244Pu Fission Xe in the Mantle and Mantle Degassing Chronology

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1. Introduction

Mantle derived materials such as MORBs and mantle xenoliths often show excess in 129Xe and 131−136Xe (hereafter represented as 136Xe) relative to the atmospheric Xe (Hennecke and Manuel, 1975; Kaneoka and Takaoka, 1978; Staudacher and Allegre, 1982; Allegre et al., 1986/7; Marty, 1989). The excess in 129Xe has been attributed to an extinct nuclide 129I (ibid). Although the excess in 136Xe must be due either to 238U spontaneous fission or to 244Pu spontaneous fission, it has not been possible to resolve their origin because of the experimental difficulty of an extremely low abundance of Xe in mantle-derived materials.

The cosmic elemental abundance ratio (244Pu/238U = 0.006 ± 0.001 at 4.56 Ga ago, Hudson et al., 1988), if applied to the Earth, favours 244Pu, since 244Pu-fissiogenic Xe would then be more than an order of magnitude abundant than 238U fissiogenic Xe in the Earth (Bernatowicz and Podosek, 1978). Atmospheric Xe also shows an excess in 136Xe and 129Xe relative to the primordial Xe, where the former excess is generally attributed to 244Pu-fissiogenic Xe (Pepin and Phinney, 1978). Common occurrence of excess 129Xe in mantle-derived materials also suggests the existence of 244Pu-
fissiogenic Xe, since the latter has a longer half life than the former.

While the above empirical data all suggest a $^{244}$Pu-fissiogenic origin of the excess in $^{136}$Xe, Xe isotopic analyses on a CO$_2$ well gas from New Mexico, which contained a sufficient amount of Xe for a precise isotopic analysis, clearly showed a $^{238}$U-fissiogenic xenon isotopic pattern setting a maximum limit of 20% for $^{244}$Pu-fissiogenic Xe (Phinney et al., 1978). Since the CO$_2$ well gas contained an excess in $^{129}$Xe, and mantle type Ne and He, the source of the excess $^{136}$Xe in the CO$_2$ well gas has also been attributed to the mantle. In addition, as the U-content in the mantle may be enough to account for the fissiogenic Xe in mantle-derived materials, some authors concluded that the excess in $^{136}$Xe in mantle-derived materials or in the mantle must be due to $^{238}$U-fissiogenic Xe (Fisher, 1985; Fisher, 1987; Allegre et al., 1986/7). Lately CO$_2$ well gases from Australia and Colorado were also reported to have $^{238}$U-fissiogenic Xe (Caffee et al., 1988).

The problem of whether the excess in $^{136}$Xe in the mantle-derived materials and therefore in the mantle is $^{238}$U-fissiogenic or $^{244}$Pu-fissiogenic bears a far-reaching implication on the evolution of the Earth. For example, if the existence of the $^{244}$Pu-fissiogenic Xe is established, this would impose a crucial constraint on the degassing chronology of the terrestrial atmosphere (see a section on Discussion). On the contrary, its non-existence would revise a long standing "$^{244}$Pu-paradox", that is, why $^{129}$I-fissiogenic Xe should be seen in spite of the shorter half life of its parent nuclide $^{129}$I, if $^{244}$Pu-fissiogenic Xe were not observed.

The purpose of the present paper is to examine whether the excess in $^{136}$Xe is due to $^{238}$U-fission or to $^{244}$Pu-fission in the light of all the published data on MORBs and diamonds, and of newly obtained data on diamonds. We will show that the excess in $^{136}$Xe is best explained by $^{244}$Pu-fissiogenic Xe. On the basis of these empirical data, we then discuss the atmospheric degassing chronology.

2. Data base

The mantle-derived materials used in this study are MORBs and diamonds. Although there are a few Xe isotopic data on mantle xenoliths, we did not use them simply because their analytical precision is poorer than those for MORBs and diamonds.
Although both MORBs and diamonds were derived from the mantle, we emphasize that while MORBs are recent derivatives from the upper mantle, diamonds are generally much older, representing the noble gas state in the ancient mantle. As discussed in a later section, comparison of the modern noble gas state with the ancient one in the mantle yields unique information about the mantle degassing chronology. Also noteworthy is the fact that some diamonds, especially the coat in a coated diamond, often contains a much larger amount of trapped noble gas (sometime more than ten times) than that contained in basalt glass. Hence, we can hope for more precise mantle Xe isotopic data by analysing these diamonds.

The diamonds analysed in this study are coated diamonds from Zaire (890801-4 in Table I) and Botswana (881227, 890109 in Table I). Samples 890801 and 890802 were coats separated from a single big Zaire diamond. The age of the kimberlite pipes of these diamonds are known to be Mesozoic. In general the crystallization age of diamond is much older than the host kimberlite (e.g., Boyd and Gurney, 1986; Meyer, 1989). In the case of the Zaire diamonds both K-Ar and $^{40}$Ar-$^{39}$Ar stepheating dating gave an apparent age of more than 6.0 Ga (Zashu and Ozima, 1986). However, this unusual age now turned out to be due to an excess in $^{40}$Ar (Ozima et al., 1989). The best Sm-Nd model age obtained on one of the Zaire diamonds suggests about 1.8 Ga (Podosek and Brannon, written communication, 1988).

The Botswana diamond was from the Jwaneng kimberlite pipe, of which emplacement age is 80$\sim$114Ma (Smith, 1983). According to Richardson et al. (1984), diamonds in Archean cratons in Southern Africa which include the Jwaneng kimberlite pipe crystallized 3.2$\sim$3.3 Ga ago, and has been stored in a cool, thick root zone (keel) of cratons. Hence, we assumed the crystallization age of about 3.2 Ga for the Botswana diamond.

All the published diamond data were obtained from a whole rock specimen. For a Botswana and two Zaire diamonds, the coat parts were separated from the core part either by laser cutting (Zaire) or by crashing (Botswana). Noble gas measurements were made on the coat (Zaire, Botswana) and core (Botswana). Although the core and coat of a coated diamond are likely to have crystallized in different mantle regions, they at least give information on the mantle noble gas state.

For the description of samples and experimental procedures, readers should refer to the respective literature. For unpublished data, the analyt-
## Table I. Xe isotopic composition of diamonds.

<table>
<thead>
<tr>
<th>Sample</th>
<th>mass (g)</th>
<th>$^{130}$Xe (10$^{-12}$ cc/g)</th>
<th>$^{124}$Xe</th>
<th>$^{126}$Xe</th>
<th>$^{128}$Xe</th>
<th>$^{129}$Xe</th>
<th>$^{130}$Xe</th>
<th>$^{131}$Xe</th>
<th>$^{132}$Xe</th>
<th>$^{134}$Xe</th>
<th>$^{136}$Xe</th>
</tr>
</thead>
<tbody>
<tr>
<td>88127</td>
<td>0.1262</td>
<td>0.029±0.013 0.0266±0.0114</td>
<td>0.511±0.023</td>
<td>6.26±0.22</td>
<td>=1</td>
<td>5.07±0.19</td>
<td>6.40±0.22</td>
<td>2.51±0.09</td>
<td>2.13±0.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td>890109</td>
<td>0.1272</td>
<td>1.4±0.06 0.05±0.01 0.0468±0.123</td>
<td>0.486±0.026</td>
<td>6.75±0.28</td>
<td>=1</td>
<td>5.24±0.22</td>
<td>6.63±0.27</td>
<td>2.68±0.11</td>
<td>2.31±0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>890801</td>
<td>0.2866</td>
<td>0.60±0.03 0.026±0.004 0.0234±0.0045</td>
<td>0.481±0.017</td>
<td>7.20±0.17</td>
<td>=1</td>
<td>5.29±0.13</td>
<td>6.80±0.15</td>
<td>2.80±0.08</td>
<td>2.44±0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>890802</td>
<td>0.4842</td>
<td>0.51±0.02 0.026±0.005 0.0235±0.0035</td>
<td>0.478±0.017</td>
<td>7.10±0.15</td>
<td>=1</td>
<td>5.19±0.11</td>
<td>6.68±0.13</td>
<td>2.78±0.07</td>
<td>2.42±0.06</td>
<td></td>
<td></td>
</tr>
<tr>
<td>890803</td>
<td>0.0881</td>
<td>0.52±0.03 0.026±0.021 0.014±0.014</td>
<td>0.470±0.036</td>
<td>7.52±0.33</td>
<td>=1</td>
<td>5.11±0.26</td>
<td>6.81±0.27</td>
<td>2.88±0.13</td>
<td>2.61±0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>890804</td>
<td>0.0802</td>
<td>0.08±0.01</td>
<td>n.m</td>
<td>n.m</td>
<td>0.607±0.203</td>
<td>8.13±1.4</td>
<td>=1</td>
<td>5.81±1.01</td>
<td>7.73±1.30</td>
<td>2.97±0.56</td>
<td>2.83±0.51</td>
</tr>
<tr>
<td>air</td>
<td></td>
<td>0.02337 0.02180</td>
<td>0.4715</td>
<td>6.496</td>
<td>=1</td>
<td>5.213</td>
<td>6.607</td>
<td>2.563</td>
<td>2.176</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*) Errors in isotopic ratios include 1σ in mass spectrometry, elemental abundance calibration and in discrimination factors (≈ 0.5%/amu), and 20% in hot blank.

**) n.m.: Peaks are too small to be measured.

***) Sample 88127: coat of a Botswana diamond, 890109: core of a Botswana diamond, 890801, 890802: coat of a Big Zaire diamond, 890803, 890804: coat of small Zaire diamonds.
ical results are given in Table I, where the retuning of a mass spectrometer and modification in the scanning procedure (to avoid discontinuous peak jumping and others) resulted in a marked improvement in the precision of the Xe isotopic analyses. This improvement as well as the use of large diamond samples (2~3 carats) enabled us to obtain the most precise Xe isotopic ratio (in terms of error bars) in our laboratory.

3. $^{238}$U-fission or $^{244}$Pu-fission?

Figure 1 shows a three isotope plot $^{136}$Xe/$^{130}$Xe--$^{129}$Xe/$^{130}$Xe, which shows a clear linear trend. We also show the correlation line determined by Staudacher (1987) for MORB data. It is remarkable that the diamonds data lie perfectly on the correlation line defined by Staudacher. Such a linear array was first reported in MORBs by Staudacher and Allègre (1982) (they used $^{134}$Xe in place of $^{136}$Xe in their three isotope plot). They argued that because of the similar half life times of $^{129}$I and $^{244}$Pu, the corresponding excess Xe trend, to appear together, and the simultaneous variation of both $^{129}$Xe and $^{134}$Xe, are a typical signature of the extinct radioactivities. In a

![Diagram](image_url)

Fig. 1. $^{136}$Xe/$^{130}$Xe--$^{129}$Xe/$^{130}$Xe three isotope plot. Note that diamond data lie on the correlation line defined for MORB by Staudacher (1987). Error bars are 1σ and shown only for newly obtained data (this work). MORB(•): Staudacher and Allègre (1982), Ozima and Zashu (1983), Staudacher and Allègre (1986), Allègre et al. (1986/7), Marty (1989). Diamond(◇): Ozima and Zashu (1988), Ozima et al. (this work).
later paper (1986/7), however, they retracted the previous view, and suggested that the excess in $^{134}$Xe, and also $^{136}$Xe, are due to $^{238}$U-spontaneous fission, since one MORB from the Indian ocean showed a pattern similar to that of the $^{238}$U-fissiogenic Xe, and also, the inventory consideration appeared to favour the $^{238}$U fission. However, the conclusion based on a single datum with large analytical errors can hardly be considered as conclusive, and as discussed in a later section, the inventory argument is not supported by recent experimental results.

To understand the linear trend in Fig. 1, let us first suppose that the excess in $^{129}$Xe and $^{136}$Xe were derived from $^{129}$I and $^{238}$U respectively. Although the exact ages of the diamonds are not known, they must be much older than the MORBs; very likely to be older than 1 Ga as discussed above. Since $^{238}$U-fissiogenic Xe has still been evolving because of its long half life ($T_{1/2} = 4.47$ Ga), it is difficult to see why these samples, formed at an entirely different time, should lie on the same linear trend. We expect the modern mantle (MORB glass) to be more enriched in $^{238}$U-fissiogenic $^{136}$Xe excess than diamonds, giving rise to a different mantle Xe or a different mixing line with a steeper slope. The almost identical linear trend both for the modern MORBs and the ancient diamonds strongly suggests that the mantle Xe, with the excess $^{129}$Xe and $^{136}$Xe, was established long before the crystallization of the diamonds. This favours the short lived $^{244}$Pu as a progenitor of the excess $^{136}$Xe in the mantle over the still living $^{238}$U. Alternatively, if we assume that the $^{129}$Xe and $^{136}$Xe were derived from $^{129}$I and $^{244}$Pu, the observed linear trend can be more reasonably explained: Xe isotopic ratio ceased its evolution soon after the formation of the Earth (within a few hundred million years) and subsequent geodynamical processes in the mantle homogenized the isotopic composition to give rise to a well defined mantle Xe, and hence the single linear correlation line.

In the above discussion, we implicitly assumed that the linear array represents a mixing line between the atmospheric Xe and some (unidentified) mantle Xe. However, if excess $^{136}$Xe was derived from $^{244}$Pu, the linear array can be interpreted to represent an isochron, since the slope of the linear array depends primarily on the mantle degassing time ($t_d$): the later the $t_d$, the more the contribution of fissiogenic Xe from a longer-lived $^{244}$Pu than from $^{129}$I, therefore, the steeper slope is produced. This is discussed in a later section.
4. Discussion

$^{238}\text{U fissiogenic Xe in the mantle}$

The above discussion shows that the excess $^{136}\text{Xe}$ in the mantle is most likely to be derived from $^{244}\text{Pu}$ fission. However, the present mantle contains a small, but non-negligible amount of U (a few ppb) and the less degassed mantle must have contained even a larger amount of U. Hence, Fisher (1985; 1987) concluded that excess $^{136}\text{Xe}$ in the mantle must derive from $^{238}\text{U}$, since if 15 ppb is assumed for the U content in the mantle, $2 \times 10^{-14}\text{cm}^3/\text{g}$ of fissiogenic $^{136}\text{Xe}$ must have been produced for 4.5 Ga, which is comparable with the observed excess $^{136}\text{Xe}$ in common volcanic rocks. The U content (and, therefore, the $^{238}\text{U}$-fissiogenic Xe) estimated by Fisher may be an overestimation, since U was likely to be enriched in mantle-derived materials such as peridotite and lherzolite (Kushiro, private communication), on which Fisher’s argument was partly based. O’Nions and Oxburgh (1986) estimated a much smaller U content of 5 ppb in the mantle on the basis of global heat flow.

It is also important to consider that an excess in an isotope becomes noticeable only in the case where the excess is significant relative to a common isotope, that is, excess $^{136}\text{Xe}$ can be seen only in the case where $^{238}\text{U}/\text{Xe}$ is sufficiently high. Hiyagon and Ozima (1986) showed that Xe has a fairly large partition coefficient between silicate melt and crystals (olivine, pyroxene), i.e., $D_{\text{Xe}} > 0.1$, which is more than an order of magnitude larger than the partition coefficient for U ($D_{\text{U}} < 10^{-2}$) (e.g., Henderson, 1982). Lately, similar large partition coefficients for Xe between melts and minerals (diopside, anorthite, forsterite) were also reported by Broadhurst and Drake (1988). Hence, the U/Xe ratio in the mantle is expected to be smaller than in common volcanic rocks. If the degree of a partial melting was small, the U/Xe ratio in the mantle could be as small as one-tenth (which is the ratio of $D_{\text{U}}/D_{\text{Xe}}$) of the ratio found in volcanic rocks, and hence $^{238}\text{U}$-fissiogenic Xe could easily be overshadowed by a common Xe in the mantle.

In the above discussion, we implicitly assumed that the Xe in diamonds is essentially of a trapped origin, or in-situ $^{238}\text{U}$-fissiogenic Xe is negligible. The justification for this assumption can again be seen in Fig. 1: if the Xe contains a significant amount of in-situ fissiogenic Xe, the latter amount
must vary from sample to sample reflecting the difference in the amount of the U content and the age of the diamonds (there could be a considerable difference in the age between Botswana and Zaire diamonds), and hence, it would be impossible to have any correlation between the in-situ fissionogenic $^{136}$Xe and the trapped $^{129}$Xe.

$^{136}$Xe/$^{130}$Xe- $^{129}$Xe/$^{130}$Xe chronology

From the preceding discussions, we assumed that excess $^{136}$Xe and $^{129}$Xe in the mantle relative to the atmospheric Xe are due to $^{244}$Pu and $^{129}$I, respectively. The existence of these excess in Xe, then, indicates that the atmospheric Xe was derived from the mantle before the total decay of $^{129}$I and $^{244}$Pu, say, within a few half life of $^{129}$I. It then follows that the ratio of excess $^{136}$Xe to excess $^{129}$Xe depends on the time of Xe degassing, that is, the time of the mantle degassing; the later the degassing time the larger the ratio, since more $^{244}$Pu relative to $^{129}$I remained in the mantle because of the longer half life of $^{244}$Pu. Therefore, the linear correlation in Fig. 1 whose gradient corresponds to the ratio of excess $^{136}$Xe to excess $^{129}$Xe, can then be interpreted to be an isochron. Below we described a mathematical formulation for the isochron.

Following Pepin and Phinney (1978), we assumed that the primordial terrestrial Xe is a fractionated U-Xe, and that the present Xe in earth has evolved with the addition of radiogenic components derived from $^{244}$Pu and $^{129}$I. As discussed in the previous section, we neglected $^{238}$U derived fissionogenic Xe. Let us consider that the mantle degassing occurred at $t_d$. The atmospheric Xe isolated from the Earth’s interior at $t_d$ ceased to evolve thereafter. Normalizing Xe isotopes to a fission shielded isotope $^{130}$Xe, Xe isotopic composition in the atmosphere can be written as (Ozima et al., 1985)

$$
\begin{align}
\left(\frac{^{129}\text{Xe}}{^{130}\text{Xe}}\right)_A & = \left(\frac{^{129}\text{Xe}}{^{130}\text{Xe}}\right)_0 + \left(\frac{^{129}\text{I}}{^{130}\text{Xe}}\right)_0 \{1 - \exp(-\lambda_{^{129}I} t_d)\}, \\
\left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_A & = \left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_0 + \left(\frac{^{244}\text{Pu}}{^{130}\text{Xe}}\right)_0 \frac{\lambda_{^{136}Xe}}{\lambda_{^{244}Pu}} \{1 - \exp(-\lambda_{^{244}Pu} t_d)\},
\end{align}
$$

(1)
where subscripts \(A\) and \(0\) refer to the present atmosphere and to the Earth 4.56 Ga ago, and \(\lambda_{129}\), \(\lambda_{244}\) denote the decay constants of \(^{129}\)I and \(^{244}\)Pu. \((^{129}\text{Xe}/^{130}\text{Xe})_0\) and \((^{136}\text{Xe}/^{130}\text{Xe})_0\) correspond to the fractionated U-Xe, and \(\lambda_{SF},^{136}\text{Y}_{Pu}\) is the decay constant of the spontaneous fission of \(^{244}\)Pu, and the fission yield for \(^{136}\)Xe. While the atmospheric Xe isotopic composition ceased to evolve after \(t_d\), Xe in the Earth’s interior has still continued to evolve due to the decay of \(^{244}\)Pu and \(^{129}\)I. For a time sufficiently longer than the half life of \(^{244}\)Pu, \(i.e., t > 1 \times 10^8\) yrs the Xe isotopic compositions in the mantle can be expressed as

\[
\begin{align*}
\left(\frac{^{129}\text{Xe}}{^{130}\text{Xe}}\right)_M & = \left(\frac{^{129}\text{Xe}}{^{130}\text{Xe}}\right)_A + \frac{(^{129}\text{I})_0}{f(^{130}\text{Xe})_0}\exp(-\lambda_{129}t_d), \\
\left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_M & = \left(\frac{^{136}\text{Xe}}{^{130}\text{Xe}}\right)_A + \frac{(^{244}\text{Pu})_0}{f(^{130}\text{Xe})_0}\frac{\lambda_{SF}}{^{136}\text{Y}_{Pu}}\exp(-\lambda_{244}t_d),
\end{align*}
\]  

(2)

where the subscript \(M\) refers to the mantle and \(f\) denotes the fraction of \(^{130}\)Xe, which remained in the mantle at the mantle degassing time (the rest of the fraction, that is, \((1-f)\) was degassed into the atmosphere-crust system). The Xe isotopic evolution is depicted in Fig. 2. Denoting \(s_1\) and \(s_2\) for the gradient of the lines (\(A_0-A\)) and (\(A-M\)) in Fig. 2, we have from Eqs.(1) and (2)

\[
\begin{align*}
\left(s_1 = \frac{(^{136}\text{Xe}/^{130}\text{Xe})_A - (^{136}\text{Xe}/^{130}\text{Xe})_0}{(^{129}\text{Xe}/^{130}\text{Xe})_A - (^{129}\text{Xe}/^{130}\text{Xe})_0} & = \frac{(^{244}\text{Pu})_0}{(^{129}\text{I})_0}\frac{\lambda_{SF}}{^{136}\text{Y}_{Pu}}\frac{1 - \exp(-\lambda_{244}t_d)}{1 - \exp(-\lambda_{129}t_d)}, \\
\left(s_2 = \frac{(^{136}\text{Xe}/^{130}\text{Xe})_M - (^{136}\text{Xe}/^{130}\text{Xe})_A}{(^{129}\text{Xe}/^{130}\text{Xe})_M - (^{129}\text{Xe}/^{130}\text{Xe})_A} & = \frac{(^{244}\text{Pu})_0}{(^{129}\text{I})_0}\frac{\lambda_{SF}}{^{136}\text{Y}_{Pu}}\frac{\exp(-\lambda_{244}t_d)}{\exp(-\lambda_{129}t_d)}.
\end{align*}
\]  

(3)

Consequently, we have

\[s_2/s_1 = \frac{\exp(\lambda_{129}t_d) - 1}{\exp(\lambda_{244}t_d) - 1}.\]  

(4)
Fig. 2. Schematic representation of Xe isotopic evolution in the Earth. A$_0$: fractionated U-Xe ($^{129}$Xe/$^{130}$Xe = 6.06, $^{136}$Xe/$^{130}$Xe = 2.075, Pepin and Phinney, 1978), A: atmospheric Xe ($^{129}$Xe/$^{130}$Xe = 6.496, $^{136}$Xe/$^{130}$Xe = 2.176), M: mantle Xe (isotopic composition is not known). The initial Xe isotopic composition (assumed to be a fractionated U-Xe) had evolved (A$_0$ → A) with the continuous addition of $^{244}$Pu-fissiogenic $^{136}$Xe and $^{129}$I-radiogenic $^{129}$Xe until the mantle degassing time ($t_d$). While the atmospheric Xe composition was quenched at $t_d$, Xe in the mantle has been evolving (A → M). The gradients for A$_0$-A and A-M can be determined from the values of the fractionated U-Xe and atmospheric Xe, and from the observed linear correlation in Fig. 1. The mantle degassing time $t_d$ can then be determined from the ratio of the gradients (see the text).

Hence, if $s_1$ and $s_2$ are known, we can calculate $t_d$ from Eq. (4). $s_2$ can be estimated from the empirical data displayed in Fig. 1. For example the gradient of the correlation line defined by Staudacher (1987) gives $s_2 \approx 0.4$. To estimate $s_1$, we must know the composition of primordial Xe in the Earth. According to Pepin and Phinney (1978), the atmospheric Xe contains about 6.7% of $^{129}$Xe decayed from $^{129}$I and about 4.7% of $^{136}$Xe decayed from $^{244}$Pu. Hence, by subtracting these later added nucleogenic components from the atmospheric Xe, we can define the primordial Xe composition, that is, $^{129}$Xe/$^{130}$Xe = 6.496 × (1 - 0.067) = 6.06 and $^{136}$Xe/$^{130}$Xe = 2.176 × (1 - 0.047) = 2.074. We then have $s_1 = 0.23$. However, the estimated values do not yield a positive $t_d$ in Eq. (4). The failure was most likely due to the improper choice of $s_1$, or of the composition of primordial Xe, especially in the estimation of fissiogenic $^{136}$Xe in the atmospheric Xe. The estimation of radiogenic $^{129}$Xe in the atmospheric Xe was made by comparing the atmospheric Xe with the primordial Xe (e.g.,
fractionated U-Xe), where the procedure is quite straightforward and there seems to be little ambiguity. However, the estimation of the nucleogenic \(^{136}\text{Xe}\) was made by a very complicated statistical analysis and involves a large uncertainty (Pepin and Phinney, 1978). If the failure in solving Eq.(4) is solely due to an error in the estimation of the fissiogenic \(^{136}\text{Xe}\), in order for Eq.(4) to yield a positive \(t_d\) the fraction of \(^{136}\text{Xe}\) in the atmospheric Xe should be smaller than 2%. In this regard it is interesting to note that Igarashi (1988) reestimated the fraction of the fissiogenic \(^{136}\text{Xe}\) in the atmospheric Xe with additional new data and a refined statistical method, and obtained a considerably smaller value of about 3% (compared to 4.7% in Pepin and Phinney (1978)) for the fissiogenic component. Because of the large uncertainty in the current estimation of primordial Xe composition, it would not be meaningful to exploit further the isotopic evolution equations. Here, we were content to note that the observed linear trend in Fig. 1 can be at least qualitatively understood in terms of an isochron nature, and that the mathematical formulation would offer a useful basis for a future quantitative discussion of mantle degassing.

*Origin of fissiogenic Xe in CO\(_2\) well gas*

All the above discussions indicated that the excess \(^{136}\text{Xe}\) in mantle derived materials is best explained by \(^{244}\text{Pu}\) fission. However, the origin of excess \(^{136}\text{Xe}\) in the CO\(_2\) well gas from Harding County, New Mexico appears to be quite different from those in the mantle derived materials. The excess \(^{131-136}\text{Xe}\) in the CO\(_2\) well gas are mostly due to \(^{238}\text{U}\) fission (Phinney *et al.*, 1978; Smith and Reynolds, 1981), which is understandable because of the storage in the crust where U is highly enriched. However, it appears to be difficult to attribute the excess \(^{129}\text{Xe}\) to a crustal origin. Since the CO\(_2\) well gas data are consistent with the Xe data in MORBs when plotted in correlation diagrams such as the \(^{20}\text{Ne}/^{22}\text{Ne}-^{21}\text{Ne}/^{22}\text{Ne}, ^{40}\text{Ar}/^{36}\text{Ar}-^{129}\text{Xe}/^{130}\text{Xe}, \) and \(^{136}\text{Xe}/^{130}\text{Xe}-^{129}\text{Xe}/^{130}\text{Xe}\) diagrams, Staudacher (1987) concluded that the excess Xe in the CO\(_2\) well gas must be of an upper mantle origin. On the contrary, Ozima *et al.* (1985) pointed out that since \((^{136}\text{Xe})_{\text{Pu}}/(^{129}\text{Xe})_1\) is smaller in the CO\(_2\) well gas Xe than in the atmospheric Xe, the CO\(_2\) well Xe cannot be related to the mantle source(s) from which the atmosphere was derived. They therefore ruled out the upper mantle origin of the CO\(_2\) well Xe.
Lately Caffee and Hudson (1987) suggested that $^{238}$U-derived fissionogenic $^{129}$I may account for the excess $^{129}$Xe in the CO$_2$ well gas, provided that the fissionogenic $^{129}$I (therefore $^{129}$I derived $^{129}$Xe) was enriched by a factor of 3000 over $^{238}$U fissionogenic Xe in the source. However, Musselwhite et al. (1989) showed experimentally that I is more incompatible than Xe, and concluded that $^{129}$I and hence its derived $^{129}$Xe could not be enriched, relative to the $^{238}$U-fissionogenic Xe in the mantle. However, in the crustal environment such a high degree of I enrichment, and therefore the enrichment of $^{129}$Xe as required for the observed excess $^{129}$Xe may be possible. For example, Srinivasan et al. (1971) found that the iodrite (AgI) of Tertiary age (minimum age) contained about $2 \times 10^{-13}$ cm$^3$/g of radiogenic $^{129}$Xe as well as $^{238}$U-fissionogenic Xe, where the excess $^{129}$Xe is undoubtedly of an in-situ radiogenic origin, but not of a mantle origin. Also some brines are known to be enormously enriched in I (up to 100 ppm) (Greenwood and Earnshaw, 1984). If I in the brine was mainly derived from igneous regions which have an equilibrium ratio of $^{129}$I/$^{127}$I = 5 $\times$ 10$^{-12}$ (Fabryka-Martin et al., 1985), we would have about $5 \times 10^{-16}$ g/g-brine of $^{129}$I, which will produce about $10^{-13}$ cm$^3$/g-brine of $^{129}$Xe for a few ten Ma, being enough to account for the observed excess $^{129}$Xe in the CO$_2$ well gas. Since thermal brine is likely to take a major role in accumulating volatiles (including CO$_2$) in the crust, it would be reasonable to suppose that the excess $^{129}$Xe as well as the excess $^{136}$Xe in the CO$_2$ well gas are of a $^{238}$U fission origin, both being produced in the crust from the fission of $^{238}$U.

The agreement of CO$_2$ well Xe with MORB Xe data in the $^{136}$Xe/$^{130}$Xe-$^{129}$Xe/$^{130}$Xe correlation plot, which has been taken as an evidence of the mantle origin of the former by Staudacher (1987), must then be regarded to be fortuitous. In support of this view, we note that CO$_2$ well gas Xe from Colorado and Australia which show excess in Xe$^{129}$ and Xe$^{136}$ (Caffee et al., 1988) do not conform to the linear trend in Fig. 1. From all these evidences we conclude that the excess $^{129}$Xe as well as the excess $^{136}$Xe in the CO$_2$ well gas was derived from $^{238}$U in the crust.

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