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Key Points:
- Xe isotopes of MORB could be consistent with chondritic Pu/U
- We reconcile MORB Xe with a model requiring no major, early degassing
- More work needs to be done before MORB Xe can be uniquely interpreted

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Xenon isotopes in the MORB source, not distinctive of early global degassing

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Abstract Although fissiogenic Xe in mid-ocean ridge basalt (MORB) has long been used inferred to infer an early (>4 Ga) catastrophic mantle degassing, decomposition of the analyzed gas in terms of its constituents requires several assumptions. The canonical interpretation has not been tested using the full spectrum of possible initial components and radiogenic inputs. We use a Markov chain Monte Carlo approach that examines a broad range of Xe isotopic components present during Earth formation and evolution. Our best fit simulations are consistent with the preservation of much higher Pu/U in MORB source Xe than previously recognized but are equally supportive of both limited and early catastrophic loss. We show that an initially Xe depleted upper mantle that becomes progressively ingassed through both radiogenic ingrowth and subduction of evolving atmospheric Xe is equally consistent with all evidence, underscoring the need for improvements to our knowledge of fission Xe spectra, MORB Xe measurements, and Pu geochemistry.

1. Introduction

Terrestrial noble gas systematics have long been used to infer conditions pertaining to the formation and evolution of Earth's mantle and atmosphere [e.g., *Staudacher and Allegre*, 1982]. Such studies are of two broad types: using noble gas elemental ratios to infer accretionary and evolutionary mechanisms and the use of isotopic variations as a record of ancient fractionation processes. Despite the generally inert nature of noble gases, their elemental ratios are affected by numerous processes, including differential degassing due to contrasting solubility/partitioning/kinetic effects [e.g., *Burnard*, 2004; *Weston et al.*, 2015]. Since these processes can depend on the specifics of melting and eruption mechanisms at mid-ocean ridges and ocean islands, secular effects (e.g., changes in the degree of mantle melting over Earth history) make drawing inferences about long-term behavior difficult [*Keller and Schoene*, 2012]. This multiplicity of possible interactions is further complicated by several contradictory observations. For example, there is experimental evidence for Ar being either incompatible [e.g., *Heber et al.*, 2007] or compatible [*Watson et al.*, 2007] in mantle phases, and some experiments and/or model calculations suggest surprising behaviors not typically assumed in modeling studies (e.g., Xe alloying with Fe in the core [*Lee and Steinle-Neumann*, 2006], Xe compatibility in olivine exceeding Ar at >2 GPa [*Sanloup et al.*, 2011], and Xe solubility of several percent in quartz under lower crustal conditions [*Sanloup et al.*, 2005]). The recognition of primordial ^{3}He loss from the mantle [*Lupton and Craig*, 1975] led some workers to infer the existence of layered mantle convection [e.g., *Kurz et al.*, 1982]. However, higher ^{3}He fluxes recently proposed appear to reconcile many noble gas systematics with whole mantle convection [*Ballentine et al.*, 2002]. Given the many ambiguities described above, the paucity of experiments documenting noble gas behavior at high pressures, the largely unknown kinetic parameters, and the disparate estimates of mid-ocean ridge basalt (MORB) source ^{3}He/^{22}Ne of (i.e., >10 [*Tucker and Mukhopadhyay*, 2014] and <4.4 [*Weston et al.*, 2015]), interpreting the relative and absolute abundances of terrestrial noble gases in terms of planetary processes remains fraught.

Restricting our attention instead to the isotopic composition of Xe, with its numerous (nine) nuclides and assumed resistance to planetary loss, has advantages over the use of elemental ratios. Despite these favorable characteristics, their meaning in terms of the formation and evolution of Earth's atmosphere and mantle is hotly debated [e.g., *Bernatowicz and Podosek*, 1978; *Marty*, 2012; *Owen et al.*, 1992; *Pepin*, 2006; *Porcelli and Ballentine*, 2002; *Pujol et al.*, 2011]. Much of this controversy, however, reflects different underlying assumptions rather than intrinsic limitations to the isotopic system.

In a seminal work, *Staudacher and Allegre* [1982] proposed that Xe in the modern atmosphere arises from upper mantle outgassing with the fissiogenic Xe component dominated by ^{244}Pu-derived isotopes. This view was challenged by several workers [e.g., *Porcelli and Ballentine*, 2002] on the basis that numerical decompositions of upper mantle-derived Xe (assuming the presence of atmospheric, fissiogenic, planetary, or solar components) indicate that ^{238}U-fission Xe (effective $t_{½} \approx 4.4$ Ga) is the dominant progenitor and thus MORB Xe cannot be the residue of atmospheric outgassing. This observation necessitated the introduction of models that either do not completely derive the atmosphere from the upper mantle [e.g., *Dauphas*, 2003] or require evolution of the upper mantle composition by addition of Xe from a deep mantle reservoir [e.g., *Porcelli and Ballentine*, 2002]. However, Xe from >1 Ga diamonds [*Ozima and Zashu*, 1991] and Hadean zircons [*Turner et al.*, 2004, 2007] provide ample evidence for ^{244}Pu-derived Xe (effective $t_{½} \approx 80$ Ma) and chondritic (i.e., 0.007 [*Hudson et al.*, 1989]) Pu/U in the early solar system and Earth. Previous investigations have demonstrated the existence of a significant primitive component (e.g., solar wind) in terrestrial Xe [*Caffee et al.*, 1999]. Based on Pb isotopes, *Elliott et al.* [1999] argued that U has been added to the MORB source over geologic time. This view is supported by analyses of U isotopes of MORB samples which are interpreted to indicate that its source was pervasively contaminated by <2.4 Ga addition of U [*Andersen et al.*, 2014]. When compounded by the essentially unknown geochemical behavior of Pu on early Earth, inferences of early mantle Pu/U from active MORB degassing are highly uncertain.

Previous statistical decompositions of upper mantle Xe have assumed that the totality of nonradiogenic Xe comes from atmospheric Xe [*Ozima et al.*, 1985; *Staudacher and Allegre*, 1982] or that there is only a single primordial component (e.g., solar wind-derived Xe [*Pepin and Porcelli*, 2006]). These assumptions ignore the variety of possible "planetary" Xe compositions that could have been inherited during accretion, such as Q-Xe [*Wieler*, 1994]. Indeed, most meteorites are seen to contain a mixture of primary Xe components (e.g., AVCC [*Eugster et al.*, 1967]) so it is difficult to conceive of a scenario in which Earth-forming materials contained but a single component. In this work we utilize all nine stable isotopes of Xe in an improved statistical framework to not only ascertain the relative radioactive decay contributions to terrestrial Xe but also to determine the time-varying input of nonradiogenic Xe components.

2. Method

2.1. Xenon Components

As published analyses of all nine Xe isotopes in MORB samples are rare, we focus only on the most recent of these measurements [*Kunz et al.*, 1998; cf. *Tucker et al.*, 2012]. We take advantage of *Pepin and Porcelli*'s [2006] detailed analysis of the *Kunz et al.*'s [1998] data by using their MORB 1 composition for modeling purposes (note that using their MORB 2 values does not significantly influence our results). Our choice of additional possible contributing components includes air (i.e., modern atmospheric Xe [*Basford et al.*, 1973]), solar wind [*Meshik et al.*, 2014], Q-Xe [*Wieler*, 1994], ^{238}U spontaneous fission [*Wetherill*, 1953], ^{244}Pu spontaneous fission [*Hudson et al.*, 1989], and ^{129}Xe produced from the decay of ^{129}I ($t_{½} \approx 16$ Ma [*Jeffery and Reynolds*, 1961]).

While several of these components are standard choices for Xe isotope decompositions [e.g., *Pepin and Porcelli*, 2006; *Caffee et al.*, 1999], this is the first work to our knowledge that investigates the presence of a wider spectrum of possible primordial Xe inputs. While *Mukhopadhyay* [2012] tested for the presence of AVCC, this only allows a fixed SW-Xe/Q-Xe rather than the full range (i.e., it assumes that carbonaceous chondrites are representative rather than allowing for different mixtures of Q and SW-Xe). For example, adding Q-Xe tests for the possible presence of primordial noble gases from meteoritic sources rather than assuming an underlying composition of solar wind Xe (SW-Xe) or the hypothetical U-Xe [*Pepin and Phinney*, 1978].

2.2. Computational Method

We utilize a Bayesian approach, calculated through a Markov chain Monte Carlo (MCMC), to search for a best fit of the *Kunz et al.*'s [1998] MORB Xe isotopic data to the various possible Xe components. This approach permits efficient exploration of the full posterior probability distribution (i.e., the solution). In order to calculate the fit to a proposed composition, we treat each component as a vector and seek to construct a component by multiplying each component by a real positive weight and summing them together by

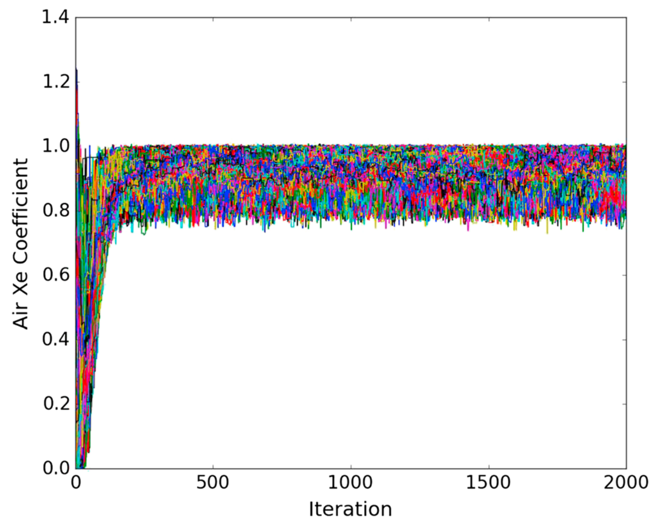

Figure 1. We plot the fractional contribution of Air Xe on ^{130}Xe for each walker in each iteration. After 200 iterations, the value remains between 0.8 and 1, suggesting that between 80% and 100% of ^{130}Xe is derived from atmospheric Xe. This steady range shows that after 200 iterations, the algorithm has converged to a stationary state.

$Xe_{\mathrm{Guess}} = \sum w_i \times Xe_i$. This summed component is then compared to MORB Xe by evaluating the error-weighted square of the difference for each isotope (i.e., the log likelihood function for normal errors).

Given that the Xe spectra of several of our components are highly correlated (e.g., ^{244}Pu- and ^{238}U-derived Xe [*Caffee et al.*, 1999]), a concern is that a standard optimization (e.g., gradient descent) routine could yield erroneous parameters and uncertainties. A further issue potentially affecting previous decompositions is that they may have multiple local minima in which an optimization algorithm could become trapped (e.g., the Microsoft Excel SOLVER routine utilized by *Pepin and Porcelli* [2006]). It is also not possible to take the output from standard optimization routines to calculate uncertainties. A Bayesian statistical approach uses a prior distribution with the maximum likelihood to produce a posterior distribution. In other words, we start with a prior distribution consisting of probabilities for the value of each xenon component in MORB, which is then updated by evaluating goodness of fit of each possible permutation of the available source components. A basic Markov chain Monte Carlo is a biased random walk through the parameter space where new solutions are proposed based on a proposal distribution (Metropolis-Hastings algorithm [*Hasting*, 1970]). This proposal distribution is usually a multivariate normal distribution with the number of free parameters corresponding to the square of the dimensional space which need to be set to allow for efficient exploration of the posterior distribution (inappropriate proposal distributions delay convergence of the algorithm). Therefore, instead of attempting to tune the 6^2 free parameters we chose to use a more complicated MCMC algorithm. Additionally, given our concerns about the structure of the solution space (i.e., the posterior distribution), we utilize an affine-invariant ensemble sampler [*Goodman and Weare*, 2010] as it is known to be insensitive to highly correlated inputs. An explanation of this algorithm is beyond the scope of this paper, but an excellent introduction is given by *Foreman-Mackey et al.* [2012]. Specifically, we employ 6000 "walkers" [*Goodman and Weare*, 2010] and 2000 iterations, with the first 1000 iterations being discarded as "burn-in" (Figure 1).

Since we are using a Bayesian approach to analysis of MORB Xe data, we need to select a plausible prior distribution so as not to bias our results. For this purpose, we chose a prior distribution that constrains the possible solutions to having positive coefficients. This limitation is simply to prevent unphysical solutions. For example, it is impossible to preferentially remove a Xe component from a reservoir (e.g., to subtract U-fission Xe from the MORB source).

We implemented the model in Python version 3.4.2 and uses numpy [*Van Der Walt et al.*, 2011] for the array structure and mathematical functions. We used the affine-invariant ensemble sampler implemented in Python by *Foreman-Mackey et al.* [2012].

3. Results

Before discussing our results in detail, we first demonstrate the convergence of our sampler to a stable posterior distribution. We do this by plotting the value of the air component as a function of iteration for each walker (Figure 1). This value is expected to be >0.8 due to pervasive air contamination (or subduction of air Xe), and indeed, after ~200 iterations, the solutions converge. A MCMC sampler that has reached the stationary distribution cannot exit from that distribution; therefore, more iterations only increase the computation time but introduce no bias.

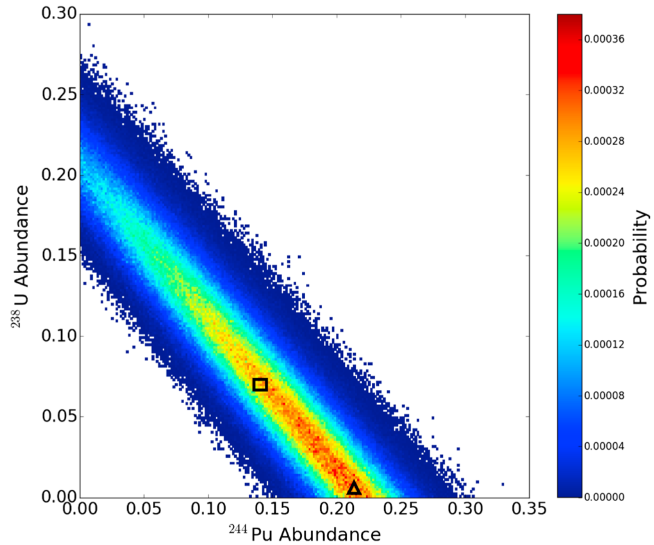

Figure 2. We show the fractional contribution on ^{136}Xe from ^{244}Pu-Xe and ^{238}U-Xe. Note the good negative correlation. The majority of solutions suggest higher Pu/U than previously inferred for the MORB source. The solutions with approximately chondritic Pu/U do not require a catastrophic early degassing and are instead consistent with a closed system mantle evolution (i.e., they do not require loss of Xe from the MORB source). The open triangle shows the solutions that are consistent with chondritic Pu/U, while the open rectangle shows a solution which requires catastrophic, early degassing.

Our primary interest is to examine the range of possible solutions for the contribution of ^{244}Pu and ^{238}U fission-derived Xe. We find that the posterior distribution for the *Kunz et al.*'s [1998] MORB data cannot uniquely resolve the relative abundances of ^{244}Pu and ^{238}U (Figure 2). Our solutions tend to cluster closer to high ^{244}Pu than high ^{238}U, whereas the canonical view is that MORB is best fit by low ^{244}Pu solutions [e.g., *Kunz et al.*, 1998]. We emphasize that we cannot uniquely identify the time-integrated ^{244}Pu/^{238}U ratio due to a lack of resolution stemming from the fact that the underlying components make up $>95\%$ of the MORB signal (air alone is on average $>80\%$) (Figure 1). As shown in Figure 3, a robust identification of extraterrestrial Xe is possible while its detailed nature (i.e., Q-Xe, SW-Xe, or both) is not. There is no correlation between the inferred Pu/U and the proportion of Q-Xe to SW-Xe, the variation results from the large uncertainties present in each component. The fact that a unique decomposition is not achieved is not surprising as various components (e.g., ^{244}Pu- and ^{238}U-derived Xe) are highly correlated (Figure 4).

4. Discussion

4.1. Dating Mantle Closure

Xenon isotope decompositions of MORB have long been used to infer a closure age (i.e., the effective time of isolation of mantle Xe from an atmospheric reservoir) for the upper mantle [e.g., *Staudacher and Allegre*, 1982; *Kunz et al.*, 1998] or used in more extensive geochemical modeling [e.g., *Tolstikhin et al.*, 2013]. These models make use of the fact that the apparent Pu/U derived from MORB source Xe is lower than that of a chondritic reservoir and thus would appear to require an early large-scale degassing event to remove ^{244}Pu derived Xe shortly after Earth accretion. We note that our arguments extend to the ^{129}I-Xe story as any loss inferred from ^{129}I-derived Xe necessitates preferential removal of ^{244}Pu, thus lowering the inferred Pu/U. As we previously noted, the accuracy of these calculations depends on the specifics of the deconvolution. Contrary to previous models, our results show that the fraction of ^{136}Xe in MORB Xe derived from ^{244}Pu is broadly consistent with either a

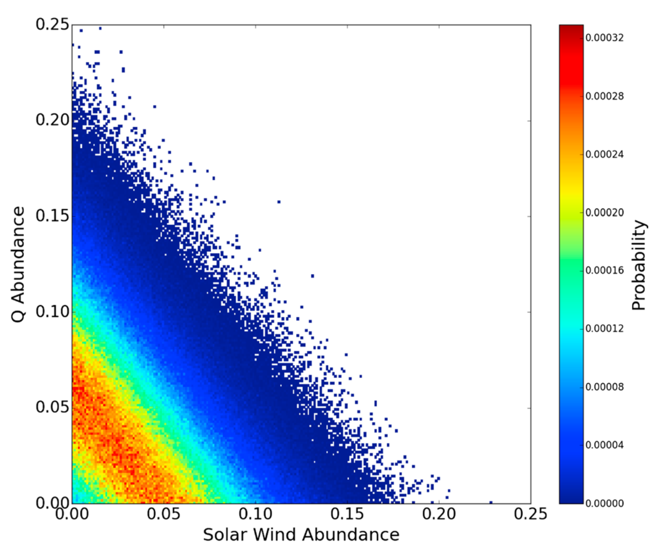

Figure 3. The contribution of SW Xe and Q-Xe on ^{130}Xe. The primordial components are generally $<20\%$ of the ^{130}Xe, and there is a negative correlation between the abundances of SW Xe and Q-Xe.

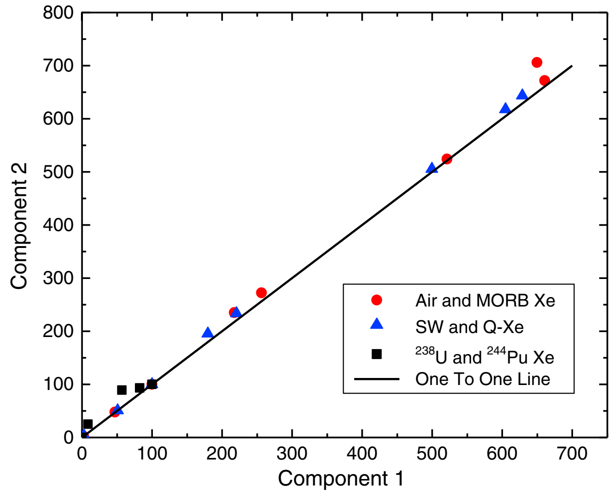

Figure 4. The correlation between Air Xe and MORB Xe, SW Xe and Q-Xe, and ^{238}U Xe and ^{244}Pu Xe. That is, for each data series, the *x* values are isotope ratios from the first listed component and the *y* values from the second (e.g., one point would be the ^{124}Xe/^{130}Xe from MORB and air and another would be the ^{126}Xe/^{130}Xe). Note that most of these pairs fall very close to a slope one line indicating their high correlation. This makes unique decompositions very difficult as the highly correlated nature of these components would require analyses far more precise to make unique interpretations.

chondritic reservoir following 4.57 Ga of closed system evolution (Figure 2) or one that experienced an early (>4 Ga) catastrophic outgassing. This range of possible relative ^{244}Pu abundances would appear to preclude accurate I-Pu-Xe dating of Earth's mantle/atmosphere until more precise measurements are available.

4.2. Ancient Atmosphere or Solar?

Pujol et al. [2011] proposed that atmospheric Xe evolved by photoionization-assisted fractionation from an original solar wind composition slowly over geologic time. Since the claim of *Pujol et al.* [2011] can be modeled by mixing SW-Xe and air-Xe, we do not need to explicitly include it in our modeling. Given the possibility of adding Xe back into the mantle through subduction [*Holland and Ballentine*, 2006], we have to consider the influence of a changing atmospheric Xe isotope composition to our model interpretations. If all the inferred SW-Xe in MORB gases represent ancient subducted atmosphere, this would imply an initially Xe free upper mantle (i.e., the atmosphere ingassed to the mantle). Since we identify relatively minor amounts of SW-Xe or Q-Xe (<20% of ^{130}Xe) in our calculations, we infer that the subducted Xe signal present is largely overwhelmed by (presumably shallow) air contamination. While *Holland and Ballentine* [2006] suggested that as much as 80% of Xe in the upper mantle could be derived via subduction (the remaining 20% being primordial SW-Xe), both the results of *Pujol et al.* [2011] and our decompositions are consistent with all nonradiogenic Xe in the upper mantle resulting from subduction recycling. It is more likely that the primordial Xe is SW-Xe rather than Q-Xe because Ne isotopes suggest solar Ne rather than planetary Ne [*Honda et al.*, 1991]. The relation of Ne to Xe does not need to strictly be preserved throughout geologic time. For our argument to hold, they simply need to have a similar origin. This finding is independent of the whether or not the mantle was outgassed early during a giant impact (i.e., it has no bearing on the Pu/U inferred from MORB Xe systematics).

4.3. Atmosphere From Degassing Mantle?

Since our decomposition returns a primordial component (SW and Q-Xe) with additional radiogenic Xe, it is entirely plausible that the mantle and atmosphere both evolved from the same primordial composition or that the atmosphere was delivered by planetesimals and meteorites [e.g., *Holland et al.*, 2009]. It is possible that the atmosphere also formed from the initial Xe of the mantle (e.g., SW-Xe) and subsequently evolved [*Pujol et al.*, 2011]. The argument of *Porcelli and Ballentine* [2002] that MORB Xe cannot be the residue of atmospheric outgassing relies on finding decompositions of MORB Xe that have a significant ^{238}U-derived Xe component. Our findings contrast with this model and require virtually no correction to the value of MORB due to ^{238}U-Xe, thus staying in the realm of possible residue compositions following atmospheric degassing (Figure 5 in *Porcelli and Ballentine* [2002]). However, since the modern atmosphere is thought to contain more Xe than the upper mantle [*Staudacher and Allegre*, 1982], any major degassing of the mantle to form the atmosphere would require that the MORB source have a low time-integrated Pu/U (which is seemingly at odds with our Figure 2).

4.4. End-Member Models

Since we are not able to ascertain whether or not MORB Xe is uniquely consistent with chondritic Pu/U, we are left considering the full range of histories, from early catastrophic degassing to relatively little Xe loss. We propose a new model for MORB Xe in which an early mantle stripped of Xe by core formation [*Lee and Steinle-Neumann*, 2006] is ingassed over time through subduction of sediments containing atmospheric Xe [*Holland and Ballentine*, 2006]. The atmosphere receives volatiles via meteorite or cometary delivery after the bulk of accretion is concluded [e.g., *Holland et al.*, 2009] and slowly evolves by processes including photoionization [*Pujol et al.*, 2011] with relatively minor loss from the MORB source. While this scenario is consistent with our results, it stands in stark contrast to the canonical view, in which early catastrophic degassing is required to produce an apparently ^{244}Pu-Xe-poor (i.e., low Pu/U) mantle. Fits between model results and Xe isotopes suggesting early degassing [e.g., *Avice and Marty*, 2014] may be more apparent than real; tuning models to match the data is not equivalent to having an independent physical model describing noble gas behavior given these conditions. While the canonical model has the appealing implication that the timing of the last major Xe loss event can be dated, our results equally well explain the Xe data without invoking major planetary processes for which there is little or no independent confirmation. We wish to note that we are not proposing this model to resolve all outstanding issues in xenology. Rather, we wish to highlight the remarkable range of interpretations that are consistent with decompositions of MORB-Xe. Challenges to our model on the basis of terrestrial ^{40}Ar systematics are difficult due to the wide range of mantle K abundance estimates [*Lyubetskaya and Korenaga*, 2007; *Palme and O'Neill*, 2003] and the poorly known partition behavior of Ar.

4.5. Non–Chondritic Pu/U?

Lead isotopes in MORB samples have been used to infer a lower integrated Th/U than that measured from elemental abundances—one of the so-called "Pb paradoxes" [*Allegre et al.*, 1980]. *Elliott et al.* [1999] explained this as resulting from subduction addition of U to the MORB source following oxidation of the atmosphere. A consequence of this would be that MORB Xe would have a somewhat lower Pu/U than chondritic due to the proposed twofold increase in U in the MORB source since ~2.5 Ga. Given that Pu is long extinct, we assume for the moment that Nd is a sufficiently close analog [e.g., *Lugmair and Marti*, 1977]. A compilation of partition coefficients (GERM database) indicates that Nd is more compatible in feldspars than U and less in olivine. That Pu preferentially partitions into crustal reservoirs relative to U permits an alternate interpretation for model solutions that yield an apparently subchondritic Pu/U. For example, fractionation during magma ocean crystallization or formation of a plagioclase floatation crust [*Warren*, 1989] would result in a low Pu/U depleted mantle. This suggests that recognition of a slightly lower than chondritic Pu/U inferred from the MORB source does not necessarily require an early catastrophic outgassing of mantle Xe.

Our intent here is not to argue strongly for our alternate model, which remains highly speculative, but to instead draw attention to the nonunique nature of models that conclude that fission Xe isotopes require an early, catastrophic degassing. More precise Xe isotopic data and future investigations to better understand the geochemical behavior of Pu are needed to rigorously test the competing models for terrestrial Xe isotopic evolution.

5. Conclusion

Our multicomponent decompositions of MORB Xe isotopic data support the presence of primordial Xe [e.g., *Caffee et al.*, 1999]. If this primordial component is SW Xe, it could be the result of Xe subduction through geologic time rather than reflecting a true primordial signal. Given the uncertainty in both the underlying composition and the similarity of fission Xe spectra derived from ^{238}U and ^{244}Pu, we find no unambiguous support for the occurrence of an early catastrophic outgassing of Xe. Instead, we reconcile the Xe isotope systematics of MORB with a new model that suggests an initially Xe-depleted mantle that did not experience catastrophic degassing followed by subduction replenishment. Future work is required to better constrain the fission spectra of U and Pu and the Xe isotopic composition of MORB. Even then, the effects of photoionized Xe loss [*Pujol et al.*, 2011], the alloying of Fe and Xe at core conditions [*Lee and Steinle-Neumann*, 2006], and the formation of Xe-O bonds at high pressures will need to be better understood before we can draw unique inferences about Earth evolution from Xe isotopes.

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