^T}{T} - 1}{1 - e^{-\beta T}}$$

We then have nine parameters which, except for β , can be independently estimated: β , μ , $({}^{40}\text{Ar}_{\text{DM}}/{}^{40}\text{Ar}_{\text{UM}})^T$, $Q_{\text{Xe}}/Q_{\text{Ar}}$, $Q_{\text{He}}/Q_{\text{Ar}}$, S_{Xe} , R_{Ar} , and S_{He} . Various other "tricks" have been used in defining the parameters to be used in the total inversion:

1. Every parameter is made dimensionless. For example, βT and μT , instead of β and μ , are used.

2. Because the uncertainties in S_{Ar} and R_{Ar} are large and correlated, and we know the difference between R_{Ar} and S_{Ar} must be greater than zero [because $({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{DM}}^T$ is greater than $({}^{40}\text{Ar}/{}^{36}\text{Ar})_{\text{AC}}^T$], we use $R_{\text{Ar}} - S_{\text{Ar}}$ instead of R_{Ar} in the calculations, where the uncertainty in $R_{\text{Ar}} - S_{\text{Ar}}$ is smaller than and not highly correlated with that of S_{Ar} .

3. When a variable can vary through a large range, especially when it can be very small but still greater than zero, its distribution is likely to be lognormal. Therefore $\ln(\beta T)$,

$\ln(\mu T)$, and $\ln({}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T)$, are used instead of βT , μT , and $({}^{40}\text{Ar}_{\text{DM}}/{}^{40}\text{Ar}_{\text{UM}})^T$. These selections insure that each variable behaves in a more or less gaussian fashion.

Selection of input parameters is as follows:

1. Regarding $\ln(\beta T)$, because we do not know anything about βT except that it must be greater than zero, we simply use 0 ± 10 for $\ln(\beta T)$; this corresponds to a range from 4.5×10^{-5} to 2.2×10^4 for βT .

2. Regarding $\ln(\mu T)$, because P_K is set to be 1, we have ${}^{39}\text{K}_{\text{DM}}^T/{}^{39}\text{K}_{\text{DM}}^0 = e^{-\mu T}$ and ${}^{39}\text{K}_{\text{DM}}^T/{}^{39}\text{K}_{\text{DM}}^0$ is estimated to be 0.08 to 0.8. We can also estimate μT from mean age of continental crust. For example, a value of 2.5 Ga would yield $\ln(\mu T) = -0.3$. Combining both approaches, we use $\ln(\mu T) = -0.3 \pm 1.2$.

3. Regarding $\ln({}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T)$: ${}^{40}\text{Ar}_{\text{UM}}$ can be estimated as 2.1×10^{-5} cm³ STP/g from the K concentration in UM. *Hart et al.* [1985] estimated the ${}^{40}\text{Ar}$ concentration in DM to be $1.7 - 3.2 \times 10^{-6}$ cm³ STP g⁻¹. This corresponds to $\ln({}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T) \approx -2.5$ to -1.9 . Considering the large uncertainty in this estimation, $\ln({}^{40}\text{Ar}_{\text{DM}}^T/{}^{40}\text{Ar}_{\text{UM}}^T)$ is set to be -2.3 ± 1.0 .

4. $Q_{\text{Xe}}/Q_{\text{Ar}}$ and $Q_{\text{He}}/Q_{\text{Ar}}$: Available solubility data are compiled in Table B1. The values used here ($Q_{\text{Xe}}/Q_{\text{Ar}} = 3.3 \pm 1.0$ and $Q_{\text{He}}/Q_{\text{Ar}} = 0.105 \pm 0.05$) are an average of the values reported by *Jambon et al.* [1986] and are very similar to an average of all available data.

5. Regarding S_{Xe} , the Xe concentration in present DM is very low. The ${}^{129}\text{Xe}/{}^{130}\text{Xe}$ ratio in DM (7.50 according to *Staudacher et al.*, [1986]) is not dramatically different from that of UM (6.48). Therefore, ${}^{129}\text{Xe}/{}^{130}\text{Xe}_{\text{DM}}$ is nearly the same as the atmospheric ratio. A value of 6.34 is taken as initial ${}^{129}\text{Xe}/{}^{130}\text{Xe}$ for DM and UM [*Staudacher and Allegre*, 1982]. Therefore, $S_{\text{Xe}} \approx 8$. The uncertainty of S_{Xe} is difficult to estimate but we somewhat arbitrarily set it at 3. In run 3 (Table 3), we set S_{Xe} to be 4 ± 10 to evaluate the effect on the solution when S_{Xe} is not well determined.

6. Regarding S_{Ar} , the selection ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in UM as 475 ± 125 is discussed in the section on the isotopic ratios in the undegassed mantle. The value of ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in DM is chosen as $28,000 \pm 5,000$ [*Staudacher et al.*, 1986]. The initial ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in UM and DM is nearly zero. Therefore $S_{\text{Ar}} = 59 \pm 20$.

7. Regarding $R_{\text{Ar}} - S_{\text{Ar}}$, ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ in AC is estimated to be 400 ± 100 . Therefore $R_{\text{Ar}} - S_{\text{Ar}} = 11 \pm 6$.

8. Regarding S_{He} , ${}^4\text{He}/{}^3\text{He}$ in DM is taken as $88,000 \pm 8,000$ ($\sim 8.2 \pm 0.8 Ra$), while ${}^4\text{He}/{}^3\text{He}$ in UM is more difficult to evaluate. The highest ${}^4\text{He}/{}^3\text{He}$ in Loihi glass is 22,500 (32 *Ra*) which is considered to be the most reliable for a high ${}^3\text{He}/{}^4\text{He}$ ratio observed in a mantle-derived rock (because He in subaerial rocks may be subject to contamination by cosmogenic ${}^3\text{He}$ [*Kurz*, 1986]) and is taken as a maximum for $({}^4\text{He}/{}^3\text{He})_{\text{UM}}^T$. Here we adopt the "planetary value" of 7,000 ($\sim 100 Ra$) for $({}^3\text{He}/{}^4\text{He})_{\text{UM}}^0$. These values together yield an S_{He} of about 5.2. The true value for S_{He} is likely to be higher because the observed highest ${}^3\text{He}/{}^4\text{He}$ is likely to be lower than that of UM, due to mixing of DM He with UM He. Therefore, we have chosen S_{He} as 7 ± 4 .

It is possible that the highly degassed segments of DM are volumetrically minor, and that the degassed reservoir is better represented by "average" MORB isotope ratios. Therefore, in run 2 of Table 3 we have used $S_{\text{Xe}} = 5 \pm 2$, $S_{\text{Ar}} = 40 \pm 10$ and $R_{\text{Ar}} - S_{\text{Ar}} = 7 \pm 4$. With the exception of these parameters, the output is similar to that from runs 1 and 3. Essentially, the difference between these cases is that in run 2 we resolve the degassed portion of the mantle into a larger, less degassed reservoir than

TABLE B1. Compilation of Solubility Ratios of Noble Gases

Temperature °C	Q_{Xe}/Q_{Ar}	Q_{Kr}/Q_{Ar}	Q_{Ne}/Q_{Ar}	Q_{He}/Q_{Ar}	Melt composition	Reference
1300	2.4	2.2	0.26	0.114	basalt	Jambon et al., [1986]
1320	3.3	2.6	0.23	0.088	basalt	Jambon et al., [1986]
1400	3.4	1.4	0.26	0.117	basalt	Jambon et al., [1986]
1400	2.9	1.9	0.24	0.102	basalt	Jambon et al., [1986]
1500	3.9	1.6	0.26	0.106	basalt	Jambon et al., [1986]
1500	3.5	1.5	0.26	0.124	basalt	Jambon et al., [1986]
1500	3.7	1.5	0.22	0.083	basalt	Jambon et al., [1986]
Average of the above ^b	3.3(±0.5)	1.8(±0.4)	0.25(±0.02)	0.105(±0.015)	-	-
1200	-	2.8	0.12	>0.041	tholeiitic basalt	Hayatsu and Waboso [1985]
1200	-	2.9	0.22	-	alkali-olivine basalt	Hayatsu and Waboso [1985]
1200	-	4.3	0.35	-	basaltic andesite	Hayatsu and Waboso [1985]
1100	-	4.0	0.25	-	basaltic andesite	Hayatsu and Waboso [1985]
1200	-	4.4	0.36	-	basaltic andesite	Hayatsu and Waboso [1985]
1300	-	3.4	0.38	-	basaltic andesite	Hayatsu and Waboso [1985]
1200	2.8	1.9	-	-	basalt	Ozima and Podosek [1983]
1500	3.3	1.5	0.29	0.17	enstatite	Ozima and Podosek [1983]
1350	~4.0	~1.4	0.083	-	alkali-olivine basalt	Lux [1985] ^a
1350	~3.4	~1.4	0.13	-	tholeiitic basalt	Lux [1985] ^a
Average of all	3.2±0.6	2.4±1.1	0.24±0.08	0.105±0.035		

The solubility ratios are $Q_i/Q_o = K_o/K_i$, where K_i is the partition coefficient between melt and vapor.

^a Estimated from the diagram in the paper.

^b These were the values used for calculations.

in runs 1 and 3. All of the uncertainties estimated above are considered to represent two standard deviations (2σ). We note that these values were halved for use in the inversion calculation which makes use of 1σ uncertainties. However, all uncertainties given in Table 3 were readjusted to represent the 2σ level.

APPENDIX C: RELATIONS BETWEEN THE NOBLE GAS CONCENTRATIONS DURING DEGASSING

We want to obtain relationships between different gas species during degassing. Let

$$K_i = \frac{C_i \text{ in melt (mol/g)}}{P_i \text{ in gas (atm)}}$$

where K_i is solubility of "i" in melt, C_i the concentration in melt and P_i the partial pressure in the vapor. Then, during fractional degassing,

$$d[C_i M] + \frac{P_i}{RT_m} dV_g = 0 \quad (C1)$$

where melt is assumed to be homogeneous, M is mass of melt, T_m is temperature of the melt, and V_g is volume of vapor. During equilibrium degassing

$$C_i M + \frac{P_i V_g}{RT_m} = C_i^0 M_0 \quad (C2)$$

or

$$\frac{C_i}{C_i^0} = \frac{M}{M_0} + \frac{P_i}{C_i} \frac{V_g}{RT_m M_0} = \frac{M}{M_0} + \frac{V_g}{K_i RT_m M_0} \quad (C3)$$

where M_0 is the initial mass. Taking $M/M_0 \sim 1$, because of the small relative mass of the vapor phase, and letting $M_0 = \rho_m V_m$, where ρ_m and V_m are the density and volume of the melt, we can finally write that

$$\frac{C_i^0}{C_i} = 1 + \frac{V_g}{K_i RT_m \rho_m V_m} = 1 + Q_i \frac{V_g}{V_m} \quad (C4)$$

where $Q_i = 1/(K_i RT_m \rho_m)$ is a constant at fixed temperature and composition, and V_g/V_m is time-integrated vesicularity. For fractional degassing, (C1) becomes

$$\frac{dC_i}{C_i} = - \frac{dV_g}{K_i RT_m \rho_m V_m} = - Q_i \frac{dV_g}{V_m}$$

Integrating, we have

$$\ln \frac{C_i}{C_i^0} = - Q_i \frac{V_g}{V_m}$$

and, finally

$$\frac{C_i}{C_i^0} = e^{-Q_i V_g/V_m} \quad (C5)$$

which is the equation for fractional degassing.

From equation (C4), we can relate the degassing function of different gases during equilibrium degassing through

$$\frac{{}^{130}\text{Xe}_{DM}^0 / {}^{130}\text{Xe}_{DM}^i - 1}{{}^{36}\text{Ar}_{DM}^0 / {}^{36}\text{Ar}_{DM}^i - 1} = \frac{{}^{3}\text{He}_{DM}^0 / {}^{3}\text{He}_{DM}^i - 1}{{}^{4}\text{He}_{DM}^0 / {}^{4}\text{He}_{DM}^i - 1} = \frac{V_g}{V_m} \quad (C6)$$

where V_g/V_m is time integrated vesicularity. From equation (C5), we can relate the degassing function of different gases during fractional degassing through

$$\frac{1}{Q_{Xe}} \ln \frac{{}^{130}\text{Xe}_{EDM}^0}{{}^{130}\text{Xe}'_{EDM}} = \frac{1}{Q_{Ar}} \ln \frac{{}^{36}\text{Ar}_{EDM}^0}{{}^{36}\text{Ar}'_{EDM}} = \frac{1}{Q_{He}} \ln \frac{{}^3\text{He}_{EDM}^0}{{}^3\text{He}'_{EDM}} = \frac{V_g}{V_m} \quad (C7)$$

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