Partitioning experiments in the laser-heated diamond anvil cell: volatile content in the Earth’s core

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The present state of the Earth evolved from energetic events that were determined early in the history of the Solar System. A key process in reconciling this state and the observable mantle composition with models of the original formation relies on understanding the planetary processing that has taken place over the past 4.5 Ga. Planetary size plays a key role and ultimately determines the pressure and temperature conditions at which the materials of the early solar nebular segregated. We summarize recent developments with the laser-heated diamond anvil cell that have made possible extension of the conventional pressure limit for partitioning experiments as well as the study of volatile trace elements. In particular, we discuss liquid–liquid, metal–silicate (M–Sil) partitioning results for several elements in a synthetic chondritic mixture, spanning a wide range of atomic number—helium to iodine. We examine the role of the core as a possible host of both siderophile and trace elements and the implications that early segregation processes at deep magma ocean conditions have for current mantle signatures, both compositional and isotopic. The results provide some of the first experimental evidence that the core is the obvious replacement for the long-sought, deep mantle reservoir. If so, they also indicate the need to understand the detailed nature and scale of core–mantle exchange processes, from atomic to macroscopic, throughout the age of the Earth to the present day.

Keywords: high pressure; laser-heated diamond anvil cell; iodine; helium; partitioning; fibre laser

1. High-pressure experiments and the planetary context

Over the past few decades, experimental high-pressure research on material physical properties has had a fundamental impact on our understanding of static Earth structure, from detailed structural phase transitions to constraints on internal temperatures at the major discontinuities of the core and mantle. The trade-off in temperature and composition in seismological models drives a need

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for increasing resolution in tomography and has led to detailed experimental investigations in mantle phase equilibria with an increasing importance of minor and trace elements in end-member dense phases, and their effect on phase transitions, transport and thermodynamic properties.

Controls on the bulk composition of the Earth remain a fundamental problem in cosmochemistry and the geochemistry of planetary formation and have been examined systematically for all elements in the periodic table (Kargel & Lewis 1993; Allègre et al. 1995, 2001). Following Ringwood’s (1966, 1979) early analysis that matched refractory lithophile elements with the composition of CI chondrites (Allègre et al. 2001), high-pressure experiments have largely focused on the nature of the dominant minor (light) element in the core (e.g. Poirier 1994; Hillgren et al. 2000; Li & Fei 2003).

Early suggestions of a giant impact of a Mars-sized body (e.g. Hartmann & Davis 1975) evolved with substantial debate on an impact-triggered origin of the Earth–Moon system (for an overview, see Canup & Righter (2000)) that continues to the present day (Stevenson 2007, 2008). Recently, the possibility of more energetic collisions has led to possible extension of the magma ocean depth through high-temperature impactor core implantation (Canup 2004; Rubie et al. 2007; Solomatov 2007) and early tidal heating. The late stage Mars-like impact scenario (Halliday & Wood 2007) suggests that final equilibration in the Earth is likely to have taken place under mid-mantle pressures or greater and at higher temperatures. If equilibration took place over an extended magma ocean depth range, then increasing the range of pressure dependence of partitioning becomes important for assessing the average signature imparted to the mantle and core Rubie et al. (2003, 2007).

The various processes of accretion itself—the classic models of homogeneous and heterogeneous accretion—must be superposed on any planetary-size signature, particularly if processing was punctuated by a few events with unknown mass-transfer dynamics. The apparatus of choice in the majority of cases is the multi-anvil apparatus (e.g. Ito 2007) in its various forms designed to provide sufficient temperature homogeneity and volume for melt–melt/–crystal segregation. A coincidental feature of the multi-anvil press for such studies is that the working pressure range generally reported reaches a maximum near 25 GPa (though the limit can be higher), thought to be typical of the depth of the dominant phase of core–mantle segregation in the early Earth.

Figure 1. (Opposite.) (a) Schematic of the LHDAC showing anvil and sample configuration. The use of a 100 W air-cooled fibre laser with emission centred at 1070 nm (e.g. Model R4, SPI Lasers UK Ltd) greatly simplifies beam delivery. (b) Use of a noble gas pressure medium combined with a finely ground mixture makes possible convective mixing in the sample chamber. The sample regions shown represent the cavity between the diamond anvils and are shown to scale and illustrate the rapid decrease of volume and increase in aspect ratio with increasing pressure as the gasket thins. Style of flow is shown by the black arrows. Streaming flow (horizontal circulation) is observed in the high-melting temperature medium solid xenon (figure 2). Prolonged exposure to the IR heating laser eventually anneals the silicate and metal phases into well-defined regions. At the larger sample sizes the experiment most likely captures the mixing process in a magma ocean by effectively creating an emulsion of metal and silicate components. (c) Alternative sample configuration where typically a metal foil is sandwiched between a silicate layer of the composition of interest and an insulation layer from the anvil culet.
He, Ar, Xe mixed with Sil and Met alloy

(a) 1070 nm ruby doped fibre laser

(b) Figure 1. (Caption opposite.)

(c) 0.05 0.05 0.03 0.005

S1 beam metal alloy diamond anvil gasket insulation layer

S2 beam silicate
In the context of changing ideas on magma ocean models and processes, there is, from an experimental point of view, little choice but to determine the behaviour of chemical systems to the maximum pressures, and then attempt to reconcile all possible parameters. There has been, in general, no need to consider an extension of the pressure limit, especially considering the problems that were assumed with equilibration in the laser-heated diamond anvil cell (LHDAC). However recent LHDAC experiments (Bouhifd & Jephcoat 2003) with compared multi-anvil data (e.g. Thibault & Walter 1995; Li & Agee 1996; O’Neill et al. 1998; Gessmann et al. 1999; Chabot et al. 2005) show good agreement between the partition coefficients obtained with both techniques. The maximum temperature limit of the multi-anvil apparatus is near 3000 K (Ito 2007), whereas the LHDAC can in principle raise sample temperatures in direct proportion to a homologous temperature (required as the magma ocean deepens), and is the subject of §2.

2. LHDAC experiments

In this section, we summarize the method and analytical procedures used to perform a partitioning experiment in the LHDAC. In figure 1, we show a typical schematic LHDAC set-up with anvil and sample configuration. New fibre laser technology has greatly simplified the use of high CW and pulsed powers with the diamond anvil cell (DAC; figure 1a) removing much of the optics required for delivery. Operating in the infrared (IR) at 1070±10 nm, they interact with a sample in the same way as the conventional YAG laser at 1064 nm. With high beam quality (M2 values 1.0), they offer superior focusing characteristics, high stability and power variability to enable fine control of the sample temperature environment. Use of a noble gas pressure medium combined with a finely ground starting mixture makes possible convective mixing in the sample chamber. With light rare gases as pressure media, self-stirring is accomplished by rastering the laser beam for periods of up to 10–20 min across the sample (figure 1b). Prolonged exposure to the IR heating laser eventually anneals the silicate and metal phases into well-defined regions that adhere to the gasket enabling sample recovery (see fig. 3 of Bouhifd & Jephcoat 2003). The style of convective mixing within the sample chamber is indicated schematically by the arrows in figure 1b based on apparent motion of particles of the opaque starting mixture. LHDAC partitioning experiments become harder with increasing pressure and thinning of the gasket (and proximity of the diamond to the sample melts) which reduces stirring efficiency. Figure 1b shows a scaled variation in aspect ratio of the sample size as pressure is increased. A rare gas both allows mixing and provides the dynamic insulation from the anvil surface with the IR input laser absorbed continuously by the metal–silicate (M–Sil) melt phases. At the highest pressures, alternative configurations may be needed such as solid media insulation and layering in the sample cavity (figure 1c), but sample recovery in this geometry requires careful polishing to remove the insulation layer adjacent to the diamond and to sample with micrometre spatial resolution the heated volume for element analysis.

We find that a (solid) helium or argon medium works well to at least 60 GPa for sample thicknesses typically corresponding to 20 μm (figure 1b). Frames captured from a heating experiment in xenon (xenon is also the sample of interest rather than a preferred pressure medium) are shown in figure 2a. Mixing and heating
under the beam leads to melt–melt segregation. The melting temperatures of the noble gases increase rapidly with pressure and can lead to unusual effects: the xenon medium produced blue emission accompanying the rapid increase in temperature on M–Sil absorption of the IR beam (figure 2a–c), and displayed streaming of the M–Sil mixture in narrow filaments across specific regions of the gasket hole (figure 2d–f). The streaming effect is attributed to increased viscosity of xenon near or just below its melting temperature, suggested by the reduced mobility of the opaque sample fragments and locally strong refractive index contrast at the xenon melt–solid interface (figure 2c).

(a) Analytical methods

Starting compositions consisted of a glass of CI chondrite mixed with Fe, Ni, Co, S, Si (metallic powders) or KI (potassium iodide). The bulk composition was prepared from oxide and carbonate mixes through repeated cycles of grinding and fusion at 1800 K and rapidly cooled to obtain the glass of CI chondrite as listed in table 1 and used for the partitioning experiments.

The chemical compositions of the run products were analysed by an electron microprobe (JEOL JXA-8800R with four wavelength-dispersive spectrometers) with an accelerating voltage of 15 kV and a beam current of 20 nA, as well as by a scanning electron microscope (SEM, JEOL JSM-840A) equipped with an Oxford Instruments Isis 300 energy-dispersive analytical system (the accelerating voltage was 20 kV, with a beam current of 6 nA). Good agreement for argon analysis for each instrument was shown by Bouhifd & Jephcoat (2006). Counting times were typically approximately 100 s and Fe, FeS, Ni and Co metals, orthoclase, jadeite, wollastonite, periclase and corundum were employed as standards for both instruments.

For noble gases analysis (He, Ne and Ar so far), we used the ultraviolet laser ablation microprobe (UVLAMP) and noble gas mass spectrometry. The run products analysed by UVLAMP need no polishing or extra preparation, as we analysed them directly after removal from the diamond anvil cell. The analyses with the UVLAMP were carried out at the Open University, UK. The combined laser–microscope system uses a 10 Hz quintupled Nd–YAG laser with a wavelength of 213 nm and 10 ns pulses. The extracted gas was cleaned using three SAES AP-10 getters at 400°C and room temperature to remove active gases before analysing with a MAP 215-50 noble gas mass spectrometer. Analyses were corrected for measured blank values taken before and after each ablation. Further details regarding the UV laser technique can be found in Kelley et al. (1994) and Heber et al. (2007). Comparison of the Ar content as analysed by electron microprobe and Ar profile determined by UVLAMP for sanidine melt quenched from 15.5 GPa and 3000 K showed close agreement between both techniques (see fig. 2 in Bouhifd et al. in press). Multiple blanks are taken before and after analysis, and, in terms of redundancy, more than one experiment is performed at a given composition and pressure and cross checks made with pure metal as well as the M–Sil mixture. A typical recovered sample processed with the UVLAMP instrument is shown in figure 3.

As mentioned above, sample mixing in the DAC is expected to become much more constrained by the reduction in sample volume. (Free space is needed for the noble gas, but also the grain size of mechanically ground starting mixtures must be small enough to capture the average composition.) As pressure increases,
solid–solid and melt–solid partitioning become important, and we have also applied focused ion beam (FIB) lift-out techniques to prepare the recovered LHDAC samples for transmission electron microscopy (TEM) study (Greaves et al. 2008) with the process shown in figure 4. The FIB technique is now widely used in Earth and planetary materials science (Heaney et al. 2001), as well as for the LHDAC samples (Irifune et al. 2005). A combination of this technique and an ex situ lift-out method (Giannuzzi & Stevie 1999) makes possible the preparation of a site-specific thin foil of the recovered sample with typical dimensions of $10 \times 10 \times 0.1 \, \mu m$ and to transfer them onto a carbon film on a copper TEM grid.

Figure 2. (a–f) Frames captured from a LHDAC experiment with xenon as a pressure medium. Atomic transitions in xenon appear to be excited as judged by a prominent blue hue not visible with argon as a pressure medium. The smooth, tubular regions in (c) indicate unusual phase structure in xenon accompanying the visibly more viscous flow patterns of the M–Sil mixture during the experiment. (d–f) Streaming and filament flow of the M–Sil particulates induced in a solid xenon pressure medium.
It is well known that metal–silicate partitioning of siderophile elements is a function of the oxygen fugacity (Drake et al. 1989; Schmitt et al. 1989). It is therefore important to estimate the $f_{O_2}$ of the quenched silicate and metal liquids.

### Table 1. Chemical composition of starting materials (wt%).

<table>
<thead>
<tr>
<th></th>
<th>CNF&lt;sup&gt;a&lt;/sup&gt;</th>
<th>CCF&lt;sup&gt;b&lt;/sup&gt;</th>
<th>CFI&lt;sup&gt;c&lt;/sup&gt;</th>
<th>CCI&lt;sup&gt;d&lt;/sup&gt;</th>
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<td>30.5</td>
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<tr>
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<td>2.5</td>
<td>2.2</td>
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<tr>
<td>FeO</td>
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<td>3.8</td>
<td>4.6</td>
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<tr>
<td>MgO</td>
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<td>20.8</td>
<td>20.7</td>
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<td>2.0</td>
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<td>1.8</td>
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<td>10.0</td>
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<tr>
<td>S</td>
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</table>

<sup>a</sup>CNF, glass CI chondrite+Ni and Fe metals—composition similar to CI–C used by Thibault & Walter (1995) and Bouhifd & Jephcoat (2003).

<sup>b</sup>CCF, glass CI chondrite+Co and Fe metals—composition similar to CI–D used by Thibault & Walter (1995) and Bouhifd & Jephcoat (2003).

<sup>c</sup>CFI, glass CI chondrite+Fe metal+KI.

<sup>d</sup>CCI, glass CI chondrite+Fe, Ni, Si and S metal powders+KI.

Figure 3. Sample processed by UVLAMP technique (see text). Ablation pits are visible in both silicate (CI composition) and a metal (Fe–Ni alloy) inclusion just avoiding the silicate matrix. Pit volumes were measured by interference methods.

(b) Oxygen fugacity

It is well known that metal–silicate partitioning of siderophile elements is a function of the oxygen fugacity (Drake et al. 1989; Schmitt et al. 1989). It is therefore important to estimate the $f_{O_2}$ of the quenched silicate and metal liquids.
relative to the iron–wüstite (IW) buffer. The oxygen fugacities that have prevailed during our experiments were calculated after the experiments relative to the IW equilibrium from the activities of Fe and FeO in the metal and silicate phases following the relation:

$$\log f_{O_2}(\Delta IW) = 2 \log \left( \frac{a_{FeO}^{silicate}}{a_{Fe}^{metal}} \right) = 2 \log \left( \frac{X_{FeO}^{silicate} \cdot \gamma_{FeO}^{silicate}}{X_{Fe}^{metal} \cdot \gamma_{Fe}^{metal}} \right),$$

(2.1)

where $a_{FeO}^{silicate}$, $X_{FeO}^{silicate}$ and $\gamma_{FeO}^{silicate}$ are, respectively, the activity, molar fraction and the activity coefficient of FeO in the silicate liquid, and $a_{Fe}^{metal}$, $X_{Fe}^{metal}$ and $\gamma_{Fe}^{metal}$ are, respectively, the activity, molar fraction and the activity coefficient of Fe in the metallic phase.

To estimate the oxygen fugacities of our experiments, we assumed an ideal behaviour (an assumption that is likely to be valid at high temperatures) for the S-free system: the activities of FeO in the silicate liquid and of Fe in the metal can be estimated as their mole fractions.

For the S-bearing system, we adopt the activity model for the Fe–FeS binary determined at ambient pressure by Lee & Morita (2002), assuming no significant pressure effect on their activity coefficients. For comparison we also estimate the oxygen fugacities of our experiments by using the activity model of Asahara et al. (2004). The difference between the two methods is within a half log unit, which is a good agreement for $f_{O_2}$ estimations. The oxygen fugacity relative to the IW buffer calculated for each experiment varies from 1.5 to 3.0 log units below the IW buffer, and is consistent with the constraints on oxygen fugacity relevant to core–mantle differentiation (Walter & Thibault 1995).

Figure 4. Steps of the FIB specimen procedure. (a) The indentation in the gasket shim created by the diamond anvils with the sample visible in the centre, (b) an area is chosen for cross sectioning, (c) two trenches are milled, one on either side of the region of interest, (d) the sample is tilted and the sides and underside are cut, (e) a glass rod is used to remove the specimen from the sample, (f) the final specimen (~10×~0.1×~10 μm) is then placed on a carbon film on a copper TEM grid.
3. The example of Ni–Co partitioning

Arising from the original ‘siderophile element anomaly’ problem, nickel and cobalt have long been elements of choice for determining a pressure effect on partitioning and the success of the partitioning studies of Li & Agee (1996) on Ni and Co confirmed the substantial idea that segregation took place in a deep magma ocean leading to extensive work on the metal–silicate partitioning of siderophile elements (see Righter 2003 for review; Walter et al. 2000).

The relative Ni : Co ratio in the Earth’s upper mantle is nearly the same as primitive Solar System materials (that can be taken as identical to chondrites), indicating that they were not fractionated from one another during core formation (e.g. O’Neill & Palme 1998). This means that, on average, the ratio of their partition coefficients during core–mantle equilibration, $D_{Ni}/D_{Co}$, was nearly unity, placing a powerful constraint on core-formation models. Models for a deep magma ocean have gained acceptance despite some disagreement on the specific condition at which this may have taken place. High-pressure and high-temperature studies produced results consistent with metal–silicate equilibration at the base of the magma ocean that would have extended to as much as 60 GPa and above 2000 K and an oxygen fugacity two orders of magnitude below IW buffer (Chabot et al. 2005 and references therein).

Our preliminary (Bouhifd & Jephcoat 2003) and more recent experimental results (Bouhifd & Jephcoat 2008) show in fact that Ni and Co partitioning coefficients are similar from approximately 30 to 52 GPa (figure 5). More importantly, in the range 30–52 GPa our partitioning results account for both absolute and relative depletions of Ni and Co, providing direct experimental evidence for a deep-magma ocean necessary to explain the high abundance of both Ni and Co in the Earth’s mantle. The experiments are designed to follow the silicate liquidus with increasing pressure maintaining melt–melt partitioning. Hence temperature increases with pressure too, but has a smaller effect on the partitioning relations for Ni and Co.

In a pioneering study, Tschauner et al. (1999) found that the ratio $D_{Ni}/D_{Co}$ (partition coefficients of Ni and Co between solid metal and Mg–silicate perovskite) is approximately unity over the range of their experimental pressures extending from 27 to 80 GPa. However, they found that both $D_{Ni}$ and $D_{Co}$ decrease with increasing pressure, with the absolute values required to match chondritic models established at much lower pressures of approximately 25 GPa. Solid metal–solid silicate partitioning results might not be relevant to the conditions during the Earth’s core-formation processes as it is only one of three magma ocean models (Rubie et al. 2007; Jacobsen 2008). Late-stage impacts with a Mars-size body may be energetic enough to form a global melt (Tonks & Melosh 1993; Canup 2008).

In the LHDAC, the experiments take place at constant oxygen fugacity (approx. 2 log units below the IW buffer), and it has been noted that siderophile element depletions in the mantle are inconsistent with equilibration with Fe-rich metal at a single oxygen fugacity (O’Neill 1991; Wade & Wood 2005). In their recent work, Wade & Wood (2005) and Wood et al. (2008) present a model in which the magma ocean deepened in proportion to the size of the proto-Earth, and in which the Earth became more oxidized as it accreted (Wänke & Dreibus 1988; O’Neill 1991; Wade & Wood 2005). In this case, the Ni, Co, V, Cr, Mn,
W and Nb contents match those calculated from the chondritic abundances of refractory elements in the Earth. More importantly, the final value of the Ni partition coefficient predicted by the model is in good agreement with our experimental results at pressures near 42 GPa. This good agreement indicates that moderately siderophile elements (in this case Ni) have their partition coefficients established in the latest stages of accretion at high pressure (see Wood 2008). In a closing comment, and as a way to indicate the difficulty of extrapolation from lower pressure data, we note that Kegler et al. (2008) reported a slope change for Ni and Co partition coefficients near 5 GPa (which may or may not be significant for a deep magma ocean), but more importantly claimed that individual Co–Fe, Ni–Fe ratios required to satisfy present mantle composition are reached at different depths, arguing against a single-stage magma ocean equilibration. The present data do not support the extrapolation and confirm a lower mantle metal-silicate equilibration.

4. Noble gas solubility experiments in the LHDAC

The agreement of LHDAC results with conventional methods extends beyond the transition metals Ni and Co. The noble gas medium itself undergoes solubility and exchange with the M–Sil sample and, by analysing the separate gas contents of each, a partitioning coefficient can be obtained as well as pressure-dependent solubility. Bouhifd & Jephcoat (2006) reported results for argon that were readily derived by the standard methods of SEM and EMP. The solubility obtained for quenched sanidine and anorthite melts agreed closely,
and showed the same pressure dependence, with earlier work by piston–cylinder methods to approximately 5 GPa (White et al. 1989). The gas-loading technique (Jephcoat et al. 1987) surrounds a solid sample by the noble gas and this agreement for argon indicates little observable effect of this saturation of the starting material. Further, because the diamond anvil seals the sample environment, the LHDAC represents perhaps one of the better ways in high-pressure experiments to ensure no loss of volatile component. Argon solubility data were obtained to near 20 GPa showing marked changes in the silicate melt depending on the aluminium content of the starting material (Bouhifd & Jephcoat 2006) and reconciled earlier apparently discordant results for other (crustal) melt compositions (see Bouhifd et al. in press).

A key implication of this study with argon is that noble gas solubility data obtained in the LHDAC are accurate to at least 20 GPa and raised the question of the pressure dependence of helium partitioning for which only one study (Matsuda et al. 1993) has been reported at pressure and showed a systematic decrease in partition coefficients for all noble gases up to 10 GPa. Data on helium were obtained to only 6 GPa by the Matsuda et al. (1993) study, yet extrapolated values of the He partition coefficient near $10^{-4}$ were being used in models assessing the Earth’s likely core helium budget that corresponded to expected depths in a magma ocean with melt–melt or melt–solid exchange (Porcelli & Halliday 2001). Experimental data on helium partitioning would be relevant to the continuing debate on the origin of high $^3$He/$^4$He sources in the mantle (Porcelli & Elliot 2008), where it is argued that recently proposed mechanisms that increase the $^3$He : U ratio in mantle domains (and hence led to high $^3$He : $^4$He without the need for a primordial reservoir) are unlikely to operate in a convecting mantle. In order to assess the relevance of a possible core reservoir for helium (Porcelli & Halliday 2001; Trieloff & Kunz 2005), it is important to develop methods to measure the low solubility of helium in metallic alloy melts in the presence of silicate.

Figure 6 shows the first profiles obtained by UVLAMP methods on a Fe–Ni–Co alloy foil heated to 2500 ± 200 K. The data provide evidence for two regimes of He solubility: a narrow, near-surface layer, characterized by high solubility, and a bulk, interior regime of much lower average concentration. Measurements were made on metallic alloy samples alone, and on M–Sil mixtures. In both cases helium solubility measured in the metal was consistent, indicating no contamination from the silicate phase. By taking the ratio of the bulk concentrations of He measured in iron and a CI chondritic mixture, a partition coefficient is obtained that appears significantly higher than Matsuda et al. (1993) and fairly flat as a function of pressure to at least 17 GPa. As also observed for argon, helium solubility in the silicate melt drops above a critical pressure effectively increasing the partition coefficient into the metal phase. Further details can be found in Bouhifd et al. (submitted).

Figure 7 shows the net He content measured in the metal component after M–Sil and pure-metal experiments. There is some fluctuation, but within error the He concentration is roughly within the range 2–8 ppm and not strongly dependent on composition of the alloy. Extensive metallurgical studies on implanted helium solubility have been performed in the context of alpha particle embrittlement of metals (e.g. Rothaut et al. 1983; Jung 1991) in which precipitation of helium as nanometre-sized clusters is observed after annealing.
at high temperature with initial concentrations in the range 10–300 atomic ppm (approx. 4/56 of the ppm He in Fe by weight at low concentrations). This range of solubility corresponds well to the surface-subtracted bulk solubility retained in

Figure 7. Helium concentrations in metal alloys quenched from the melt. The measured concentrations are used to determine the partition coefficients for helium between molten silicates and Fe-rich alloy liquids (Bouhifd et al. submitted). UVLAMP Blank corrections have been subtracted. Circle, Fe 54–Ni 29–Co 17 alloy; diamond, pure iron metal; square, Fe 75–Ni 25 alloy. The line drawn at 7 ppm represents a typical concentration (100 atomic ppm) in experiments on He-implanted steel (Rothaut et al. 1983) at which nanometre-sized clusters form in the metal after high-temperature annealing.
the metal measured by UVLAMP (figure 7) and indicates that we are capturing the substitutional solubility of helium in the metal alloy (Rothaut et al. 1983) and not mechanically isolated pockets in a quenched melt.

Our recent LHDAC measurements indicate that the M–Sil partition coefficient of helium is increased by two orders of magnitude and using estimates of the helium supply in, for example, an early dense atmosphere (Porcelli & Halliday 2001) imply more than enough total $^3$He could have been partitioned into a segregating core to supply the total ocean-island basalt (OIB) flux (Bouhifd et al. submitted). Despite strong evidence for subsequent mantle degassing (see Porcelli & Pepin (2000) for review), enough helium may have been retained in the core from the early atmosphere for the core to continue to perturb mantle signatures up to the present day: variations in mantle $^3$He–$^4$He could in fact represent stochastic and infrequent transfer processes at the core–mantle boundary (CMB). The transfer of core material across the CMB into the mantle was judged viable for much lower expected core helium levels (Porcelli & Halliday 2001); the new partitioning data, showing increased helium content in the metal, reduce the level of core material transfer that would be required at the CMB.

The passage of an element out of the core is likely to be highly dependent on bonding. Helium exsolution and incorporation into the mantle may operate differently from transition metal and lanthanide exchange that is likely to be strongly related to perovskite or post-perovskite defect chemistry. Helium and other light noble gases behave differently, with their interactions with host material dominated by repulsive forces (Jung 1991). Single-site, perfect-crystal control is unlikely to dominate the transfer of He in a high-temperature environment, and a more energetically favourable process would be occupation of defect or grain boundary sites by nanometre-scale clusters as described by Rothaut et al. (1983) for metals. In fact, the observation of clustering and diffusion and growth at high temperatures in metals provides a mechanism for concentration of dissolved helium and migration out of the core flow to quiescent liquid-metal regions at the core–mantle boundary (where material is not entrained back into the core). Such an atomic-level enhancement of the helium local concentration at the CMB might outweigh any remaining mantle He signature after strong degassing and provide a further scenario for a core contribution to high $^3$He/$^4$He mantle samples. A clearer understanding awaits TEM of quenched CMB materials. Helium transfer need not be accomplished with pockets of core material infiltrating the mantle convection system and there may be no need therefore to invoke a mass balance of all trace elements when accounting for a mantle helium source from the core.

5. Metal–silicate iodine partitioning in the LHDAC

In their best bulk silicate Earth model, Kargel & Lewis (1993) noted from their calculated partition ratios as a function of atomic number that the halogens (Cl, Br and I) appear to have been strongly partitioned into the core. The calculation, as for all elements, is strongly dependent on the assumed volatility. Volatility corrections include both the degree of retention in the condensing nebula and other loss mechanisms once a planet is formed. Given the uncertainty of volatility processes specific to iodine, Kargel & Lewis (1993) allowed for a
weighted uncertainty, but the apparent iodine depletion remained substantial. A further interest in iodine lies directly in the extinct nuclide system \(^{129}\text{I} -^{129}\text{Xe}\) \((T_{1/2} = 15.7 \text{ Myr})\). Early core formation is likely to have resulted in iodine entering the core and production of radiogenic \(^{129}\text{Xe}\). There is no published experimental work to date on iodine partitioning at these conditions.

Liquid metal–silicate partitioning experiments were carried out on iodine in a LHDAC, at high temperature (2550 K) and high pressures (3.9–20 GPa). The effect of variable composition of the Fe-metal phase was investigated with the addition of Ni, FeS and FeSi to the starting composition (table 1). Figure 8 plots the partition coefficients obtained for both sulphur-bearing (with Ni) and sulphur-free compositions. There is a significant difference in the \(D_I\) measured for partitioning into either pure iron metal \((D_I \approx 1.2)\) or the sulphur–iron–nickel alloy \((D_I \approx 4.4)\). There is consistent meteoritic evidence for iodine’s chalcophile behaviour (Goles & Anders 1962) and sulphur has been shown to have an effect on the partitioning behaviour of other siderophile elements (e.g. Jana & Walker 1997) that is probably underpinned by the changes sulphur induces in the local structure of liquid Fe (Sanloup et al. 2002). A key feature of figure 8 is that pressure has no clear effect on the distribution of iodine between the molten metal and silicate liquid phases up to 20 GPa (Armytage et al. in preparation).

Immediate implications are that the volatility factors assumed for iodine are, not surprisingly, incorrect, and presumably the other halogens too, but are within the range of a generous uncertainty that reflects the poorly known nebular chemistry and planetary loss processes (Kargel & Lewis 1993). It is not clear whether a single volatility trend must apply to all elements and the scatter around such trends is not constrained. A general consequence is that the presence of other elements (such as perhaps any of the minor light components postulated...
for reducing core density) can substantially affect the distribution of trace elements between mantle and core. It is known that coupling between elements can complicate the simple classification of elements in terms of their individual distribution in the Earth (Allègre et al. 2001). A late-stage sulphur-rich metallic liquid composition (postulated to arise from the evolving oxygen fugacity of the mantle; Wade & Wood 2005; Wood et al. 2006) may preferentially sweep iodine and trace elements into the core with time. Given the high sulphur budgets for the core, however, iodine partitioning in sulphur-bearing liquids probably also factored in the early stages of core formation too.

(a) Implications for the xenon isotope inventory

The implications for the role of iodine on the $^{129}\text{Xe}$ budget will be developed elsewhere (Armytage et al. in preparation), but there are some implications that reflect on the interplay between partitioning experiments and noble gas isotope systematics. For example, given more recent ideas on a late-stage giant impact at 100 Myr, it is possible that much of the $^{129}\text{I}$ decayed to $^{129}\text{Xe}$ before the main process of core–mantle equilibration.

Xenon isotope systematics indicate that more than 99 per cent rare gas loss has occurred up to $10^8$ years after formation (Porcelli & Pepin 2000). For Xe, unlike He, the distinction between OIB/MORB is not important, and there are no accurate isotope data for OIB Xe. The atmosphere is strongly fractionated with respect to solar (due to early losses to space), and also may have started with a different heavy Xe isotope composition. MORB and well-gases appear less fractionated, which could be explained by trapped solar Xe in the mantle (which was then never fractionated) along with subducted Xe. ‘Solar Xe’, in the context of a mantle source, can just imply ‘not atmospheric’ and so not from subducted contamination. If there is primordial $^{3}\text{He}$, there should also be primordial Xe in the mantle, but the atmosphere is also anomalous in the heavy isotopes, regardless of fractionation (possibly of a composition called U–Xe) and the origin of this difference is not clear. Whether the interior has solar Xe or U–Xe is not constrained within the current precision of the data. The problem is more complicated because it appears that well gases and MORB, which are probably similar for mantle He and Ne, are not related in Xe isotopes (Pepin & Porcelli 2006). How Xe relates to mantle reservoirs is far more complex than the $^{3}\text{He}$ problem.

Incorporation of $^{129}\text{I}$ into the core is not related to ‘missing $^{129}\text{Xe}$’ that is missing with respect to the iodine composition of the mantle, and so was probably lost from the Earth. Further, any additional iodine in the core, if it lost $^{129}\text{Xe}$ to the mantle, increases the required loss. If substantial I is sequestered in the core, and it formed very early, then there is more $^{129}\text{Xe}$ expected than in the mantle. How much it adds depends upon the behaviour of Xe, and how it changes the isotopic composition depends upon the amount of $^{130}\text{Xe}$ in the core. However, it could not have had a large effect, since it is not observed in the isotopic evolution of the mantle: either there was a large amount of Xe in the core as well, so that the $^{129}\text{Xe}–^{130}\text{Xe}$ did not change despite all the radiogenic production, or there was enough $^{130}\text{Xe}$ in the mantle to dilute the radiogenic $^{129}\text{Xe}$ in the same way. Either scenario requires large losses of Xe subsequently, though this fits with current Xe models.
In no mantle Xe-isotope models is there a need for an addition from the core of $^{129}$Xe. Data for OIB are sparse, but it seems that there are no unusual ratio analogues to $^3$He/$^4$He. If the core contributes $^3$He to OIB, whether it affects Xe depends upon the He:Xe ratio of the core compared with the mantle. It could be either much higher or lower depending on the He content of the core, which in turn depends on early atmosphere composition and again is not well constrained.

There is no apparent $^{129}$Xe missing on the Earth, since it clearly must have been lost to space and there are also arguments against missing $^{129}$Xe based on Pu-derived $^{136}$Xe. Core Xe composition is not required to solve any immediate Xe anomaly. Nevertheless, partitioning of iodine into the core, eventually decaying to $^{129}$Xe, is not disallowed based on mantle Xe systematics.

6. Concluding remarks

Our studies so far with the LHDAC indicate that, from transition metal to light and heavy volatile components, the LHDAC technique yields results consistent with previous work. The partitioning of different elements between an Fe-rich alloy and silicate melts can now be performed at pressures appropriate to a major part of the Earth’s lower mantle.

A systematic increase in the pressure range of partitioning studies will provide valuable insight into the processes of core formation and the validity of high-temperature magma-ocean models. A weak pressure dependence of partitioning behaviour, or asymptotic trends, can leave the depth of segregation open. One would then be forced to examine more closely other contributing factors such as the extreme temperature dependence and oxygen fugacity at constant pressure to define unique segregation conditions. Ultimately, all element partitioning must be compositionally consistent, but that also requires that we understand the nebular formation process and degree of volatility in initial accretion, as well as perhaps the uniformity of mantle sampling.

At some stage, planetary accretion probably involved all three phases of matter in the solid, liquid and vapour phases. Here we have described the case in which exchange with an early, dense atmosphere and melt–melt partitioning were critical stages in the incorporation of volatiles. Measurements of volatile partitioning enable tests of the volatility corrections in nebular formation, for which many elements are poorly constrained. As well as a repository for a suite of minor elements, the Earth’s core may act as a permanent reservoir both for trace and for immiscible volatile components.

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