What CO₂ well gases tell us about the origin of noble gases in the mantle and their relationship to the atmosphere

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Study of commercially produced volcanic CO₂ gas associated with the Colorado Plateau, USA, has revealed substantial new information about the noble gas isotopic composition and elemental abundance pattern of the mantle. Combined with published data from mid-ocean ridge basalts, it is now clear that the convecting mantle has a maximum \(^{20}\text{Ne}/^{22}\text{Ne}\) isotopic composition, indistinguishable from that attributed to solar wind-implanted (SWI) neon in meteorites. This is distinct from the higher \(^{20}\text{Ne}/^{22}\text{Ne}\) isotopic value expected for solar nebula gases. The non-radiogenic xenon isotopic composition of the well gases shows that 20 per cent of the mantle Xe is ‘solar-like’ in origin, but cannot resolve the small isotopic difference between the trapped meteorite ‘Q’-component and solar Xe. The mantle primordial \(^{20}\text{Ne}/^{132}\text{Xe}\) is approximately 1400 and is comparable with the upper end of that observed in meteorites. Previous work using the terrestrial \(^{129}\text{I}/^{129}\text{Xe}\) mass balance demands that almost 99 per cent of the Xe (and therefore other noble gases) has been lost from the accreting solids and that Pu–I closure age models have shown this to have occurred in the first ca 100 Ma of the Earth’s history. The highest concentrations of Q-Xe and solar wind-implanted (SWI)-Ne measured in meteorites allow for this loss and these high-abundance samples have a Ne/Xe ratio range compatible with the ‘recycled-air-corrected’ terrestrial mantle. These observations do not support models in which the terrestrial mantle acquired its volatiles from the primary capture of solar nebula gases and, in turn, strongly suggest that the primary terrestrial atmosphere, before isotopic fractionation, is most probably derived from degassed trapped volatiles in accreting material.

By contrast, the non-radiogenic argon, krypton and 80 per cent of the xenon in the convecting mantle have the same isotopic composition and elemental abundance pattern as that found in seawater with a small sedimentary Kr and Xe admix. These mantle heavy noble gases are dominated by recycling of air dissolved in seawater back into the mantle. Numerical simulations suggest that plumes sampling the core–mantle boundary would be enriched in seawater-derived noble gases compared with the convecting mantle, and therefore have substantially lower \(^{40}\text{Ar}/^{36}\text{Ar}\). This is compatible with observation. The subduction process is not a complete barrier to volatile return to the mantle.

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1. Introduction

The mechanism, timing and origin of the formation of the Earth’s atmosphere and oceans remain enigmatic. While this is ultimately responsible for creating the conditions for life and the tectonic character of our own planet, small differences in planetary volatile acquisition, in the case of Venus and Mars, have resulted in totally different planet surfaces. In particular, the origin of the inner planetary exospheres has variably been attributed to volatiles trapped in accreting material, those from a residual solar nebula or those deposited as a late cometary veneer (e.g. Dauphas et al. 2000; Dauphas 2003). It has been clear for some time from both the major gas species and its inert or ‘noble’ gas isotopic composition that the Earth’s atmosphere today is not a simple relic of primary nebula gas capture (Brown 1949; Suess 1949), nor indeed of degassed infalling accretionary or later cometary material. The noble gas isotopic composition and elemental abundance pattern of the modern atmosphere alone require significant primary atmosphere processing and loss (e.g. Porcelli & Pepin 2004). Nevertheless, identifying the primary atmosphere origin and composition is critical in being able to develop a quantitative understanding of the mechanism and process of early planetary atmosphere modification. The mechanism and magnitude of planetary gas loss itself provides, in turn, stringent mass-balance constraints on the accretionary origin of the volatiles.

One of the most important developments in our understanding of planetary accretion from the early solar nebula is modelling work that suggests that multiple Mars-sized bodies impacting on an accreting planet are a natural part of the accretionary process (Wetherill 1994; Morbidelli 2002). In the more detailed giant impactor simulations that indicate the extent of planetary-scale vaporization, melting and material dispersal before re-accretion (Canup 2004, 2008), it is perhaps a question of whether or not we would expect to find any volatiles trapped within the solid planets at all. However, we do, and an important additional clue to planetary volatile origin lies in the isotopic and elemental composition of the noble gases degassing from the solid Earth today. We briefly review our current understanding of noble gases in the mantle together with recent advances made since the comprehensive reviews by Graham (2002) Hilton et al. (2002), Pepin & Porcelli (2002), Porcelli & Ballentine (2002) and Porcelli & Pepin (2004). In the light of recent results, we discuss what noble gases tell us about the planetary accretionary process, the subsequent evolution of the Earth’s interior and, indeed, what relationship they have with the present-day atmosphere.

2. Helium: the case for an accretionary volatile reservoir in the terrestrial mantle

One of the most important observations is that of deep-Earth $^3$He degassing into the oceans from mid-ocean ridges (Clarke et al. 1969). Unlike any other element except hydrogen, helium has a residence time in the atmosphere of approximately $10^6$ years (Torgersen 1989) before being lost to space. This results in the atmosphere having a very low He concentration and enables helium enriched in $^3$He relative to $^4$He.
degassing from mid-ocean ridges to be readily identified. This also means that, unlike any other element, helium cannot be recycled from the atmosphere back into the mantle; the isotopic anomalies observed at mid-ocean ridges are a result of the release of $^3$He trapped during accretion and modified only by radiogenic $^4$He produced by U and Th decay in the mantle.

An equally important observation is the small $^3$He/$^4$He ratio variance in mid-ocean ridge basalts (MORB; figure 1). Away from oceanic plateaux and ocean islands, these samples preserve, across the entire approximately 65 000 km length of the mid-ocean ridge systems, a uniform $^3$He/$^4$He isotopic composition $(8.75 \pm 2.14R_a$, where $R_a$ is the atmospheric ratio of $1.40 \times 10^{-6}$; Graham 2002). This points to a terrestrial mantle reservoir supplying the mid-ocean ridges that is relatively homogeneous with respect to its $^3$He/(U+Th) composition and provides a critical insight into the volatile–solid evolution of the mantle system (e.g. Kurz et al. 1982; Allègre et al. 1983; O’Nions & Oxburgh 1983). Isotopic evidence for the existence of a mantle reservoir separate and distinct from the convecting mantle is provided by high $^3$He/$^4$He ocean island volcanism (Kurz et al. 1982; figure 1). Fluid dynamics require the plume to be initiated from a boundary layer in the mantle, with the most recent seismic tomographic imaging of many ocean island plume systems placing this reservoir near to or at the core–mantle boundary (Montelli et al. 2004, 2006). Nevertheless, the source, preservation and character of the mantle high $^3$He/$^4$He reservoir remain a current topic of debate.

Although the isotopic composition of He on accretion has some model dependence (pre-deuterium burning $= 120R_a$ and solar wind $= 330R_a$; Mahaffy et al. 1998; Podosek et al. 2000), owing to the small amount of $^4$He compared with

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**Figure 1.** Compilation of He isotope data showing the low $^4$He/$^3$He ratio and isotopic heterogeneity of some ocean island systems compared with the relatively well-mixed isotopic composition of mid-ocean ridges (MORB, mid-ocean ridge basalts; HIMU, high mu mantle). Adapted from Barfod et al. (1999).
current terrestrial values and model uncertainties, the actual endmember used makes little difference to the mantle evolution models discussed. For a closed system and known U+Th content, it is then simple to calculate the mantle helium concentration that would produce a particular $^{3}\text{He}/^{4}\text{He}$, and this provides a critical insight into the source or process responsible for introducing volatiles into the deep planet and its subsequent evolution.

The Earth’s convecting mantle is degassing and also has a changing U+Th content due to continental crust extraction. The present-day U+Th concentration in the MORB-source or ‘convecting’ mantle, however, is reasonably well known (e.g. Jochum et al. 1983). An estimate of the $^{3}\text{He}$ concentration in this mantle reservoir can be made from the present-day $^{3}\text{He}$ flux into the ocean (Lupton & Craig 1975) and the average oceanic crust production rate (Parsons 1981). The estimated $^{3}\text{He}$ concentration is too low to have preserved the observed $^{3}\text{He}/^{4}\text{He}$ ratio for the given U+Th concentration and cannot be a simple closed system. Three approaches have been adopted to explore how the He isotope system in the mantle works: (i) analytically (e.g. Tolstikhin 1975; Staudacher & Allègre 1982; Anderson 1998; Porcelli & Elliot 2008), (ii) through numerical simulations of mantle convection and degassing (e.g. Van Keken & Ballentine 1998, 1999; Tackley 2000), or (iii) by considering a steady-state He flux through the convecting mantle from a deep volatile-rich mantle reservoir (Kellogg & Wasserburg 1990; O’Nions & Tolstikhin 1994; Porcelli & Wasserburg 1995). We first discuss the steady-state models.

A widely accepted explanation for the He observations has been a steady-state flux of high $^{3}\text{He}/^{4}\text{He}$ material from beneath the 670 km discontinuity in the mantle into the convecting upper mantle. High $^{3}\text{He}/^{4}\text{He}$ in plumes provides evidence for a reservoir capable of supplying this flux (Kellogg & Wasserburg 1990; O’Nions & Tolstikhin 1994; Porcelli & Wasserburg 1995). A combination of seismic tomography (Grand 1987; Van der Hilst et al. 1997) and numerical models (Van Keken & Ballentine 1998, 1999) demonstrated that the 670 km mantle phase change does not prevent efficient mixing, and that the mantle cannot preserve a compositional boundary at this depth. This does not rule out a flux of volatile-rich and high $^{3}\text{He}/^{4}\text{He}$ material from a yet deeper geochemical reservoir within the Earth (e.g. Kellogg et al. 1999; Porcelli & Halliday 2001; Tolstikhin & Hofmann 2005), but makes any assumption of steady state in a much larger convecting system less certain. Numerical simulations do not need to make an assumption of steady state and are equally capable of balancing such a deep $^{3}\text{He}$ flux into a convecting mantle system with the observed $^{3}\text{He}/^{4}\text{He}$ and $^{3}\text{He}$ concentration (e.g. Ballentine et al. 2007).

Alternative explanations to a deep $^{3}\text{He}$ flux require higher than currently accepted $^{3}\text{He}$ concentrations in the convecting mantle or faster degassing rates in the past to have only recently brought the He concentration to current ‘low’ values. A consequence of the former would require that the present-day $^{3}\text{He}$ flux into the oceans is a factor of 3.5 times lower than the average over the time required to produce the ocean crust and is called the ‘zero-paradox’ reference concentration (Ballentine et al. 2002). While there is considerable uncertainty in the variance of the past $^{3}\text{He}$ degassing flux (Van Keken et al. 2001), there is no evidence to support such a high zero-paradox convecting mantle $^{3}\text{He}$ concentration (e.g. Saal et al. 2002).

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A recent parametrized analytical study by Porcelli & Elliot (2008) assumes an exponentially decreasing degassing rate over time and a U\textsuperscript{238}Th decrease in the convecting mantle linked to different crustal growth rates. This work explores the evolution of $^{3}\text{He}/^{4}\text{He}$ in the mantle and provides a conservative estimate of the highest $^{3}\text{He}/^{4}\text{He}$ produced by this reservoir over time. One analytical approach has been to explore the concept of the high $^{3}\text{He}/^{4}\text{He}$ mantle reservoir originating from a depletion in U+Th, thereby preserving the ambient $^{3}\text{He}/^{4}\text{He}$ at the time of radio-element depletion without requiring a reservoir with a high $^{3}\text{He}$ concentration (e.g. Anderson 1998). The study by Porcelli & Elliot (2008) in a similar model context does not provide any support for the required ancient high $^{3}\text{He}/^{4}\text{He}$ convecting mantle required by the ‘low U+Th, not high $^{3}\text{He}$’ branch of enquiry.

The high-helium high-degassing model explored by Porcelli & Elliot (2008) also raises an interesting problem. In order to match the present-day convecting mantle, $^{3}\text{He}/^{4}\text{He}$ ($8R_a$) and He concentration ($3.2\times10^{-11}$ cm$^3$ (STP) $^{3}\text{He}$ g$^{-1}$), a mantle initial $^{3}\text{He}$ of $4.1\times10^{-9}$ cm$^3$ (STP) $^{3}\text{He}$ g$^{-1}$ is required. In the last 4 Ga, the model then requires the whole convecting mantle to have lost approximately 99 per cent of its volatiles to the atmosphere. $^{40}\text{Ar}$ mass balance between the mantle and the atmosphere, discussed in §5, provides evidence of only approximately 50 per cent mantle outgassing efficiency (Hart et al. 1979), and is reasonably well reproduced by numerical models of mantle convection (Van Keken & Ballentine 1998, 1999) and more recent models that attempt to take into account changes in past heat flow (Ballentine et al. 2007). The same fluid dynamical models only outgas up to 70 per cent of their original $^{3}\text{He}$. To effect the extreme convection required for such efficient outgassing will require a substantial advance in our understanding of the mantle rheology of the early Earth. Until then, we argue that the strongest explanation for the observed mantle $^{3}\text{He}/^{4}\text{He}$, low [$^{3}\text{He}$] and [U+Th] remains a flux of high $^{3}\text{He}/^{4}\text{He}$ material from a gas-rich reservoir deeper in the mantle system (Kurz et al. 1982; Allègre et al. 1983; O’Nions & Oxburgh 1983; Kellogg & Wasserburg 1990; Tolstikhin & O’Nions 1994; Porcelli & Wasserburg 1995).

3. Neon: a trapped meteorite origin for terrestrial mantle volatiles?

Key information on the source composition of the volatiles in the mantle is provided by the Ne isotopic system. Some of the earliest terrestrial neon isotopic anomalies, different from atmospheric values, were observed in natural gases and radioactive minerals (Wetherill 1954; Sharif-Zade et al. 1972, 1973; Verchovsky & Shukolyukov 1976). These allowed the identification of the different Ne isotope production mechanisms, often referred to as ‘Wetherill’ reactions (Wetherill 1954). A combination of laboratory observation (Hunemore 1989) and modelling work (Yatsevich & Honda 1997) provides a good understanding of the rates of production as a function of radio-element, target element and respective spatial distribution (Ballentine et al. 2002). In the terrestrial mantle, production of $^{20}\text{Ne}$ and $^{22}\text{Ne}$ is negligible, while nucleogenic $^{21}\text{Ne}$ addition is readily observed.

The initial observation of $^{20}\text{Ne}/^{22}\text{Ne}$ values above atmospheric values in both CO$_2$-rich well gas (Phinney et al. 1978) and MORB (Sarda et al. 1988) was then due to either mass fractionation of an atmospheric component or an original

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accretionary signature. Honda et al. (1991) were able to show that the resolved \(^{3}\text{He}/^{22}\text{Ne}\), assuming an accretionary origin, was similar to solar values. This interpretation was reinforced by Patterson et al. (1990), who successfully argued against any fractionation of a shallow air contaminant. It is worth noting at this point that recent work (Holland & Ballentine 2006) rules out a recycled-air component significantly contributing to the mantle \(^{20}\text{Ne}/^{22}\text{Ne}\) isotope system; this is discussed in more detail later in this paper.

The Ne isotopic composition observed in mantle-derived samples is then a three-component mixture of an atmospheric component most probably introduced during the eruption process or even during sample handling (Patterson et al. 1990; Ballentine & Barfod 2000), nucleogenic \(^{21}\text{Ne}\) and the original accretionary \(^{20}\text{Ne}/^{22}\text{Ne}\) isotope signature (figure 2).

Identification of the accretionary origin of Ne is particularly important because, alone of all of the noble gases, there is a clear and simple isotopic difference between Ne trapped within meteorites and solar Ne. Solar Ne has a \(^{20}\text{Ne}/^{22}\text{Ne}=13.8\) (Benkert et al. 1993; Grimberg et al. 2006), while the maximum observed trapped in meteorites is \(^{20}\text{Ne}/^{22}\text{Ne}=12.5\) (Black 1972; Wieler 2002; Trieloff et al. 2000, 2002). Models of terrestrial volatile acquisition invoking a major role for solar nebula gases are predicted to produce a mantle \(^{20}\text{Ne}/^{22}\text{Ne} \sim 13.8\). Solar nebula models include, for example, gravitational capture of a massive early atmosphere and magma ocean equilibration (Mizuno et al. 1980; Porcelli et al. 2001; Zahnle et al. 2007). By contrast, models of mantle volatile

Figure 2. Resolution of the mantle Ne isotopic composition from Ne isotopes in CO\(_2\) well gas (Ballentine et al. 2005; Holland & Ballentine 2006). Groundwater that has accumulated crustal \(^{21}\text{Ne}\) contains dissolved air Ne with a natural radiogenic \(^{21}\text{Ne}\) isotope ‘spike’. When magmatic CO\(_2\) contacts the groundwater, mixing between the groundwater and the magmatic fluid produces a unique mixing line. Intersection of this mixing line with the well-defined MORB air–mantle mixing line provides an unambiguous resolution of the convecting mantle \(^{20}\text{Ne}/^{22}\text{Ne}\) value (Ballentine et al. 2005), unobtainable with either dataset alone. SWI, solar wind-implanted. Data adapted from Holland & Ballentine (2006).
capture that require solar wind irradiation of accreting material (Podosek et al. 2000; Trieloff et al. 2000, 2002; Ballentine et al. 2005; Tolstikhin & Hofmann 2005) would predict a lower $^{20}\text{Ne}/^{22}\text{Ne}$ value. But it is critical to distinguish between a solar Ne isotopic composition that has been reduced by eruption-related air contamination (we rule out atmospheric Ne recycling later) and a systematic mantle $^{20}\text{Ne}/^{22}\text{Ne}$ upper limit (Ballentine et al. 2001; Trieloff et al. 2001).

Until recently, most work has simply relied on the uppermost observed values. For example, Ozima & Zashu (1991) concluded from diamonds that the mantle upper limit was $^{20}\text{Ne}/^{22}\text{Ne} < 12.0$, and therefore included a significant meteorite-trapped ‘planetary’ component in their model. Farley & Poreda (1993) noted that the mantle value appeared to ‘top out’ at $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$ but, owing to limited data, did not place any significance on this value. More recently, variable $^{40}\text{Ar}/^{36}\text{Ar}$ for a constant maximum $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$ from both Iceland and Loihi (Hawaiian seamount) and newer high-quality MORB data (Moreira et al. 1998) were used to argue for a SWI origin for the Ne in the mantle (Trieloff et al. 2000). It was not possible, however, to rule out a ubiquitous air component mixing with solar wind with a higher $^{20}\text{Ne}/^{22}\text{Ne}$ (Ballentine et al. 2001; Trieloff et al. 2001). Interpretation was further complicated by reports of $^{20}\text{Ne}/^{22}\text{Ne} > 12.5$, but these either had large error bars, or were non-reproducible or both (e.g. Sarda et al. 1988; Harrison et al. 1999). The only indication of reproducible $^{20}\text{Ne}/^{22}\text{Ne} > 12.5$ is in aliquots of gas released from inclusions from one Kola plume sample (Yokochi & Marty 2004).

4. Neon: evidence from CO$_2$-rich well gases

A major breakthrough occurred by transferring focus from ocean island and mid-ocean ridge basalts to continental natural gases. In particular, CO$_2$-rich natural gases in New Mexico were used to identify the first terrestrial isotopic anomalies ($^{129}\text{Xe}/^{130}\text{Xe}$) that could be ascribed to the presence of an extinct radionuclide ($^{129}\text{I}$) within the Earth (Butler et al. 1963). From their particular Xe isotopic composition, these gases were soon identified as also being remarkably similar to those found in MORB (Staudacher 1987), although with the addition of more radiogenic noble gases from the crust.

It has been known for a long time that crustal radiogenic noble gases accumulate in groundwater (Torgersen & Clarke 1985). Groundwater $^4\text{He}$ ages are now routinely used in ancient groundwater studies (e.g. Kipfer et al. 2002), while the accumulation of $^4\text{He}$ in natural gases that have equilibrated with the groundwater is well documented (Ballentine & Sherwood Lollar 2002; Zhou & Ballentine 2006). The latter is particularly important when a magmatic gas passes through or contacts an ‘old’ groundwater. Instead of picking up simple air ‘contamination’, the air component has been ‘spiked’ with a natural crustal radiogenic/nucleogenic addition. In the case of the Ne isotopes, this means that mixing between the premixed dissolved air and crustal component and the magmatic endmember will define a mixing line with a different starting composition and gradient from those of simple air–mantle mixing. With the principal assumption that the convecting mantle has supplied the magmatic gases, intersection of the (crust + air)–mantle mixing line with

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the air–MORB mixing line then uniquely defines the mantle upper limit
$^{20}\text{Ne}/^{22}\text{Ne}$. This value, $^{20}\text{Ne}/^{22}\text{Ne}=12.5$ (Ballentine et al. 2005; Holland & Ballentine 2006; figure 2), is indistinguishable from the upper limit found from SWI meteorites. Models requiring simple solar nebula gas input into the early planet need a rethink.

5. Argon: a note on mantle degassing

The main thrust of this paper is to review the advances made in understanding the accretionary origin of volatiles in the solid Earth. Nevertheless, the evolution and magnitude of degassing of the planet play an important role in developing an understanding of the interaction between the deep-Earth volatile reservoir and the atmosphere. Foremost among the tools we have is $^{40}\text{Ar}$. Comparing the solar $^{40}\text{Ar}/^{36}\text{Ar}=3 \times 10^{-4}$ (Anders & Grevesse 1989) with the terrestrial atmosphere value of 295 clearly shows the important input of $^{40}\text{Ar}$ into the atmosphere derived from the decay of $^{40}\text{K}$ from the solid Earth. If we take bulk silicate Earth (BSE) estimates of the K concentration based on the K/U$_{\text{w}}=12,500$ ratio found in basalts (Jochum et al. 1983), then some 45–50 per cent of the planet’s $^{40}\text{Ar}$ is now found in the Earth’s atmosphere (e.g. Hart et al. 1979; Allègre et al. 1996). This reflects not only the ability of the Earth over 4.5 Ga to concentrate the lithophile elements (including K) in the continental crust, but also the efficiency of the Earth to degas the $^{40}\text{Ar}$ produced within it.

We can estimate the MORB-source mantle $^{40}\text{Ar}$ concentration from the mantle $^{3}\text{He}/^{40}\text{Ar}$ defined from well gases and MORB (Moreira et al. 1998; Ballentine et al. 2005) and the $^{3}\text{He}$ mantle concentration derived above. If we take the whole mantle to have this $^{40}\text{Ar}$ concentration, the total $^{40}\text{Ar}$ in the atmosphere and the mantle combined is significantly less than the total amount of $^{40}\text{Ar}$ estimated to have been produced since the Earth’s accretion. Hart et al. (1979) concluded that this could be explained by a hidden $^{40}\text{Ar}$-rich reservoir in the deep mantle. It is often assumed that the $^{3}\text{He}$- and $^{40}\text{Ar}$-rich reservoirs are one and the same, although there is no a priori reason for this assumption.

We note that if the convecting mantle had a $^{40}\text{Ar}$ concentration 3.5 times higher (the zero-paradox noble gas concentration), there would be no need for a hidden $^{40}\text{Ar}$ reservoir (Ballentine et al. 2002). This is exactly the same as the $^{3}\text{He}$ and $^{4}\text{He}$ concentration discrepancy discussed previously and illustrates a strong coherence between radiogenic $^{4}\text{He}$ and $^{40}\text{Ar}$. Arguments to explain the $^{40}\text{Ar}$ paradox by, for example, low BSE K/U (e.g. Lassiter 2004) or high compatibility of Ar (Watson et al. 2007) do not account for this coherence and are weaker accordingly.

6. Non-radiogenic argon: no evidence of a solar component

There is no significant production of either $^{36}\text{Ar}$ or $^{38}\text{Ar}$ in the terrestrial mantle (Ballentine & Burnard 2002). These isotope species then represent either an air component that has been recycled into the mantle, an accretionary signature,
or a hybrid of the two. Although deviations from air $^{38}\text{Ar}/^{36}\text{Ar}$ in MORB have been reported (Niedermann et al. 1997; Pepin 1998), these were not reproduced in later detailed studies of the same MORB samples (Trieloff et al. 2002).

We present here $^{38}\text{Ar}/^{36}\text{Ar}$ data from the mantle volatile-rich well-gas samples detailed in Holland & Ballentine (2006). One-sigma error envelopes of $^{38}\text{Ar}/^{36}\text{Ar}$ ratios in all the samples are within error of air ($^{38}\text{Ar}/^{36}\text{Ar}$ dashed line), irrespective of $^{40}\text{Ar}/^{36}\text{Ar}$. Gases dominated by a crustal radiogenic signature (open diamond, McElmo Dome) with high $^{40}\text{Ar}/^{36}\text{Ar}$ are expected to have air values of $^{38}\text{Ar}/^{36}\text{Ar}$ and show that these values are not an experimental artefact caused by high partial pressures of $^{40}\text{Ar}$ at high $^{40}\text{Ar}/^{36}\text{Ar}$. The mantle has $^{38}\text{Ar}/^{36}\text{Ar}$ values irresolvable from air. The data are presented in table 1.

Figure 3. CO$_2$ well-gas $^{38}\text{Ar}/^{36}\text{Ar}$ versus $^{40}\text{Ar}/^{36}\text{Ar}$. Data adapted from Holland & Ballentine (2006). Bravo Dome (filled square) and Sheep Mountain (open square) samples with resolvable mantle-derived noble gases show no deviation from air $^{38}\text{Ar}/^{36}\text{Ar}$ (dashed line), irrespective of $^{40}\text{Ar}/^{36}\text{Ar}$. Gases dominated by a crustal radiogenic signature (open diamond, McElmo Dome) with high $^{40}\text{Ar}/^{36}\text{Ar}$ are expected to have air values of $^{38}\text{Ar}/^{36}\text{Ar}$ and show that these values are not an experimental artefact caused by high partial pressures of $^{40}\text{Ar}$ at high $^{40}\text{Ar}/^{36}\text{Ar}$. The mantle has $^{38}\text{Ar}/^{36}\text{Ar}$ values irresolvable from air. The data are presented in table 1.

Solar $^{38}\text{Ar}/^{36}\text{Ar}$ ratios are distinct from air with estimates ranging from 0.172 to 0.18 (Becker et al. 1998; Pepin et al. 1999) compared with 0.1880 for air. Other possible accretionary components such as ‘Q’ have $^{38}\text{Ar}/^{36}\text{Ar}=0.1873$ (Busemann et al. 2000), almost indistinguishable from air, while fractionated solar Ar can have $^{38}\text{Ar}/^{36}\text{Ar}$ ratios greater than air ($^{38}\text{Ar}/^{36}\text{Ar}=0.205$; Benkert et al. 1993) due to implantation fractionation analogous to that observed in Ne isotopes (Grimberg et al. 2006).

While it is clear that simple consideration of only $^{38}\text{Ar}/^{36}\text{Ar}$ cannot in itself enable resolution of a potential Q-component or hybrid solar/implanted solar Ar contribution to the mantle $^{38}\text{Ar}/^{36}\text{Ar}$, the simplest explanation is that this Ar isotope pair is dominated by air that has been recycled into the mantle (Holland & Ballentine 2006). We develop this argument further in the discussion of mantle Kr and Xe.

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Krypton: both hidden and ignored

The krypton isotopic composition of mantle gases remains largely unreported, with most analyses providing isotopic compositions little different from modern air. Unlike the unambiguous identification of the isotopic composition of mantle Ne, similar to mantle $^{38}\text{Ar}/^{36}\text{Ar}$, it has been impossible to distinguish mantle Kr from atmosphere contamination. The mantle and atmosphere Kr isotopic composition is uniformly depleted in light isotopes by approximately 0.8 per cent/amu from solar. The Q-component in carbonaceous chondrites is depleted in light isotopes by approximately 1.1 per cent/amu compared with solar (e.g. Pepin & Porcelli 2002). Again, it is impossible to use simple consideration of mantle Kr isotopes to distinguish between a recycled-air and a possible

Table 1. Ar isotopic ratios from Bravo Dome, Sheep Mountain and McElmo Dome (all data 1σ).

<table>
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<th>sample</th>
<th>$^{40}\text{Ar}/^{36}\text{Ar}$</th>
<th>error</th>
<th>$^{38}\text{Ar}/^{36}\text{Ar}$</th>
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7. Krypton: both hidden and ignored

The krypton isotopic composition of mantle gases remains largely unreported, with most analyses providing isotopic compositions little different from modern air. Unlike the unambiguous identification of the isotopic composition of mantle Ne, similar to mantle $^{38}\text{Ar}/^{36}\text{Ar}$, it has been impossible to distinguish mantle Kr from atmosphere contamination. The mantle and atmosphere Kr isotopic composition is uniformly depleted in light isotopes by approximately 0.8 per cent/amu from solar. The Q-component in carbonaceous chondrites is depleted in light isotopes by approximately 1.1 per cent/amu compared with solar (e.g. Pepin & Porcelli 2002). Again, it is impossible to use simple consideration of mantle Kr isotopes to distinguish between a recycled-air and a possible
Q-component origin for Kr in the Earth’s mantle. However, the mantle $^{84}\text{Kr}/^{36}\text{Ar}$ in both the MORB-source mantle and well-gas mantle are remarkably similar to the elemental abundance (and isotopic composition) of seawater (figure 4). This is used to support a recycled air-dissolved-in-seawater origin for these species in the mantle (Holland & Ballentine 2006).

8. Xenon: massive early planetary volatile loss and fractionation

The full detail of the Xe isotope system is reviewed in several papers (Pepin 2000; Pepin & Porcelli 2002, 2006; Porcelli & Ballentine 2002). A key observation is that the terrestrial atmosphere is depleted in the light isotopes of Xe by approximately 4.2 per cent/amu compared with solar and is significantly more fractionated than Kr. The terrestrial atmosphere in addition contains $^{129}\text{I}$ contributions to $^{129}\text{Xe}$, and $^{244}\text{Pu}$ and U + Th contributions to $^{131,132,134,136}\text{Xe}$. Nevertheless, if the $^{244}\text{Pu}$ and U + Th additions to the atmosphere are subtracted, the resulting non-radiogenic atmosphere composition cannot be simply related to the fractionation of solar Xe, being underabundant in the two heaviest isotopes of Xe. This has led to the use of ‘U–Xe’ as the non-radiogenic precursor Xe isotopic composition of the Earth (Pepin 2000). The non-radiogenic fractionated U–Xe, called NEA-Xe, provides the main reference for resolving subsequent addition of U-, Pu- and I-derived isotopes of Xe to the atmosphere (Pepin & Porcelli 2006).

The timing of this volatile loss can be accessed by consideration of model ‘closure’ ages for both the I–Xe and Pu–Xe systems separately (e.g. Wetherill 1975) or by combining the two decay systems (Pepin & Phinney 1976). There are variants of this approach (e.g. Pepin & Porcelli 2006), but all converge on a closure age for terrestrial volatile loss at ca 80 Ma after Solar System formation. It should
be noted that the $^{129}\text{Xe}^*/^{130}\text{Xe}^*$ (where the asterisk designates $^{129}$I-derived Xe and $^{244}$Pu-derived Xe) in the convecting mantle (MORB-source) and atmosphere are identical—it is not possible to resolve closure of one reservoir from the other (Pepin & Porcelli 2006). Critically for this work, from I–Pu systematics, it can be calculated that the silicate Earth has lost almost 99 per cent of its Xe and therefore other noble gases during the accretionary process (Porcelli et al. 2001).

9. Non-radiogenic xenon: an accretionary component in the mantle mixed with air-derived Xe

The non-radiogenic Xe isotopes, $^{124,126,128,130}\text{Xe}$, in the convecting mantle (MORB-source) are dominated by Xe with an isotopic composition very similar to air. An excess in these isotopes was first shown by Caffee et al. (1999) in mantle-rich CO$_2$ well gases, with samples lying on the air–solar mixing line. The most solar-rich gas, from Bravo Dome in New Mexico, had a 10 per cent excess above air value. Since solar and Q-Xe are so similar in composition, it is not possible from these samples to distinguish isotopically between sources.

Holland & Ballentine (2006), collecting and analysing a full suite of samples, were able to investigate the Xe isotope system at Bravo Dome in more detail. In particular, we were able to define, independent of Ne, the mantle endmember to be $^{129}\text{Xe}/^{130}\text{Xe}=7.90\pm0.14$ (figure 5), similar to the highest observed value in

![Figure 5. The intersection of the Bravo Dome Xe array with the MORB array defines the Xe mantle composition. In an analogous way to Ne isotope systematics, the Xe data from the Bravo Dome system show a two-component air–crust mixture that intersects with the MORB air–mantle mixing line to define the mantle Xe isotopic endmember to be $^{129}\text{Xe}/^{130}\text{Xe}=7.90\pm0.14$. The MORB–air mixing line is defined by poping rock data (Moreira et al. 1998). Vertical and horizontal dashed lines are the intersection of the MORB array with the Bravo Dome array and indicate the convecting mantle values.](#)
MORB (Kunz et al. 1998). This dataset then showed that, even for the most mantle-rich sample, approximately 50 per cent of the Xe was due to shallow air contamination. For the first time, we were then able to define the convecting mantle as a mixture of 20 per cent solar or Q-derived Xe, but dominated (80%) by a component with an isotopic composition identical to air. The mantle accretionary/primitive 20Ne/132Xe ratio is approximately 1400. This is clearly not a solar ratio (solar 20Ne/130Xe $\times$ 500 000–1 000 000; Wieler 2002), is similar to the values observed in meteorites (figure 6) and compatible with a model in which the source of mantle Xe is also a trapped accretionary component.

The well-gas sample suite of Holland & Ballentine (2006) is able to unambiguously resolve, for the first time, the mantle endmember components for all noble gas isotopes. It is now possible to compare the elemental abundance pattern of the non-radiogenic heavy noble gases in the mantle, $^{36}$Ar/$^{84}$Kr/(80%)$^{130}$Xe, with those in MORB and potential sources of these species, the atmosphere and oceans. The well-gas and least degassed MORB sample, ‘popping rock’ 2PDD43 (Moreira et al. 1998), have indistinguishable mantle elemental abundance patterns. In the simplest case, one might expect the degassing residue (MORB) and gas released from a magma (well gases) to fractionate in opposite directions. The similar value in both sample suites strongly suggests that both represent a minimally fractionated mantle system. This system is identical to a seawater composition admixed with sedimentary-derived Kr and Xe (figure 4). Since Ne (and He) has such a low solubility in seawater, this source would have no effect on the primitive Ne (or He) isotopic composition of the mantle. If the noble gases are not decoupled from the

Figure 6. Carbonaceous chondrite $^{20}$Ne/$^{132}$Xe versus $^{20}$Ne. The range of Ne concentration observed in carbonaceous chondrites is sufficient to provide Ne in the gas-rich mantle source reservoir (vertical dot-dashed line; see text). Also, the Ne/Xe ratio observed in the highest-concentration meteorites is similar to accretionary Ne/Xe in the terrestrial mantle (horizontal dot-dashed line). Carbonaceous chondrite (CC) data (diamonds, CC type 1; squares, CC type 2; triangles, CC type 3; circles, CC type 4) from Mazor et al. (1970) and Scherer & Schultz (2000).
seawater in which they are dissolved during the subduction process, an ongoing area of research, recycled seawater accounts for approximately 50 per cent of the water now in the convecting mantle and is compatible with constraints imposed by deuterium isotope considerations (Holland & Ballentine 2006).

We add one note of caution. High-precision well-gas and MORB Xe isotope data have been compared and shown to be different in their plutogenic fission Xe spectrum (Pepin & Porcelli 2006). These authors have attributed this difference to a different closure age of distinct reservoirs in the mantle. The well-gas samples are, however, otherwise almost identical to MORB popping rock in noble gas elemental and isotopic compositions, including $^{129}\text{Xe}/^{130}\text{Xe}$. It is difficult to understand how differential closure and therefore differential volatile loss would then balance with the noble gas input over time from U, Th and K decay, and possibly air recycling, in different reservoirs yet still provide for such similar noble gas compositions. While the Xe-fission isotopic difference between MORB and well gases remains unresolved, this does not affect the conclusions above drawn from the non-radiogenic Xe isotopes, $^{124,126,128,130}\text{Xe}$.

10. Support for subducted ‘air’ noble gases in the terrestrial mantle

The concept of seawater recycling into the mantle has been controversial, with authors, respectively, arguing for a possible air component in Ar and Xe (Porcelli & Wasserburg 1995) or a subduction barrier effectively preventing any surface return to the mantle (Staudacher & Allegre 1988). While observations of air-derived components in MORB have been used to support a recycling model (Bach & Niedermann 1998; Sarda et al. 1999), shallow air contamination of the samples has been a significant complicating factor (Ballentine & Barfod 2000).

Serpentine inclusions within olivine from the Higashi-akaishi peridotite body, Japan, provide a new insight into the subduction process. These have been exhumed from the depths of approximately 120 km and originate through dewatering of the subducting slab and subsequent hydration reactions with the host mantle-wedge olivine (Mizukami & Wallis 2005). These inclusions contain atmosphere-derived noble gases in seawater proportions and halogen ratios indistinguishable from marine pore fluids. First results indicate that subduction of fluids with a seawater (marine pore fluid) noble gas signature occurs to depths of at least 120 km (Sumino et al. 2007).

The global impact of seawater noble gas subduction can be investigated by adapting the numerical modelling approach of Van Keken & Ballentine (1998, 1999). In these models, a seawater noble gas flux into the mantle can be balanced with the model $^{40}\text{Ar}$ production by K decay to reproduce the observed convecting mantle (MORB-source) $^{40}\text{Ar}/^{36}\text{Ar}$. These models produce a plume-forming region at the core–mantle boundary with a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio three to four times lower than the average convecting mantle (Ballentine et al. 2007). This compares well with observation, where we now know the convecting mantle (MORB-source) $^{40}\text{Ar}/^{36}\text{Ar}=42\,450\pm4420$ (Holland & Ballentine 2006), which is between 5.1 and 9.3 times higher than plume maximum values of $^{40}\text{Ar}/^{36}\text{Ar}=4530$ (Iceland—Trieloff et al. 2000), 8000 (Juan Fernandez—Farley & Craig 1994), 8300 (Loihi—Trieloff et al. 2000) and 7600 (Reunion—Trieloff et al. 2002).
11. Mass balance for a mantle-‘trapped’ noble gas meteorite source

Using a $^3$He concentration in the MORB-source region of $4.4\times10^{-11}\,\text{cm}^3(\text{STP})\,^3\text{He}\,\text{g}^{-1}$ (Porcelli & Ballentine 2002), convecting mantle He/Ne and He/Xe ratios at $^{20}\text{Ne}/^{22}\text{Ne}=12.5$ (Moreira et al. 1998) and knowledge that even these samples are 80 per cent atmospheric Xe (Holland & Ballentine 2006), we obtain a primordial Ne concentration of $1.1\times10^{-10}\,\text{cm}^3(\text{STP})\,^{20}\text{Ne}\,\text{g}^{-1}$ and a primordial Xe concentration of $7.8\times10^{-14}\,\text{cm}^3(\text{STP})\,^{132}\text{Xe}\,\text{g}^{-1}$ in the convecting mantle.

We have already established earlier in this paper that we require a gas-rich mantle reservoir to flux $^3$He into the convecting mantle. The concentration of $^3$He in this mantle reservoir can be estimated if we assume a closed system, BSE U+Th, an initial $^3$He/$^4$He of $120R_a$ and a present-day $^3$He/$^4$He similar to the maximum observed in plumes of $50R_a$, which is approximately 100 times the $^3$He concentration of the convecting mantle itself (e.g. Porcelli & Wasserburg 1995).

Scaling Ne and Xe concentrations to $^3$He then gives us gas-rich mantle source reservoir concentrations of $1.1\times10^{-8}\,\text{cm}^3(\text{STP})\,^{20}\text{Ne}\,\text{g}^{-1}$ and $7.8\times10^{-12}\,\text{cm}^3(\text{STP})\,^{132}\text{Xe}\,\text{g}^{-1}$.

These values compare with the highest concentrations observed in bulk meteorite samples of approximately $1\times10^{-5}\,\text{cm}^3(\text{STP})\,^{20}\text{Ne}\,\text{g}^{-1}$ (figure 6) and approximately $1\times10^{-8}\,\text{cm}^3(\text{STP})\,^{132}\text{Xe}\,\text{g}^{-1}$ (compiled from Mazor et al. (1970) and Scherer & Schultz (2000)). As discussed earlier, Xe isotopes require that we must allow for at least a 100-fold loss of noble gases during the accretionary process (Porcelli et al. 2001). This reduces the maximum noble gas concentrations that could have been present on the Earth at the end of accretion to $1\times10^{-7}\,\text{cm}^3(\text{STP})\,^{20}\text{Ne}\,\text{g}^{-1}$ and $1\times10^{-10}\,\text{cm}^3(\text{STP})\,^{132}\text{Xe}\,\text{g}^{-1}$. These are still approximately an order of magnitude higher than the gas-rich mantle source reservoir concentrations calculated above.

While a necessarily crude calculation, we do not need to resort to special circumstances or to only the most gas-rich material to form the source of the volatile-rich terrestrial mantle reservoir—this is well within the range of observed concentrations in bulk meteorite samples, even allowing for 99 per cent volatile loss.

12. Synthesis and conclusions

(i) The terrestrial atmosphere is unique in its noble gas isotopic and elemental composition within the Solar System.

(ii) This isotopic signature dominates the mantle Ar/Kr/(80%)Xe non-radiogenic isotopes but in seawater proportions, allowing for a small ocean sediment contribution.

(iii) Ocean island volcanic systems have significantly lower maximum observed $^{40}\text{Ar}/^{36}\text{Ar}$ values at $^{20}\text{Ne}/^{22}\text{Ne}=12.5$ than the convecting mantle.

(iv) This last observation is consistent with numerical models that investigate recycled atmosphere-derived noble gases into the convecting mantle and show the mantle source region of plumes to have lower $^{40}\text{Ar}/^{36}\text{Ar}$ than the convecting mantle.
It would be an extreme coincidence if the unique isotopic composition and abundance pattern of the atmosphere, modified by the respective noble gas solubility in water, were to be found in the mantle by any process other than subduction of air dissolved in seawater into the mantle system. The dominant source of the non-radiogenic heavy noble gases (Ar, Kr and (80%)Xe) in the convecting mantle is due to the subduction of air dissolved in seawater-derived pore fluids. These species do not then represent a primary or accretionary reservoir within the mantle that later degassed to form the atmosphere. Further observations of the mantle strongly suggest that we have evidence for a primitive reservoir within the Earth, unfractionated since accretion.

(v) The helium isotopic composition of the convecting mantle is too high for a closed system model to simply match the observed $^{3}\text{He}$ and $\text{U} + \text{Th}$ concentrations.

(vi) A $^{3}\text{He}$ flux into the convecting mantle from a deep volatile-rich mantle reservoir provides one explanation for the high convecting mantle $^{3}\text{He}/^{4}\text{He}$.

(vii) The Ne isotopic composition of the convecting reservoir is $^{20}\text{Ne}/^{22}\text{Ne} = 12.5$, and is indistinguishable from that expected for a SWI accretionary source.

(viii) Twenty per cent of the convecting mantle non-radiogenic Xe is primordial but its isotopic composition cannot distinguish between a solar nebula and trapped (Q) meteorite source.

(ix) The primordial $^{20}\text{Ne}/^{132}\text{Xe}$ ratio in the mantle of approximately 1400 (figure 6) is within the range observed in the higher concentration component of bulk meteorites and distinct from the solar ratio (approx. 500 000–1 000 000).

The presence of neon indistinguishable from meteorite SWI neon in the terrestrial mantle together with meteorite proportions of primitive Ne/Xe strongly supports a trapped accretionary noble gas source for these volatiles now in a deep volatile-rich reservoir in the mantle. The mechanism and timing of formation of this reservoir remain enigmatic. Possible explanations may be dry subduction of a late solar wind-irradiated veneer (Tolstikhin & Hofmann 2005). This would allow for bulk planetary degassing, volatile loss and fractionation of the atmosphere to its current noble gas state independently of arrival. Alternatively, the Earth may have retained some volatiles from the earliest phase of accretion. Xe isotopes require extensive gas loss (more than 99%) during accretion, with only a small percentage of the mantle preserving any accretionary signature at all. In the light of the recent modelling work pointing to multiple massive impacts in the formation of planets with Earth-like orbits (Morbidelli 2002), it is no surprise that, during the process of accretion, there has been a substantial loss of volatile elements from the accreting material.

Nonetheless, after correction for atmospheric contamination and water recycling, we have identified primordial noble gas signatures in the deep Earth that strongly suggest they were acquired from meteorites rather than gravitationally captured from the solar nebula. Trapped meteorite gases should therefore provide the starting point for a more refined understanding of the accretionary and post-accretionary loss processes that occurred to leave the volatile abundances observed in the terrestrial planets today.
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References


Hünenmohr H. 1989 Edelgase in U- und Th-reichen Mineralen und die Bistimmung der \(^{21}\text{Ne}\)-Dicktarget der \(^{18}\text{(a,n)}\)^{21}\text{Ne}-Kernreaction im Bereich 4.0–8.8 MeV. PhD thesis, Johannes-Gutenberg-Universität.


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What noble gases tell us about the mantle


