



**HAL**  
open science

## Resolving atmospheric contaminants in mantle noble gas analyses

D. Harrison, P. G. Burnard, M. Trieloff, G. Turner

► **To cite this version:**

D. Harrison, P. G. Burnard, M. Trieloff, G. Turner. Resolving atmospheric contaminants in mantle noble gas analyses. *Geochemistry, Geophysics, Geosystems*, 2003, 4, <10.1029/2002GC000325>. <insu-03619224>

**HAL Id: insu-03619224**

**<https://insu.hal.science/insu-03619224v1>**

Submitted on 25 Mar 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Copyright - All rights reserved



## Resolving atmospheric contaminants in mantle noble gas analyses

**D. Harrison**

*Department of Earth Sciences, University of Manchester, Manchester, M13 9PL, UK*

*Now at Institute for Isotope Geology and Mineral Resources, Department of Earth Sciences, ETH Zentrum, Sonneggstrasse 5, CH-8092, Zurich, Switzerland (harrison@erdw.ethz.ch)*

**P. G. Burnard**

*Division of Geological and Planetary Sciences, California Institute of Technology, MS100-23, Pasadena, California 91125, USA*

*Now at Centre de Recherches Pétrographiques et Géochimiques (CRPG-CNRS), 15 rue Notre Dame des Pauvres, B. P. 20, 54501 Vandoeuvre-les-Nancy Cedex, France (peteb@crpg.cnrs-nancy.fr)*

**M. Trieloff**

*Mineralogisches Institut, Universität Heidelberg, Im Neuenheimer Feld 236, D-69120 Heidelberg, Germany (trieloff@min.uni-heidelberg.de)*

**G. Turner**

*Department of Earth Sciences, University of Manchester, Manchester, M13 9PL, UK (grenville.turner@man.ac.uk)*

[1] As part of an ongoing initiative to constrain mantle noble gas budgets, we evaluate both recently published high-quality noble gas data and report new data in order to rationalize the use of three-dimensional (3-D) modeling techniques. Modeling of these data shows that traditional 2-D mixing plots are not adequate tools to fully constrain mixing systems and mantle end-member compositions. We show that these mantle noble gas analyses are compromised to varying degrees by the addition of a fractionated atmospheric contaminant, irrespective of eruption setting. This component can also be present in analyses with mantle-like neon or argon isotope ratios. Previous estimates for the mantle end-member  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  compositions of most of these samples are likely to be minimum values. In fact it may well be that there are no analyses in the present literature that have completely unadulterated mantle volatiles present.

**Components:** 7103 words, 4 figures, 3 animations.

**Keywords:** atmospheric contamination; mantle; noble gases.

**Index Terms:** 1025 Geochemistry: Composition of the mantle; 1040 Geochemistry: Isotopic composition/chemistry.

**Received** 6 February 2002; **Revised** 26 June 2002; **Accepted** 9 August 2002; **Published** 7 March 2003.

Harrison, D., P. G. Burnard, M. Trieloff, and G. Turner, Resolving atmospheric contaminants in mantle noble gas analyses, *Geochem. Geophys. Geosyst.*, 4(3), 1023, doi:10.1029/2002GC000325, 2003.

## 1. Introduction

[2] The Earth's interior contains primordial noble gases, particularly solar-type helium and neon that are isotopically different from atmospheric or crustal compositions [Clarke *et al.*, 1969; Sarda *et al.*, 1988; Honda *et al.*, 1991; Valbracht *et al.*, 1997; Harrison *et al.*, 1999]. Mantle-derived samples also contain excesses of radiogenic noble gases relative to the atmosphere indicating massive mantle degassing early in Earth's history [Allègre *et al.*, 1986; Turner, 1989; Tolstikhin and O'Nions, 1994]. Mantle degassing is an ongoing process, and the present-day terrestrial heat flow budget implies that radiogenic  $^4\text{He}$  is being produced from the decay of (U + Th) in the mantle at  $\sim 20$  times the rate at which it is emerging from oceanic ridges [O'Nions and Oxburgh, 1983]. This He-Heat paradox is most easily reconciled with models of a degassed convecting upper mantle which loses radiogenic heat and volatiles efficiently but which is chemically isolated from a deeper mantle reservoir from which  $\sim 90\%$  of the terrestrial heat flux is derived. Furthermore, the noble gas isotope data currently available supports this observation by identifying separate reservoirs within sections of the mantle that have different time-integrated parent/noble gas daughter ratios (e.g.,  $^{40}\text{K}/\text{Ar}$ , U + Th/He, and U + Th/Ne) and that have remained isolated for long periods of time. In particular, the He and Ne isotopic compositions of mantle-derived rocks demonstrate that some ocean islands and seamount chains (OIB) sample a more primitive region of the mantle than the majority of basalts which erupt at mid-ocean ridges (MORB) [Sarda *et al.*, 1988; Staudacher *et al.*, 1989; Valbracht *et al.*, 1997; Harrison *et al.*, 1999]. Noble gas geochemistry is central to the classical concept of a primordial component in the mantle [Allègre *et al.*, 1986; Sarda *et al.*, 1988; Honda *et al.*, 1993; Moreira *et al.*, 1995, 2001; Porcelli and Wasserburg, 1995a, 1995b; Honda and McDougall, 1997; Niedermann *et al.*, 1997].

[3] However, deconvolving mantle volatile signatures from atmospheric contaminants, in sample analyses is notoriously difficult but of utmost importance to understanding the heavy noble gas

isotopic compositions of mantle-derived samples. For example,  $^{129}\text{Xe}$  excesses (over and above the atmosphere) have only been measured in three plume-related sample sets [Poreda and Farley, 1992; Harrison *et al.*, 1999; Trieloff *et al.*, 2000] owing to atmospheric overprints obscuring the mantle signature [Patterson *et al.*, 1990] despite predictions by steady state models of the mantle that excess  $^{129}\text{Xe}$  is present in the plume mantle source region.

[4] In this report we show how four isotopes plotted on three axes can be used to deconvolve mixtures of air and mantle noble gases. The three-axis discrimination plots are used to evaluate previously published noble gas data from two hot spot localities, Iceland and Loihi, and a MORB sample. We also report new step-crushing data for an Icelandic glass sample, Dice 10. Dice 10 has been the subject of a number of studies [Harrison *et al.*, 1999; Ballentine and Barfod, 2000; Trieloff *et al.*, 2000]; similar samples were analyzed by Dixon *et al.* [2000] and Moreira *et al.* [2001]. The original study of this sample [Harrison *et al.*, 1999] appears to have overestimated  $^{21}\text{Ne}/^{22}\text{Ne}$  in comparison to data from two other laboratories (Trieloff *et al.* [2000] and data presented in Table 1). Although all other compositions compare favorably with the repeat analyses of the samples, the Ne isotope measurements of Dice 10 and Dice 11 reported by Harrison *et al.* [1999] have been compromised and should not be used. The cause of the  $^{21}\text{Ne}$  overestimate in the original study is likely due to a mixture of issues: the mass spectrometer was exposed to a  $^{21}\text{Ne}$ -enriched "spike" in an earlier life; not separating Ne from He; and a Ne sensitivity that was only just adequate to measure  $^{21}\text{Ne}$ . Note, however, that separation of He from Ne is traditionally done because noble gas labs calibrate  $^3\text{He}/^4\text{He}$  using an air pipette; air has a very high Ne/He ratio, consequently there is a pressure effect from neon on helium during these calibrations, not because of any potential effect on the Ne isotope measurements. During the study by Harrison *et al.* [1999] calibrations were made using an artificial gas standard with Ne/He ratios similar to the samples being analyzed. However, the quoted errors on these original data reflect all these problems.

## 2. Fractionating Mantle Noble Gases

[5] As well as overprinting by atmospheric contamination, mantle noble gas signatures may be modified by elemental fractionation during magma ascent by posteruptive diffusive loss from the sample, particularly of He and by shallow-level crustal contamination by radiogenic nuclides, principally  $^4\text{He}$  [Hilton *et al.*, 1995; Marty and Zimmermann, 1999]. Degassing of a silicate melt during ascent from the mantle fractionates the noble gases according to their relative solubilities (solubility decreases with increasing atomic mass) [Lux, 1987; Carroll and Webster, 1994]. However, it is possible to predict the likely  $(^4\text{He}/^{40}\text{Ar})_r$ ,  $(^{21}\text{Ne}/^{40}\text{Ar})_r$ , and  $(^{21}\text{Ne}/^4\text{He})_r$  ratios in a mantle source region based on estimates of mantle K, U + Th compositions, and nucleogenic  $^{21}\text{Ne}$  yields (subscript “r” indicates an isotope production ratio). These predicted ratios can be used to quantify the degree of fractionation (equilibrium or kinetic) in any given analysis, provided the production ratios are constant. A mantle reservoir isolated for 4Ga will have an accumulated  $(^4\text{He}/^{40}\text{Ar})_r$  of  $\approx 2$  ( $\text{K}/\text{U} = 12,700$ ,  $\text{Th}/\text{U} = 2.6$ ), whereas mantle isolated 1 Ga ago will result in an accumulated  $(^4\text{He}/^{40}\text{Ar})_r$  of  $\approx 4$  for the same K/U and Th/U [Ozima and Podosek, 1983; Allègre *et al.*, 1986; Burnard *et al.*, 1997a]. Nucleogenic  $^{21}\text{Ne}$  is largely produced from  $^{18}\text{O}$  and  $^{24}\text{Mg}$  target nuclei, which are homogeneously distributed in the mantle. As a result, the rate of  $^{21}\text{Ne}$  production in the mantle is determined by U + Th concentrations, as is  $^4\text{He}$  production. The most recent estimate of the  $(^{21}\text{Ne}/^4\text{He})_r$  production ratio is  $4.5 \times 10^{-8}$  [Yatsevich and Honda, 1997; Leya and Wieler, 1999]. Combining the predicted range in  $(^4\text{He}/^{40}\text{Ar})_r$  and the most recent  $(^{21}\text{Ne}/^4\text{He})_r$  production estimate gives a  $(^{21}\text{Ne}/^{40}\text{Ar})_r$  of between  $9 \times 10^{-8}$  to  $1.8 \times 10^{-7}$ .

[6] The radiogenic and nucleogenic isotopes of He, Ne and Ar are powerful tools for tracing mantle processes. The  $(^{21}\text{Ne}/^4\text{He})_r$  ratio is not affected by mantle chemistry and traces recent gas fractionation, while the  $(^4\text{He}/^{40}\text{Ar})_r$  and  $(^{21}\text{Ne}/^{40}\text{Ar})_r$  ratios are in addition a function of time and of mantle chemistry. In combination these ratios can be used

to identify samples containing unfractionated mantle gases and otherwise an estimation of the degree of, and processes controlling fractionation [Honda and Patterson, 1999; Marty and Zimmermann, 1999; Moreira and Sarda, 2000; Sarda and Moreira, 2002].

[7] Irrespective of fractionation processes, a seemingly ubiquitous atmosphere-derived contaminant (ADC) clouds the mantle isotopic signatures of Ne, Ar, and Xe such that noble gas analyses appear to be mixtures of mantle and atmospheric derived gases [Patterson *et al.*, 1990; Farley and Poreda, 1993; Burnard *et al.*, 1997b; Fisher, 1997; Valbracht *et al.*, 1997; Moreira *et al.*, 1998; Burnard, 1999; Harrison *et al.*, 1999; Ballentine and Barfod, 2000]. Atmospheric noble gases invade the analyzed gases in a number of ways, for example, magma interaction with surface equilibrated fluids can contaminate vesicle-trapped gases; posteruptive adsorption onto the sample surface; adsorption of atmospheric gases in the extraction system; air-filled microfractures created during sample collection and preparation [Ballentine and Barfod, 2000]. Heating at up to  $150^\circ\text{C}$  for several hours prior to analysis is insufficient to remove this contaminant. Helium is largely immune to these problems owing to its low abundance in the atmosphere.

## 3. Samples, Experimental Techniques, and Results

[8] Table 1 summarizes our new data for Dice 10, including  $\text{CO}_2$  contents. Sample descriptions have been reported elsewhere [Harrison *et al.*, 1999]. Previously reported data for Iceland, Loihi, and MORB are described in the following sections. Dice 10 was reanalyzed at the Division of Geological and Planetary Sciences, California Institute of Technology (Caltech) using the following procedures. Glassy rinds of the DICE pillows were gently broken up to about 5–8 mm diameter chunks (the largest that would fit in the crushing apparatus). Between four and six chunks were ultrasonically cleaned in dilute  $\text{HNO}_3$  followed by several washes with water and ethanol, then loaded into online crushing devices essentially the same as those described by Burnard *et al.* [1992].

The samples were baked under ultrahigh vacuum for  $\sim 6$  hours at  $120^\circ\text{C}$  then pumped at room temperature for a further 18 hours to remove surficial contaminants.

[9] The samples were analyzed by sequential crushing in the Caltech noble gas lab. The isotopes and abundances of He and Ne were measured on a MAP 215-50 noble gas mass spectrometer and Ar on a modified Nuclide 12 cm  $90^\circ$  instrument. The gases were purified using two SAES NP10 Zr-Al getters (one at  $450^\circ\text{C}$ , the other at room temperature) in an all-metal extraction system, then sorbed onto charcoal for cryogenic separation. Prior to gas purification, the amount of gas released by crushing was measured as a pressure change on a Baratron 222B 1-torr capacitance manometer. Helium, Ne, and Ar were sequentially desorbed off the charcoal then individually admitted into the relevant mass spectrometer. Abundances of the noble gases were determined by peak-height comparison ( $^4\text{He}$  and  $^{40}\text{Ar}$  on a Faraday cup, the remaining isotopes on a Galileo 4869 Channeltron in pulse-counting mode) with standard pipettes from a tank of reduced pressure air that had been modified by adding He. The “air” pipette has a  $^3\text{He}/^4\text{He}$  ratio of 2.04 Ra and  $^4\text{He}/^{40}\text{Ar}$  ratio of 1.42; all other isotopes and abundances are air-like, and each pipette delivers  $0.1 \mu\text{cc STP } ^{40}\text{Ar}$ . Nonlinearities in the response of the mass spectrometer were addressed by running multiple standards in the same size range as the samples. Isobaric interferences with  $^{20}\text{Ne}$  and  $^{22}\text{Ne}$  (by  $^{40}\text{Ar}^{++}$  and  $^{12}\text{C}^{16}\text{O}_2^{++}$ , respectively) were corrected by independently determining the  $^{40}\text{Ar}^{++}/^{40}\text{Ar}^+$  ratio and  $\text{CO}_2^{++}/\text{CO}_2^+$  ratio; these were  $<25\%$  and typically 1.3–1.5% respectively. Corrections at  $m/z = 20$  were usually negligible ( $\ll 1\%$  due to a liquid nitrogen trap close to the ion source that maintained low Ar pressures in the mass spectrometer) but relatively high  $\text{CO}_2$  backgrounds in the mass spectrometer meant that significant corrections had to be made at  $m/z = 22$ . Analyses where the correction exceeded 20% of the  $m/z = 22$  signal are not considered reliable and have not been quoted. Virtually all the error in  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{21}\text{Ne}/^{22}\text{Ne}$  ratios results from the large corrections at  $m/z = 22$ . Note that the quoted errors combine the reproducibility of at least 10 air pipettes with the

within-run counting statistics. This procedure may overestimate measurement uncertainties because errors can be counted twice. However, in practice, the within-run statistical errors are usually trivial relative to the reproducibility of the air pipettes.

[10] Blank contributions ( $^{40}\text{Ar} \leq 0.4 \times 10^{-9} \text{ cm}^3 \text{ STP}$ ;  $^{21}\text{Ne} \leq 2 \times 10^{-15} \text{ cm}^3 \text{ STP}$ ;  $^4\text{He}$  was below detection) were  $\ll 1\%$  of the total gas released, except for Ne. Neon blanks were  $\approx 3\%$  of some of the steps, but because blanks are air-like, blank correcting the data does not improve precision but merely moves the analysis along a well-defined mixing line between air and the measured ratio. Ne measurements were not corrected for blank contribution. The new Ne data for Dice 10 has a correlation similar to the Loihi line in  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{21}\text{Ne}/^{22}\text{Ne}$  space, consistent with the analyses of the same sample by *Trieloff et al.* [2000].

[11] We recognize that  $^{36}\text{Ar}$  is the most sensitive gas to analytical blank corrections. However, assuming that the uncertainties in blank corrections are incorporated into the reported data, there should be no problem using the  $^{36}\text{Ar}$  or  $^{36}\text{Ar}/^{22}\text{Ne}$  of any published analysis as we detail below. However, our approach to this issue is to consider that we never actually know what the “blank” contribution to the analysis is; this is particularly true for crushing where mechanical action in the crusher releases an indeterminate amount of atmospheric noble gas from the equipment. Static blanks and/or running blanks with no sample present cannot accurately assess this contribution. Therefore every noble gas analysis will contain an unknown amount of “blank” (atmospheric gases released from the vacuum equipment) and it is important to assess the composition of these contributions when estimating the composition of magmatic gases trapped in the sample.

#### 4. Mixing Systems and Ne Extrapolations

[12] One of the most useful advances in mantle geochemistry in recent years has been the recognition that the primordial  $^{20}\text{Ne}/^{22}\text{Ne}$  isotope signature of the mantle is significantly higher than that of the atmosphere (9.8) and similar to solar values

( $\geq 12.5$ – $13.8$ ) [Sarda *et al.*, 1988; Honda *et al.*, 1991; Honda and McDougall, 1997; Harrison *et al.*, 1999; Trieloff *et al.*, 2000]. This clear distinction provides a procedure for calculating the proportion of atmospheric component in any given analysis [Farley and Poreda, 1993; Moreira *et al.*, 1998]. Correlations of Ne isotope ratios with for instance,  $^{40}\text{Ar}/^{36}\text{Ar}$  (also  $^{129}\text{Xe}/^{130}\text{Xe}$ ) arise because, at least on a local scale, both ratios are a function of the same process, the addition of air-derived to mantle-derived gases. These correlations can be extrapolated to the mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio to estimate the mantle composition of the other ratio. Uncertainty in the actual mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio does not invalidate this approach, provided that (1) the mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  is constant and (2) that corrections are made to a constant ratio. A mantle end-member  $^{20}\text{Ne}/^{22}\text{Ne}$  value of 13.8, the solar wind value, has been chosen in this contribution.

## 5. Two Axis, Four Isotope Plots

[13] Figures 1a–1f are Ne-Ar and Ne-Xe mixing plots for the Icelandic, Loihi, and MORB data. Assuming that only two components are involved in producing the range of compositions observed in these data, mixing hyperbolae can be fitted to these data to estimate end-member compositions [Valbracht *et al.*, 1997; Moreira *et al.*, 1998; Trieloff *et al.*, 2000]. However, the distribution of variable  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  values at near constant Ne values requires the presence of a third component: two component mixtures will produce a unique  $^{40}\text{Ar}/^{36}\text{Ar}$  or  $^{129}\text{Xe}/^{130}\text{Xe}$  ratio at a given  $^{20}\text{Ne}/^{22}\text{Ne}$ .

[14] Furthermore, plotting two independently varying isotope ratios, such as  $^{40}\text{Ar}/^{36}\text{Ar}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$  (also  $^{129}\text{Xe}/^{130}\text{Xe}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$ ), on two axes result in a series of hyperbolae, each of which represents a range in end-member compositions depending on  $(^{36}\text{Ar}/^{22}\text{Ne})_{\text{ADC}}/(^{36}\text{Ar}/^{22}\text{Ne})_{\text{MANTLE}}$  [Langmuir *et al.*, 1978]. Unless  $^{36}\text{Ar}/^{22}\text{Ne}$  is known a priori in one of the end-members, the composition of the second end-member cannot be constrained even for two-component mixtures. For example, mixing between a mantle end-member with  $^{36}\text{Ar}/^{22}\text{Ne}$  of 6.5 [Moriera *et al.*,

1998] and unfractionated air ( $^{36}\text{Ar}/^{22}\text{Ne} = 19$ ) will result in the same mixing hyperbola as between a mantle end-member with  $^{36}\text{Ar}/^{22}\text{Ne} \sim 22.4$  and air saturated water ( $^{36}\text{Ar}/^{22}\text{Ne} = 65$ ); both mixing lines have the same “r” correlation. Because the  $^{36}\text{Ar}/^{22}\text{Ne}$  ratio of the air-derived contaminant is not known (and may be variable in composition), the  $^{40}\text{Ar}/^{36}\text{Ar}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$  plot does not properly constrain mantle  $^{36}\text{Ar}/^{22}\text{Ne}$  and therefore  $^{40}\text{Ar}/^{36}\text{Ar}$  cannot be constrained either (the same argument applies for determining the mantle end-member  $^{129}\text{Xe}/^{130}\text{Xe}$ ). However, we recognise that three-isotope two-dimensional (2-D) plots are unaffected by fractionation of a two-component system during and/or after trapping of gases and as such are a valuable tool.

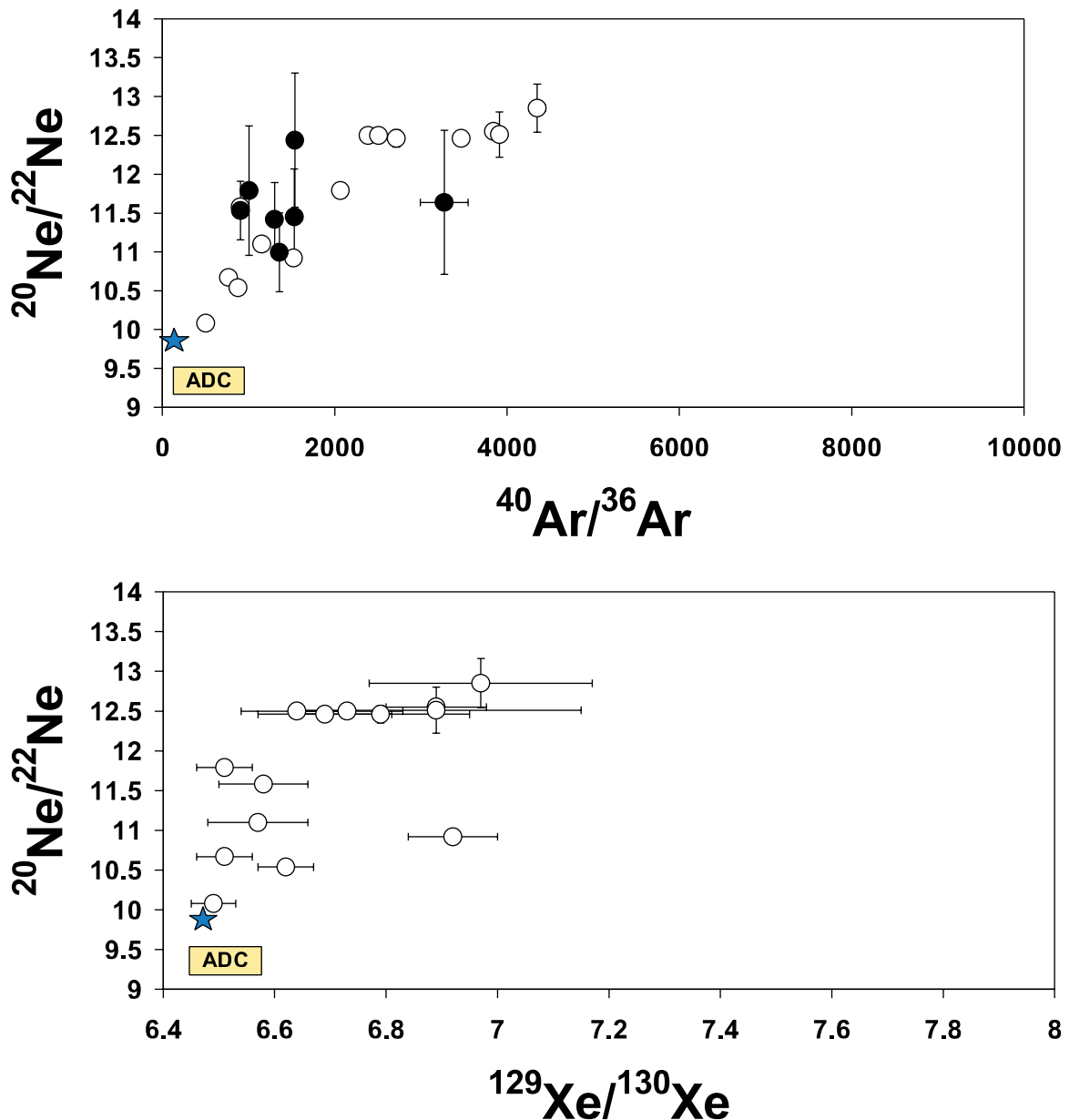
## 6. Three Axis, Four Isotope Plots

[15] When three components are clearly indicated in a 2-D mixing diagram it is advantageous to normalize the data to a common denominator and represent the four isotopes on a 3-D mixing plot. The interpretation of four-isotope 3-D mixing diagrams is an extension of the more familiar three-isotope 2-D diagrams. Normalizing to a common denominator ensures that mixing between end-members will define a plane in these 3-D plots, and using  $^{22}\text{Ne}$  as the denominator allows the plane to be most readily extrapolated to a mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  composition. Absence of a correlation in 3-D implies at least a four-component system. These diagrams have been used intermittently in the past to represent noble gas data [Reynolds and Turner, 1964; Turner, 1971; Kennedy *et al.*, 1987; Harrison *et al.*, 1999; Kendrick *et al.*, 2001]. We illustrate 3-D mixing systematics using synthetic Ne-Ar data in Figure 2 and animation 1 and reported data in Figure 3 and animations 2 and 3.

## 7. Ne-Ar System

### 7.1. Iceland

[16] The data discussed here are from step-crushing experiments of two subglacially erupted Icelandic glasses, Dice 10 and 11 [Trieloff *et al.*, 2000] and a



**Figure 1.**  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{40}\text{Ar}/^{36}\text{Ar}$  mixing plots (same applies to  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{129}\text{Xe}/^{130}\text{Xe}$ ). Correlations in two-dimensional (2-D) space of two independent isotope values produces a range of hyperbolic mixing lines constrained by  $(i^{22}\text{Ne})_{\text{ADC}}/(i^{22}\text{Ne})_{\text{MANTLE}}$  [Langmuir *et al.*, 1978] where  $i$  = either  $^{36}\text{Ar}$  or  $^{130}\text{Xe}$ ; ADC is air-derived contaminant. It is clear that in most samples there is variation in  $^{36}\text{Ar}/^{22}\text{Ne}$  (and  $^{130}\text{Xe}/^{22}\text{Ne}$ ) in the atmospheric contaminants, resulting in a range in  $^{40}\text{Ar}/^{36}\text{Ar}$  (and  $^{129}\text{Xe}/^{130}\text{Xe}$ ) ratios at a given  $^{20}\text{Ne}/^{22}\text{Ne}$  value. (a and b) Data from Icelandic Dice 10 glass sample, open circles [Trieloff *et al.*, 2000] and new data from the same samples, filled circles (Table 1). Xe was not analyzed in the repeat analysis of Dice 10 reported here. (c and d) Dunite xenolith data from Trieloff *et al.* [2000] (filled triangles) and total fusion and crush data from glasses and olivine phenocrysts from Valbracht *et al.* [1997] (open triangles). Extrapolating the dunite data, it is possible to estimate the mantle end-member  $^{40}\text{Ar}/^{36}\text{Ar}$  to be of the order  $8100 \pm 200$  (at a  $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$ ). It is not possible to fit a line to the Ne-Xe data. (e and f) Data from the mid-ocean ridge (MORB) glass “Popping Rock” [Moreira *et al.*, 1998]. Similar to the Iceland and Loihi data, variable  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  values are present at near constant  $^{20}\text{Ne}/^{22}\text{Ne}$  values and hyperbolic mixing lines, if fitted, would not correctly constrain the mantle end-member  $^{40}\text{Ar}/^{36}\text{Ar}$  or  $^{129}\text{Xe}/^{130}\text{Xe}$  values.

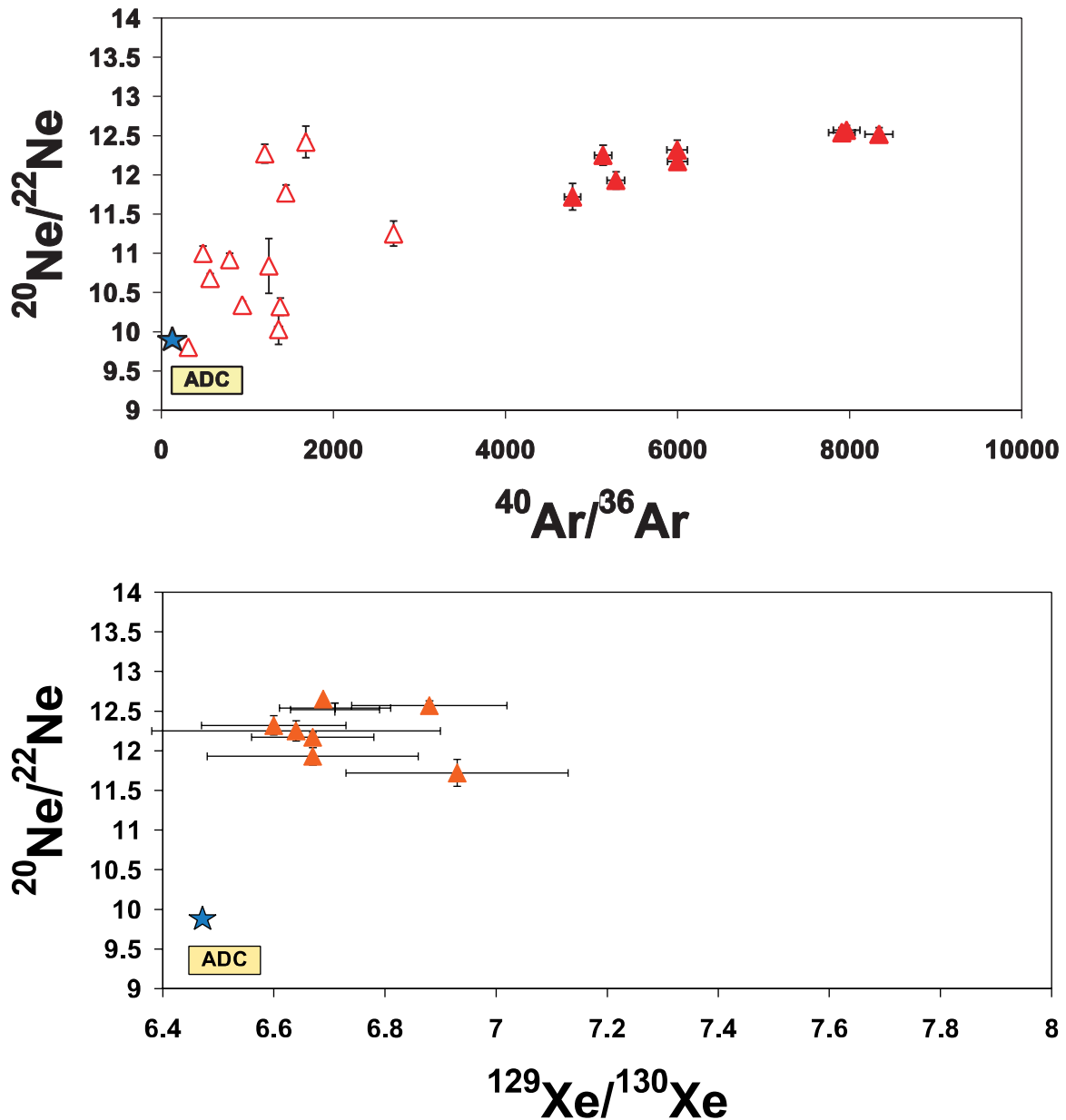


Figure 1. (continued)

repeat analysis of Dice 10 (Table 1). The  $^3\text{He}/^4\text{He}$  ratio for these samples is in the range 17–20  $R_a$ . The  $^4\text{He}/^{40}\text{Ar}^*$  values for all crushing steps are between 1.9 and 4.1 (the asterisk denotes corrected for atmospheric contamination). Extractions with  $^{20}\text{Ne}/^{22}\text{Ne} \approx 12.5$  have  $^4\text{He}/^{40}\text{Ar}^*$  values between 2.7 and 4.1. Minor fractionation of the trapped mantle gases has occurred; variable  $^4\text{He}/^{40}\text{Ar}^*$  within a single basaltic glass is to be expected as the glass preserves volatiles from different stages in the magmatic outgassing history [Burnard, 1999;

Burnard, 2001]. Variation in the measured  $^3\text{He}/^{22}\text{Ne}$  values is also seen (those with  $^{20}\text{Ne}/^{22}\text{Ne}$  extractions  $\approx 12.5$ ). While He/Ar varies about a factor of 1.52, magmatic Ne-Ar fractionation is less pronounced (e.g.,  $^{21}\text{Ne}^*/^{40}\text{Ar}^* = (1.1\text{--}1.6) \times 10^{-7}$ ). Hence this cannot explain a factor of 2 variation of  $^{36}\text{Ar}/^{22}\text{Ne}$  ratios at high mantle-like Ne values that correlate with  $^{40}\text{Ar}/^{36}\text{Ar}$ . Moreover these  $^{36}\text{Ar}/^{22}\text{Ne}$  variations contradict expected solubility controlled degassing patterns that predict lower Ar/Ne ratios in degassed magmas (Figure

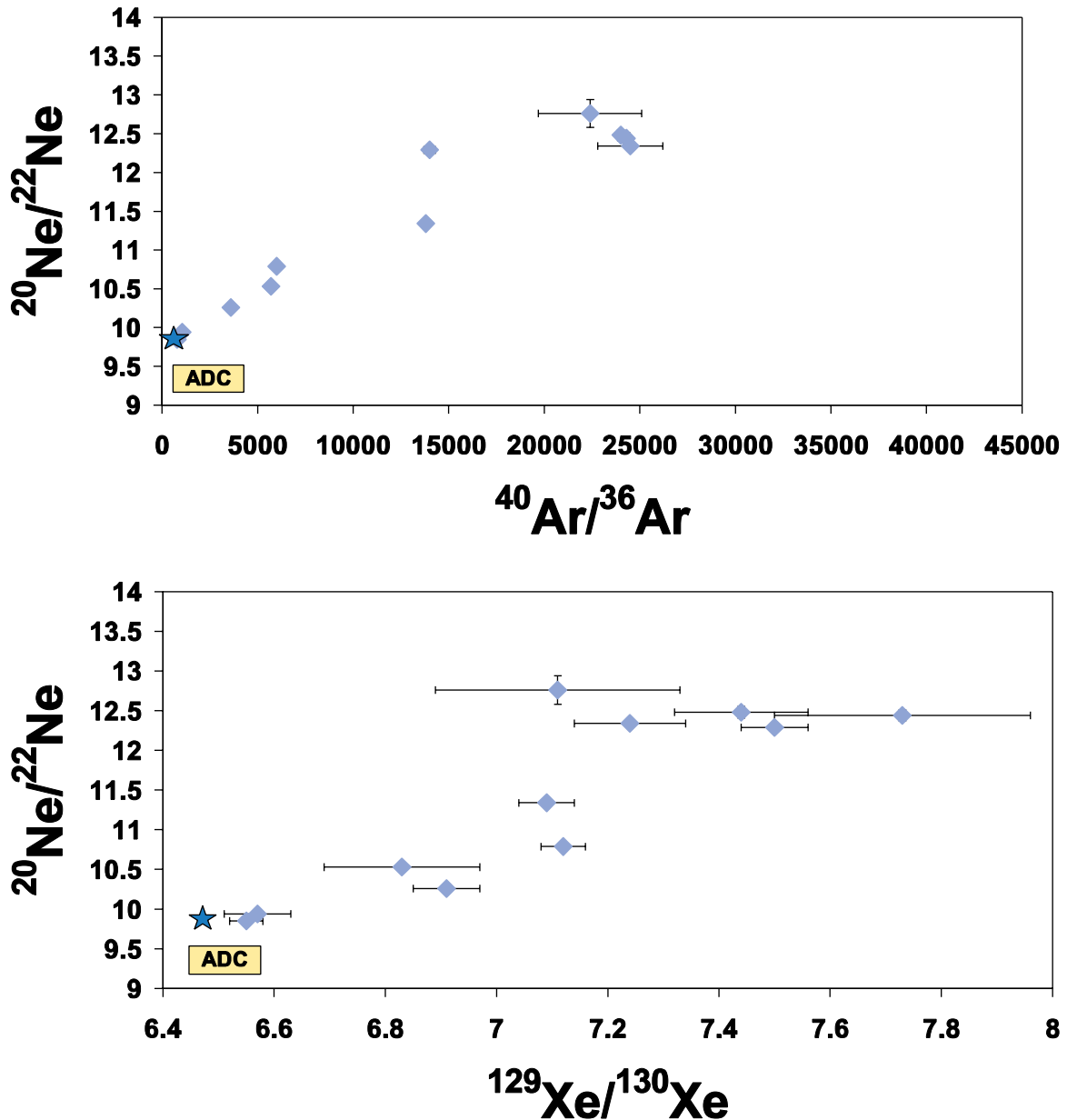
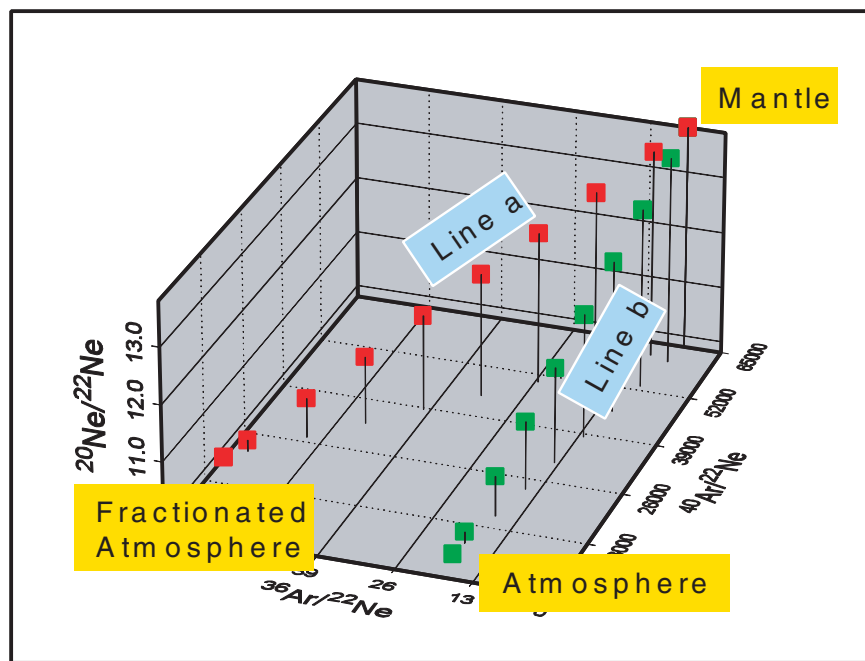
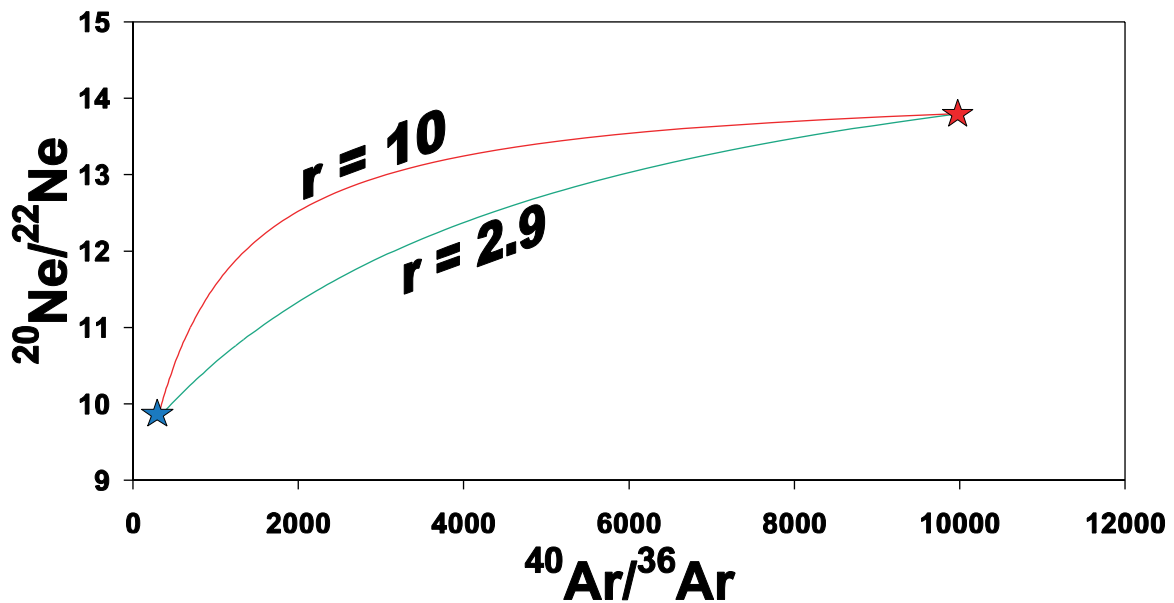


Figure 1. (continued)

3a); similarly, adsorption of Ar onto previously crushed glass powders in the crushing system would produce lower Ar/Ne ratios. While magmatic degassing or the extraction technique may have resulted in minor Ar-Ne fractionation, the major variation in Ar/Ne in these data is due to mixing between mantle and atmospheric noble gases, not solubility controlled fractionation. Estimates of the mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  value using hyperbolic four-isotope 2-D diagrams [e.g., *Moreira et al.*, 1998] are strongly controlled by the  $^{36}\text{Ar}/^{22}\text{Ne}$  values (Fig-

ures 1a–1f and captions). Analyzing the data using a 3-D plot shows that three (or more) components mix to generate the range in compositions observed in these Icelandic samples. From the plane defined by the data (Figure 3a) the three end-members in this system are (1) unfractionated atmospheric noble gases, (2) a mantle component, (3) a contaminant with atmospheric isotope ratios but high Ar/Ne which may be from surface equilibrated aqueous fluids or from an adsorbed atmospheric component.



**Figure 2.** Schematic Ne-Ar mixing diagrams. (a) Two-dimensional, four-isotope plots. Two mixing hyperbolae are presented with “ $r$ ” = 2.9 (lower mixing line) and “ $r$ ” = 10 (upper mixing line). The “ $r$ ” = 2.9 line could, for example, result from mixing between unfractionated atmosphere and a mantle component with  $^{36}\text{Ar}/^{22}\text{Ne} = 6.5$  (as proposed by *Moreira et al.* [1998]) or by mixing between air-saturated water and a mantle component with  $^{36}\text{Ar}/^{22}\text{Ne} = 22$ . The upper mixing line (“ $r$ ” = 10) is that expected for mixing between the mantle component predicted by *Moreira et al.* [1998] ( $^{36}\text{Ar}/^{22}\text{Ne} = 6.5$ ) and air-saturated water ( $^{36}\text{Ar}/^{22}\text{Ne} = 65$ ). Unless  $^{36}\text{Ar}/^{22}\text{Ne}$  is known a priori in one of the end-members, the composition of the second end-member cannot be fully constrained. (b) Three-axis, four-isotope plots showing predicted mixing between mantle and unfractionated atmosphere (line a) and mantle and a fractionated atmospheric component (line b). If only one of the atmospheric components is present, then the analyses will fall on a line between the end-member compositions. However, if three components are present (e.g., atmosphere, fractionated atmosphere, and mantle), the data will define a plane (c) between the three end-member compositions, depending on the exact Ar/Ne ratios and concentrations.

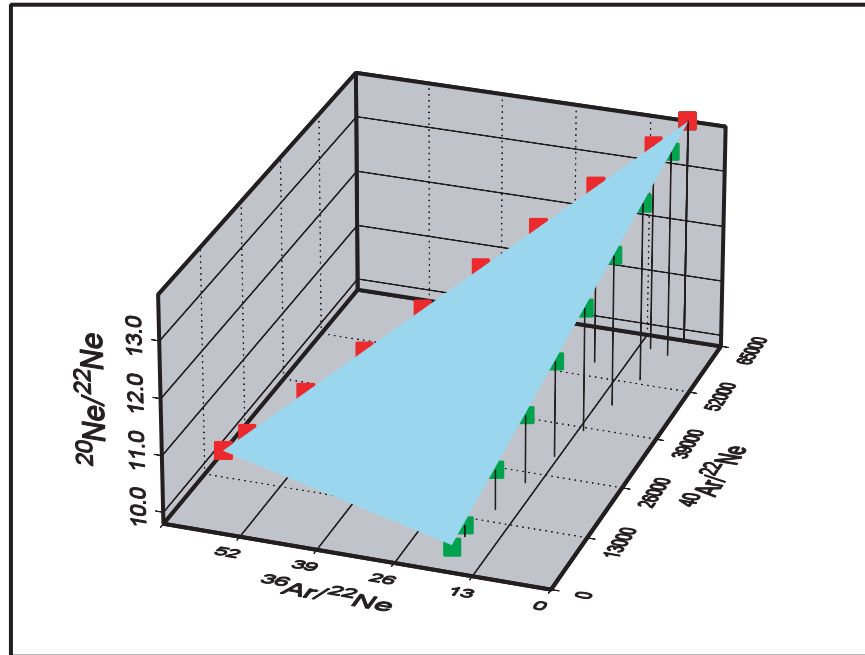


Figure 2. (continued)

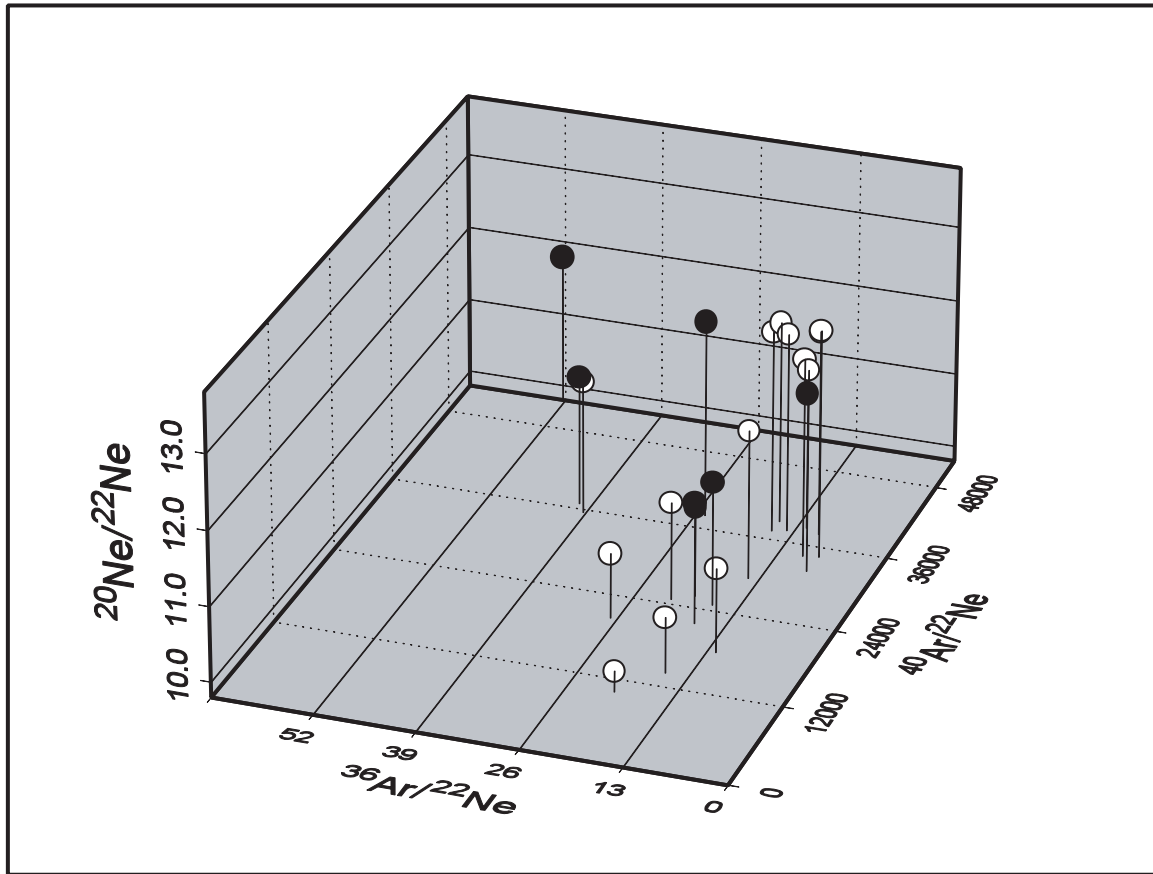
[17] This method of data representation shows that the variable  $^{40}\text{Ar}/^{36}\text{Ar}$  at near-constant  $^{20}\text{Ne}/^{22}\text{Ne}$  (of  $\approx 12.5$  as seen in Figure 1a) is due to addition of a fractionated contaminant with high  $^{36}\text{Ar}/^{22}\text{Ne}$ . This component is predominantly seen in extraction steps with high  $^{20}\text{Ne}/^{22}\text{Ne}$ , thereby producing variable  $^{40}\text{Ar}/^{36}\text{Ar}$  ratios. It is probable that this fractionated contaminant is present in all analyses (not just high  $^{20}\text{Ne}/^{22}\text{Ne}$  extractions), but its signature is swamped by unfractionated atmospheric contaminants in the low  $^{20}\text{Ne}/^{22}\text{Ne}$  releases. Note that extrapolations to the mantle  $^{20}\text{Ne}/^{22}\text{Ne}$  ratio are sensitive to these high  $^{20}\text{Ne}/^{22}\text{Ne}$  measurements. As a consequence, the fractionated atmospheric contaminant may be volumetrically small (in comparison to the unfractionated contaminant) but exerts a large influence on estimates of mantle  $^{40}\text{Ar}/^{36}\text{Ar}$ .

[18] The DICE compositions represent a three component mixture, including an atmospheric component that has a high but unknown Ar/Ne ratio, therefore the only constraint on the uncontaminated Icelandic mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio is that it must be higher than the highest measured value. This is evident considering that the maximum measured  $^{40}\text{Ar}/^{36}\text{Ar}$  by *Trieloff et al.* [2000] is

$4350 \pm 90$ , whereas high ratios have been measured in the same sample (up to  $6500 \pm 310$ ) [*Harrison et al.*, 1999]. These apparently inconsistent analyses can be explained by variable addition of a fractionated atmospheric component.

## 7.2. Loihi

[19] Two data sets are discussed here: (1) step-crushing extractions from dunite-xenolith olivine separates [*Trieloff et al.*, 2000] and (2) total fusion (plus three crush extractions) from glassy rinds and olivine phenocrysts [*Valbracht et al.*, 1997]. The  $^4\text{He}/^{40}\text{Ar}^*$  values are in the range 0.9–17.9 (Valbracht) and 0.27–0.95 (Trieloff). Measured  $^4\text{He}/^{40}\text{Ar}^*$  values  $\leq 2$  are lower than the range predicted for probable mantle production ratios. The low  $^4\text{He}/^{40}\text{Ar}^*$  values indicate that either these dunites trapped an early formed vapour phase, exsolved from the magma (which will have lower He/Ar ratios than the residual magma because He is more soluble than Ar in silicate melts), or the samples preferentially lost He after eruption. Samples containing unfractionated mantle volatiles will have  $^{21}\text{Ne}/^{40}\text{Ar}^*$  ratios of between  $\approx 9 \times 10^{-8}$  and  $\approx 2 \times 10^{-7}$  (assuming likely theoretical production ratios for  $(^4\text{He}/^{40}\text{Ar})_r$  and  $(^{21}\text{Ne}/^4\text{He})_r$ ). Values for



**Figure 3.** (a)  $^{40}\text{Ar}/^{22}\text{Ne}$  versus  $^{36}\text{Ar}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$ . Step-crushing data for subglacially erupted Icelandic basaltic glasses [Trieloff *et al.*, 2000] and new data from same samples (Table 1). All data are coplanar (plane not shown). Symbols are as in Figures 1a–1f. From the parameters of the mixing plane (not shown for clarity) we can determine both the relative timing of mixing and which end-members are fractionated. Because the analyses most affected by the fractionated atmospheric component have high  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios, this suggests that the fractionated atmospheric component was introduced into the system prior to unfractionated air. Thus variable contamination of the mantle noble gases by a fractionated component (such as air saturated water) produced intermediate compositions with high  $^{20}\text{Ne}/^{22}\text{Ne}$  but relatively low  $^{40}\text{Ar}/^{36}\text{Ar}$  prior to contamination by unfractionated atmosphere. These data show the importance of using multi-isotope plots and the influence of fractionated atmospheric contaminants on the data. Without a prior knowledge of the mantle  $^{36}\text{Ar}/^{22}\text{Ne}$ , it is not possible to constrain the “uncontaminated”  $^{40}\text{Ar}/^{36}\text{Ar}$  of these basalts other than it must be equal to or higher than the highest ratio measured. (b)  $^{40}\text{Ar}/^{22}\text{Ne}$  versus  $^{36}\text{Ar}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$ . Data from Loihi. Open triangles denote glass and olivines [Valbracht *et al.*, 1997] and closed triangles denote dunite-olivines [Trieloff *et al.*, 2000]. The data define a straight line, indicating mixing is dominated by only two components. Minor spread in Ar/Ne values within the data of Valbracht *et al.* [1997] could be due to solubility-controlled degassing processes, consistent with variable  $^4\text{He}/^{40}\text{Ar}^*$  ratios (as discussed in text). (c)  $^{40}\text{Ar}/^{22}\text{Ne}$  versus  $^{36}\text{Ar}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$ . Data from the MORB glass “Popping Rock” [Moreira *et al.*, 1998]. There is no simple correlation between  $^{20}\text{Ne}/^{22}\text{Ne}$  and  $^{36}\text{Ar}/^{22}\text{Ne}$ , particularly at high  $^{20}\text{Ne}/^{22}\text{Ne}$  values. However, these data lie on a plane; therefore the influence of a fractionated atmospheric component in these extractions is evident. Drop lines are fitted to the plane. As a result of the spread in  $^{36}\text{Ar}/^{22}\text{Ne}$ , it is not possible to define the mantle  $^{36}\text{Ar}/^{22}\text{Ne}$ , and therefore it is not possible to constrain the mantle  $^{40}\text{Ar}/^{36}\text{Ar}$ . For example, the trajectories predicted for mixing between air and a mantle with  $^{40}\text{Ar}/^{36}\text{Ar} = 40,000$  and  $80,000$  are illustrated (solid green and dashed red lines respectively;  $^{20}\text{Ne}/^{22}\text{Ne} = 13.8$ ).

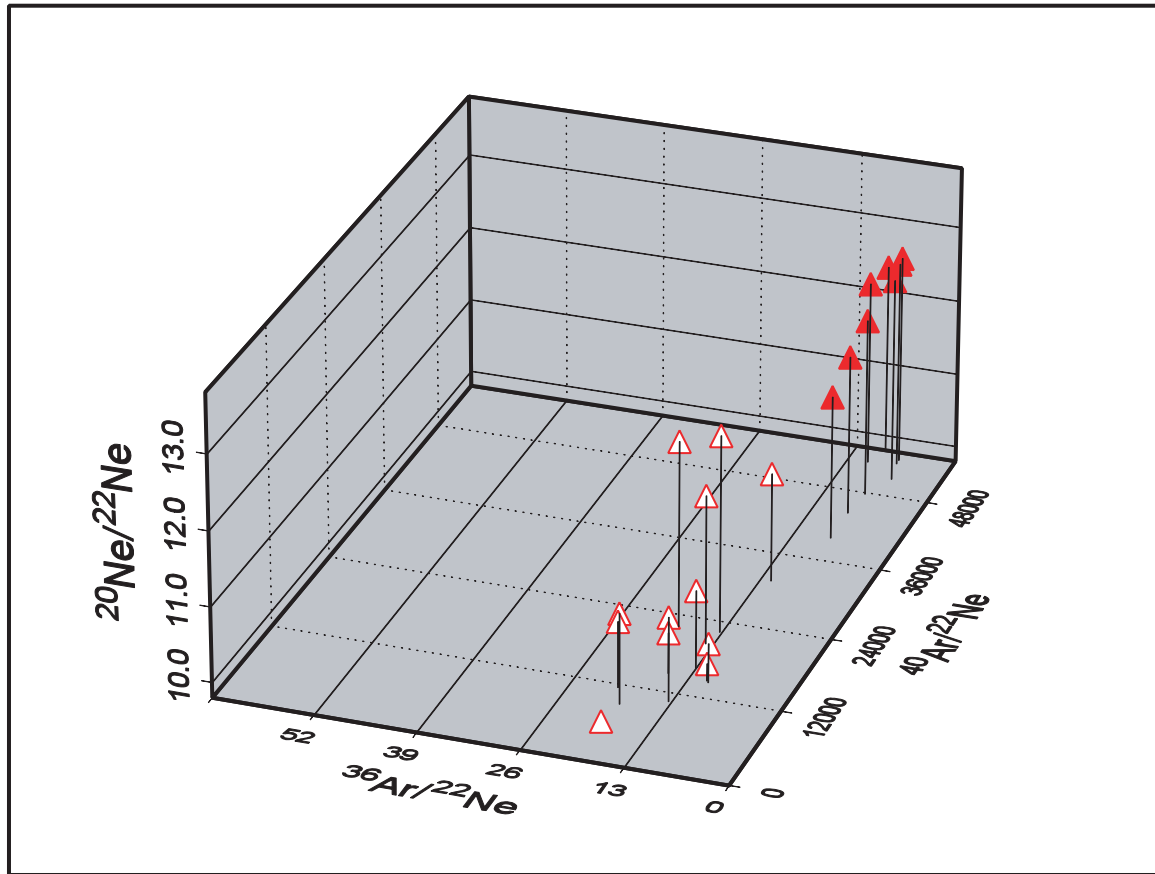


Figure 3. (continued)

the dunites [Trieloff *et al.*, 2000] are within this range; however, the glasses and olivine phenocryst data are higher than predicted production values consistent with the high  $^4\text{He}/^{40}\text{Ar}^*$  values indicating volatile loss through degassing [Moreira and Sarda, 2000; Sarda and Moreira, 2002].  $^3\text{He}/^4\text{He}$  values are between 24–27  $R_a$  for all samples.

[20] The range in  $^{36}\text{Ar}/^{22}\text{Ne}$  at a given  $^{20}\text{Ne}/^{22}\text{Ne}$  value is relatively restricted in the Loihi dunite data (in comparison with the Iceland data) consistent with mixing being dominated by two components: (1) unfractionated atmosphere and (2) a mantle component (Figure 3b). Small variations in Ar/Ne in the glasses and olivines can be readily accounted for by volatile fractionation that occurred during magmatic processes without requiring addition of a third, high Ar/Ne atmospheric contaminant. The fact that all Loihi data, dunites, phenocrysts, and glasses, all plot along a single line suggests that contamination by fractionated atmosphere has not

occurred in all these samples. Addition of fractionated atmospheric noble gases (as seen in the Icelandic glasses) does not appear to be related to sample preparation or extraction processes (as this would contaminate all samples equally), but this contaminant invades the samples either prior to or at eruption.

[21] The estimate of Trieloff *et al.*, [2000] for the  $^{40}\text{Ar}/^{36}\text{Ar}$  for the Loihi source region ( $\sim 8000$  at  $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$  or assuming  $^{20}\text{Ne}/^{22}\text{Ne} = 13.8$ ,  $\sim 13000$ ) is likely to be robust because only two components are involved in mixing to generate the observed compositions: mantle and unfractionated air. Since the composition of one (air) is well known it is possible to estimate the composition of the other.

### 7.3. MORB “Popping Rock”

[22] A number of noble gas studies have been reported for MORB glasses; however, most have

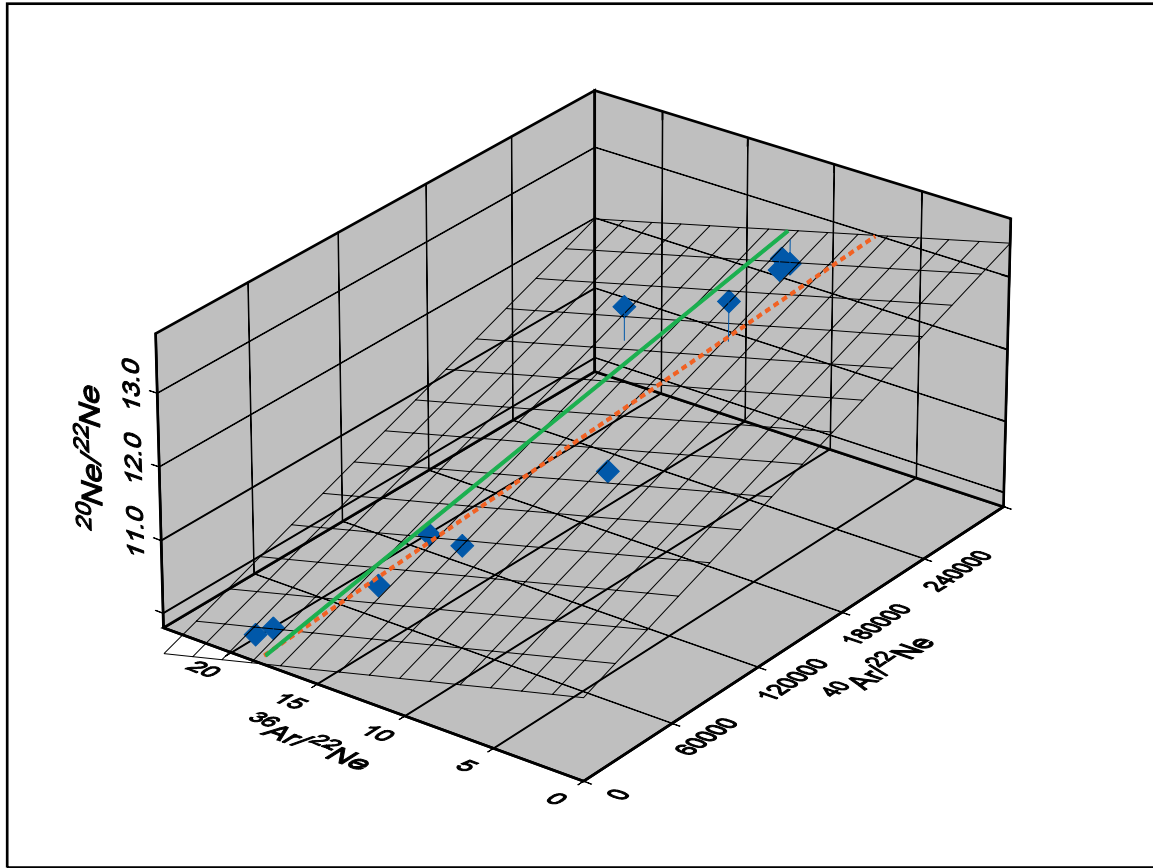


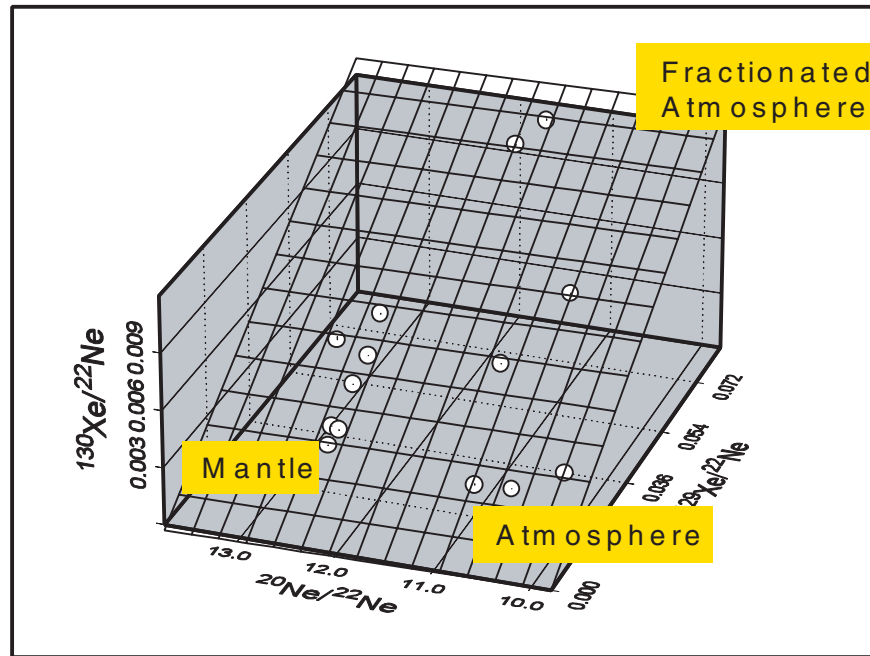
Figure 3. (continued)

high and variable  $^{21}\text{Ne}^*/^4\text{He}$  and  $^4\text{He}/^{40}\text{Ar}^*$  ratios due to magmatic fractionation [see *Burnard et al.*, 2002]. Significant variations in Ar/Ne result from this magmatic fractionation, and therefore most MORB glasses will not plot on a single mixing plane but will define a series of planes, each one unique for the degree of fractionation of that particular sample. However, the “Popping Rock” 2 $\pi$ D43 has radiogenic and nucleogenic noble gas ratios close to predicted  $^{21}\text{Ne}^*/^{40}\text{Ar}^*$  production ratios; we use the unsurpassed step crushing data of the “Popping Rock” [*Moreira et al.*, 1998] to deconvolve the various end-member components in this MORB glass.  $^4\text{He}/^{40}\text{Ar}^*$  values from the crushing steps are between 1.4 and 1.8, slightly lower than the predicted production value for the upper mantle (2–4), as outlined previously. Calculated  $^{21}\text{Ne}^*/^4\text{He}$  ratios,  $((7.4\text{--}8.5) \times 10^{-8})$  are slightly higher than the predicted production ratio, suggesting minor He loss may have occurred in

this sample. Alternatively, this may result from dissolved He remaining in the glass (which is not sampled using the crushing technique employed), although, given the high vesicularity of “Popping Rock,” virtually all the noble gases are predicted to be in the vesicles, not the glass.

[23] At any given  $^{20}\text{Ne}/^{22}\text{Ne}$  there is slight variability in the  $^{36}\text{Ar}/^{22}\text{Ne}$  values (in particular at high  $^{20}\text{Ne}/^{22}\text{Ne}$  values) (Figure 3c). This relationship is entirely consistent with mixing in a three-component system, although the high Ar/Ne component is less pronounced than for the Icelandic data.

[24] Identifying a fractionated atmospheric Ar/Ne component in these data is important in that the  $^{36}\text{Ar}/^{22}\text{Ne}$  of the mantle is still unknown (assuming that a single  $^{36}\text{Ar}/^{22}\text{Ne}$  value can actually represent the whole mantle). Estimates of the upper mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  (i.e.,  $\geq 40,000$  [*Moreira et al.*, 1998]) should be revised, although it remains impossible



**Figure 4.** (a)  $^{129}\text{Xe}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{130}\text{Xe}/^{22}\text{Ne}$ . Icelandic data [Trieloff *et al.*, 2000]. Plane fit to these data is shown along with captions describing end-member positions in four-isotope 3-D space. The data do not lie on a simple two-component mixing line between mantle and air, and the fractionated atmospheric component is more easily identified in extractions with moderate to high  $^{20}\text{Ne}/^{22}\text{Ne}$  ratios. (b)  $^{129}\text{Xe}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{130}\text{Xe}/^{22}\text{Ne}$ . Loihi data [Trieloff *et al.*, 2000]. Variation in Xe/Ne at constant, high  $^{20}\text{Ne}/^{22}\text{Ne}$  values indicates the presence of a fractionated atmospheric component. (c)  $^{129}\text{Xe}/^{22}\text{Ne}$  versus  $^{20}\text{Ne}/^{22}\text{Ne}$  versus  $^{130}\text{Xe}/^{22}\text{Ne}$ . MORB glass “Popping Rock” data [Moreira *et al.*, 1998]. Similar to the Iceland and Loihi data, the fractionated component is present at high  $^{20}\text{Ne}/^{22}\text{Ne}$  values.

to place a precise number on the upper mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio; most of the “Popping Rock” stepped crush data are consistent with mixing between air-derived noble gases and mantle component with  $^{40}\text{Ar}/^{36}\text{Ar}$  in the range 40,000–80,000 (see Figure 3c).

## 8. Ne-Ar Summary

[25] Four-isotope 3-D plots have the potential to distinguish variable atmospheric components in mantle noble gas analyses. Ne-Ar systematics can identify a major contribution in the Iceland data from a fractionated atmospheric component, as well as the mantle and normal atmospheric noble gases. It is therefore not possible to estimate the end-member mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  value except that such a value must be higher than the maximum  $^{40}\text{Ar}/^{36}\text{Ar}$  measured. The situation with regards to the “Popping Rock” data is similar in that the data are a three-component mixture. The variation

in  $^{36}\text{Ar}/^{22}\text{Ne}$  at constant  $^{20}\text{Ne}/^{22}\text{Ne}$  is less in the “Popping Rock” data than in the Iceland data, consistent with a smaller contribution from, or a less fractionated, high Ar/Ne atmospheric component. The recognition of this component however again precludes accurate estimates of the mantle source  $^{40}\text{Ar}/^{36}\text{Ar}$ .

## 9. Ne-Xe Systematics: Iceland, Loihi, and MORB

[26] Similar to the Ne-Ar plots, we can show that the Ne-Xe system for these data consists of three-component mixtures (Figures 4a, 4b, and 4c): (1) normal atmosphere, (2) a mantle component, and (3) a contaminant with atmospheric isotope ratios and high Xe/Ne. For these plots the data is best viewed with  $^{20}\text{Ne}/^{22}\text{Ne}$  along the y axis. A plane has been fitted to the Icelandic data in Figure 4a along with captions highlighting the positions of the end-members.

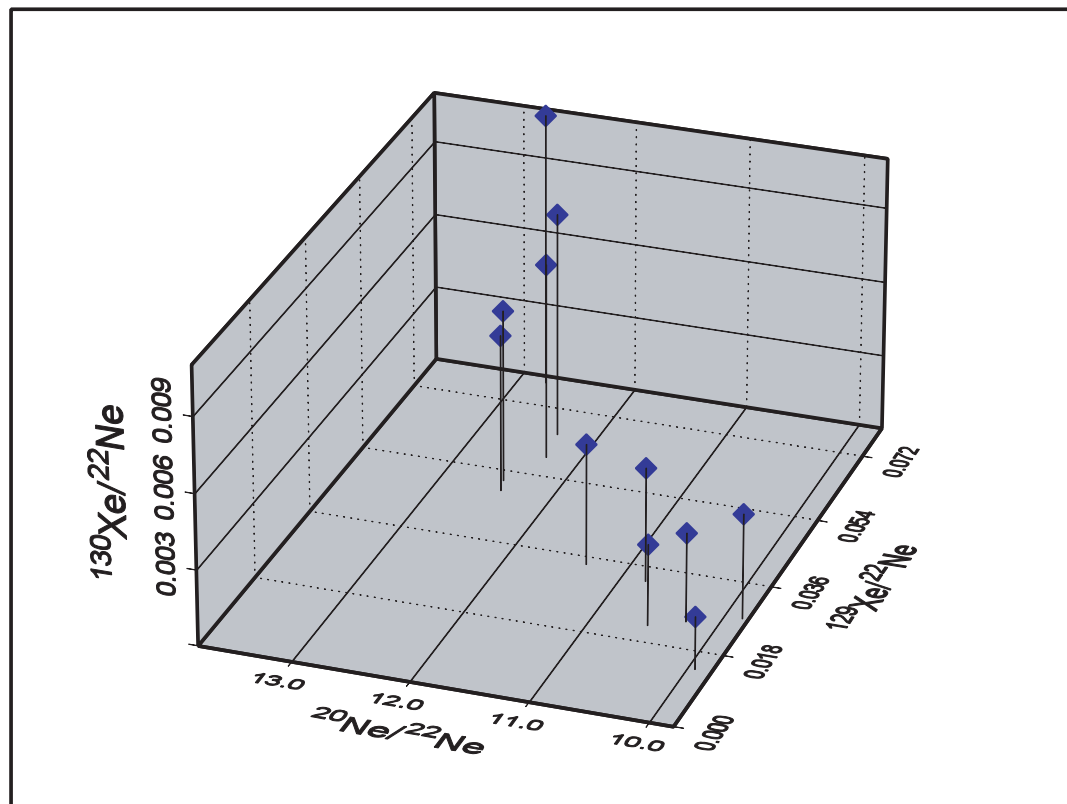
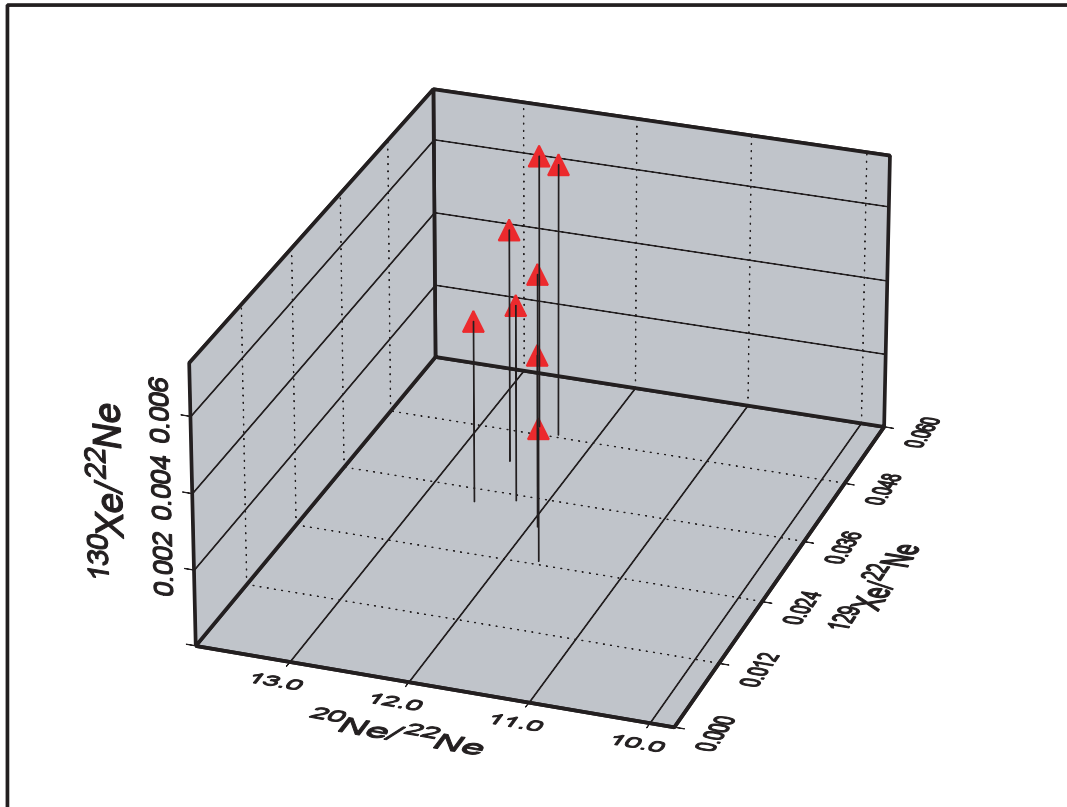


Figure 4. (continued)

[27] As previously mentioned, the  $^{40}\text{Ar}/^{36}\text{Ar}$  ratio in the various mantle reservoirs is poorly constrained, likewise the end-member mantle  $^{129}\text{Xe}/^{130}\text{Xe}$  composition. [Allègre *et al.*, 1986; Tolstikhin and O’Nions, 1994; Porcelli and Wasserburg, 1995a; Kunz *et al.*, 1998; Harrison *et al.*, 1999; Trieloff *et al.*, 2000]. The data for Iceland and Loihi, along with previous analyses from Samoa [Poreda and Farley, 1992], are the only plume-related analyses with a discernable  $^{129}\text{Xe}^*$  (the asterisk denotes excess over and above the atmosphere). The component with measurable  $^{129}\text{Xe}^*$  (i.e.,  $^{129}\text{Xe}/^{130}\text{Xe}$  higher than air, 6.45) is only discernable in extractions with low Xe/Ne and high  $^{20}\text{Ne}/^{22}\text{Ne}$ , i.e., those with minimal input from the fractionated atmospheric component. Irrespective of eruption setting (deep sea or subglacial), it is apparent that the incorporation of a fractionated atmospheric contaminant significantly influences these noble gas data. Magmatic fractionation will decrease the magmatic Xe/Ne and therefore emphasise preferential contamination effects on Xe when compared with Ar. Although this is only a limited explanation for the relatively unfractionated samples discussed here, it could be the principal explanation for other samples where fractionated contaminants are readily recognised in Ne-Xe space but barely distinguishable in Ne-Ar space.

[28] The MORB data discussed here fall on a trajectory between (1) atmosphere and a component containing (2) mantle and (3) fractionated contaminant. Only the most extreme values with high  $^{20}\text{Ne}/^{22}\text{Ne}$  and low  $^{130}\text{Xe}/^{22}\text{Ne}$  could (but not necessarily does) contain unadulterated pristine mantle volatiles.

## 10. Summary

[29] This 3-D, multiisotope procedure highlights the complexities in noble gas contamination mechanisms. We have shown that assuming simple two-component mixing between air and mantle noble gases is incorrect for most samples. Mantle signatures can be easily disturbed by the incorporation of fractionated atmospheric contaminants (ice-water/seawater) prior to or during eruption or by addition of adsorbed fractionated atmosphere after eruption. In all the samples examined, the presence

of a fractionated atmospheric contaminant is evident, even in extractions with mantle-like isotope ratios. Most current estimates of end-member mantle  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios are therefore likely to be lower limits to the actual composition. The actual  $^{40}\text{Ar}/^{36}\text{Ar}$  and  $^{129}\text{Xe}/^{130}\text{Xe}$  ratios of most mantle reservoirs remain unknown, unless the influence of fractionated atmospheric contaminants can be quantified.

## Acknowledgments

[30] DH would like to thank everyone in the Manchester Cosmochemistry Group for numerous discussions regarding 3-D isotope plots. We acknowledge M. Honda, M. Moreira, and A. Shaw for in-depth reviews, whose comments improved this script. DH was funded by a NERC grant (GR3/11637).

## References

- Allègre, C. J., T. Staudacher, and P. Sarda, Rare gas systematics: Formation of the atmosphere, evolution, and structure of the Earth’s mantle, *Earth Planet. Sci. Lett.*, *81*, 127–150, 1986.
- Ballentine, C. J., and D. N. Barford, The origin of air-like noble gases in MORB and OIB, *Earth Planet. Sci. Lett.*, *180*, 39–48, 2000.
- Burnard, P. G., The bubble-by-bubble volatile evolution of two mid-ocean ridge basalts, *Earth Planet. Sci. Lett.*, *174*, 199–211, 1999.
- Burnard, P. G., Correction for volatile fractionation in ascending magmas: Noble gas abundances in primary mantle melts, *Geochim. Cosmochim. Acta*, *65*, 2605–2614, 2001.
- Burnard, P. G., F. M. Stuart, L. Ayliffe, G. Turner, and C. Curtis, Combined noble gas and quadrupole mass spectrometer analysis of volatiles trapped in fluid inclusions, in *Water - Rock Interaction*, edited by Y. K. Kharakha and A. S. Maest, pp. 903–906, A.A. Balkema, Brookfield, Vt., 1992.
- Burnard, P. G., D. W. Graham, and K. A. Farley, Mechanisms of magmatic gas loss along the Southeast Indian Ridge and the Amsterdam-St Paul Plateau, *Earth Planet. Sci. Lett.*, *203*, 131–148, 2002.
- Burnard, P. G., K. A. Farley, and G. Turner, Multiple fluid pulses in a Samoan harzburgite, *Chem. Geol.*, *147*, 99–148, 1997a.
- Burnard, P. G., D. W. Graham, and G. Turner, Vesicle-specific noble gas analyses of “popping rock”: Implications for primordial noble gases in the Earth, *Science*, *276*, 568–571, 1997b.
- Carroll, M. R., and J. D. Webster, Solubilities of sulfur, noble gases, nitrogen, chlorine and fluorine in magmas, in *Volatiles in Magmas, Reviews in Mineralogy*, edited by M. R. Carroll and J. R. Holloway, pp. 231–271, Mineral. Soc. of Am., Washington, D. C., 1994.
- Clarke, W. B., M. A. Beg, and H. Craig, Excess  $^3\text{He}$  in the sea: Evidence for terrestrial primordial He, *Earth Planet. Sci. Lett.*, *6*, 213–220, 1969.

- Dixon, E. T., M. Honda, I. McDougall, I. H. Campbell, and I. Sigurdsson, Preservation of near-solar neon isotopic ratios in Icelandic basalts, *Earth Planet. Sci. Lett.*, *180*, 309–324, 2000.
- Farley, K. A., and R. J. Poreda, Mantle neon and atmospheric contamination, *Earth Planet. Sci. Lett.*, *114*, 325–339, 1993.
- Fisher, D. E., Helium, argon, and xenon in crushed and melted MORB, *Geochim. Cosmochim. Acta*, *61*(14), 3003–3012, 1997.
- Harrison, D., P. Burnard, and G. Turner, Noble gas behaviour and composition in the Mantle: Constraints from the Iceland Plume, *Earth Planet. Sci. Lett.*, *171*, 199–207, 1999.
- Hilton, D. R., J. Barling, and G. E. Wheller, Effect of shallow-level contamination on the helium isotope systematics of ocean-island lavas, *Nature*, *373*, 330–333, 1995.
- Honda, M., and I. McDougall, Primordial helium and neon in the Earth: A speculation on early degassing, *Geophys. Res. Lett.*, *25*, 1951–1954, 1997.
- Honda, M., and D. Patterson, Systematic elemental fractionation of mantle-derived helium, neon and argon in mid-oceanic ridge glasses, *Geochim. Cosmochim. Acta*, *63*, 2863–2874, 1999.
- Honda, M., I. McDougall, D. Patterson, A. Doulgeris, and D. Clague, Possible solar noble gas component in Hawaiian basalts, *Nature*, *349*, 149–151, 1991.
- Honda, M., I. McDougall, D. Patterson, A. Doulgeris, and D. Clague, Noble gases in submarine pillow basalt glasses from Loihi and Kilauea, Hawaii: A solar component in the Earth, *Geochim. Cosmochim. Acta*, *57*, 859–874, 1993.
- Kendrick, M. A., R. Burgess, R. A. D. Patrick, and G. Turner, Halogen and Ar-Ar age determinations of inclusions within quartz veins from porphyry copper deposits using complementary noble gas extraction techniques, *Chem. Geol.*, *177*, 351–370, 2001.
- Kennedy, B. B., J. H. Reynolds, S. Smith, and A. Truesdell, Helium isotopes: lower Geyser Basin, Yellowstone National Park, *J. Geophys. Res.*, *92*, 12,477–12,489, 1987.
- Kunz, J., T. Staudacher, and C. J. Allègre, Plutonium-fission xenon found in Earth's mantle, *Science*, *280*, 877–880, 1998.
- Langmuir, C. H., R. D. Vocke, G. N. Hanson, and S. R. Hart, A general mixing equation with applications to Icelandic basalts, *Earth Planet. Sci. Lett.*, *37*, 380–392, 1978.
- Leya, I., and R. Wieler, Nucleogenic production of Ne isotopes in Earth's crust and upper mantle induced by alpha particles from the decay of U and Th, *J. Geophys. Res.*, *104*(B7), 15,439–15,450, 1999.
- Lux, G., The behaviour of noble gases in silicate liquids: Solution, diffusion, bubbles and surface effects, with applications to natural samples, *Geochim. Cosmochim. Acta*, *51*, 1549–1560, 1987.
- Marty, B., and L. Zimmermann, Volatiles (He, C, N, Ar) in mid-ocean ridge basalts: Assessment of shallow-level fractionation and characterization of source composition, *Geochim. Cosmochim. Acta*, *63*, 3619–3633, 1999.
- Moreira, M., and P. Sarda, Noble gas constraints on degassing processes, *Earth Planet. Sci. Lett.*, *176*, 375–386, 2000.
- Moreira, M., T. Staudacher, P. Sarda, J.-G. Schilling, and C. J. Allègre, A primitive plume neon component in MORB: The Shona Ridge anomaly, South Atlantic (51–52 degrees South), *Earth Planet. Sci. Lett.*, *133*, 367–377, 1995.
- Moreira, M., J. Kunz, and C. Allègre, Rare gas systematics in popping rock: Isotopic and elemental compositions in the upper mantle, *Science*, *279*, 1178–1181, 1998.
- Moreira, M., K. Breddam, J. Curtice, and M. D. Kurz, Solar neon in the Icelandic mantle: New evidence for an undegassed lower mantle, *Earth Planet. Sci. Lett.*, *185*, 15–23, 2001.
- Niedermann, S., W. Bach, and J. Erzinger, Noble gas evidence for a lower mantle component in MORBs from the southern East Pacific Rise: Decoupling of helium and neon isotope systematics, *Geochim. Cosmochim. Acta*, *61*, 2697–2715, 1997.
- O'Nions, R. K., and E. R. Oxburgh, Heat and helium in the Earth, *Nature*, *306*, 429–431, 1983.
- Ozima, M., and F. A. Podosek, *Noble Gas Geochemistry*, Cambridge Univ. Press, New York, 1983.
- Patterson, D. B., M. Honda, and I. McDougall, Atmospheric contamination: A possible source for heavy noble gases in basalts from Loihi Seamount, Hawaii, *Geophys. Res. Lett.*, *17*, 705–708, 1990.
- Porcelli, D., and G. Wasserburg, Mass transfer of xenon through a steady-state upper mantle, *Geochim. Cosmochim. Acta*, *59*, 1991–2007, 1995a.
- Porcelli, D., and G. J. Wasserburg, Mass transfer of helium, neon, argon and xenon through a steady-state upper mantle, *Geochim. Cosmochim. Acta*, *59*, 4921–4937, 1995b.
- Poreda, R., and K. Farley, Rare gases in Samoan xenoliths, *Earth Planet. Sci. Lett.*, *113*, 129–144, 1992.
- Reynolds, J. H., and G. Turner, Rare gases in the Chondrite Renazzo, *J. Geophys. Res.*, *69*, 3263–3281, 1964.
- Sarda, P., and M. Moreira, Vesiculation and vesicle loss in mid-ocean ridge basalt glasses, *Geochim. Cosmochim. Acta*, *68*, 1449–1458, 2002.
- Sarda, P., T. Staudacher, and C. Allègre, Neon isotopes in submarine basalts, *Earth Planet. Sci. Lett.*, *91*, 73–88, 1988.
- Staudacher, T., et al., Noble gases in basalt glasses from a Mid-Atlantic Ridge topographic high at 14 N: Geodynamic consequences, *Earth Planet. Sci. Lett.*, *96*, 119–133, 1989.
- Tolstikhin, I., and R. K. O'Nions, The Earth's missing Xenon: A combination of early degassing and of rare gas loss from the atmosphere, *Chem. Geol.*, *115*, 1–6, 1994.
- Trieloff, M., J. Kunz, D. A. Clague, D. Harrison, and C. Allègre, The nature of pristine noble gases in mantle plumes, *Science*, *288*, 1036–1038, 2000.
- Turner, G., <sup>40</sup>Ar-<sup>39</sup>Ar ages from the Lunar Maria, *Earth Planet. Sci. Lett.*, *11*, 169–191, 1971.
- Turner, G., The outgassing history of the Earth's atmosphere, *J. Geol. Soc. London*, *146*, 147–154, 1989.
- Valbracht, P. J., T. Staudacher, A. Malahoff, and C. J. Allègre, Noble gas systematics of deep riftzone glasses from Loihi Seamount, Hawaii, *Earth Planet. Sci. Lett.*, *150*, 399–411, 1997.
- Yatsevich, I., and M. Honda, Production of nucleogenic neon in the Earth from natural radioactive decay, *J. Geophys. Res.*, *102*, 10,291–10,298, 1997.