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A Refined Solution to the First Terrestrial Pb-isotope Paradox

D. T. MURPHY*, B. S. KAMBER AND K. D. COLLERSON

ADVANCED CENTRE FOR QUEENSLAND UNIVERSITY ISOTOPE RESEARCH EXCELLENCE (ACQUIRE), DEPARTMENT OF EARTH SCIENCES, STEELE BUILDING, ST. LUCIA CAMPUS, ST. LUCIA, BRISBANE, QLD. 4072, AUSTRALIA

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The first terrestrial Pb-isotope paradox refers to the fact that on average, rocks from the Earth's surface (i.e. the accessible Earth) plot significantly to the right of the meteorite isochron in a common Pb-isotope diagram. The Earth as a whole, however, should plot close to the meteorite isochron, implying the existence of at least one terrestrial reservoir that plots to the left of the meteorite isochron. The core and the lower continental crust are the two candidates that have been widely discussed in the past. Here we propose that subducted oceanic crust and associated continental sediment stored as garnetite slabs in the mantle Transition Zone or mid–lower mantle are an additional potential reservoir that requires consideration. We present evidence from the literature that indicates that neither the core nor the lower crust contains sufficient unradiogenic Pb to balance the accessible Earth. Of all mantle magmas, only rare alkaline melts plot significantly to the left of the meteorite isochron. We interpret these melts to be derived from the missing mantle reservoir that plots to the left of the meteorite isochron but, significantly, above the mid-ocean ridge basalt (MORB)-source mantle evolution line. Our solution to the paradox predicts the bulk silicate Earth to be more radiogenic in $^{207}Pb/^{204}Pb$ than present-day MORB-source mantle, which opens the possibility that undegassed primitive mantle might be the source of certain ocean island basalts (OIB). Further implications for mantle dynamics and oceanic magmatism are discussed based on a previously justified proposal that lamproites and associated rocks could derive from the Transition Zone.

KEY WORDS: *Pb isotopes, paradox, mantle Transition Zone, undegassed mantle, core formation*

INTRODUCTION

The Pb-isotope system is arguably one of the most powerful tools available to geochemists for deciphering terrestrial differentiation processes. It is particularly useful for tracing the extraction history of continental crust from the mantle. Uranium and Th are strongly lithophile refractory elements and were concentrated in the bulk Earth during accretion whereas the moderately volatile daughter element Pb is believed to be depleted. There is the added possibility that because of its chalcophile character, appreciable amounts of Pb are concentrated in the core. Thus, the U/Pb and Th/Pb ratios of the various silicate Earth reservoirs are high and, with the exception of some ancient samples, all terrestrial rocks contain a very significant proportion of radiogenic Pb. Silicate Earth Pb-isotope systematics reflect the fact that U and Th are highly incompatible and very strongly concentrated in the continental crust, yet only U is redox-sensitive. Lead, which is less incompatible than its parent elements, is highly mobile in fluids and as a result, over-abundant in the continental crust relative to elements with similar partition coefficient for anhydrous mantle melting (Miller *et al.*, 1994; Brenan *et al.*, 1995).

The U–Pb isotope system is complex not only because of the contrasting chemistry of U and Pb but also because there are two U isotopes that decay to two different isotopes of Pb. There is a near order of magnitude difference in half-life between the two U isotopes, which means that Pb isotopes evolve in a highly non-linear fashion. This provides valuable temporal resolution in geochemical modelling that is not available for other isotope systems and allows geochronology by measurement of the daughter (Pb) isotope ratios only. As a result, a family of rocks of the same age and initial Pb-isotope composition that have evolved with different U/Pb ratios in a closed system define a Pb–Pb isochron in a $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ plot. The Pb-isotope characteristics

*Corresponding author. Telephone: ++61 7 3365 9776. Fax: ++61 7 3365 1277. E-mail: d.murphy@earth.uq.edu.au

of meteorites exemplify this idea because most meteorites have not undergone significant U–Pb fractionation since their formation. They define a 4·56 Ga isochron, which approximates the time of initial condensation from the solar nebula. Importantly, irrespective of the time of accretion, all Solar System material, including the bulk Earth, is expected to plot on this isochron.

It has long been known that there exists a paradox in the U–Pb systematics of the Earth, the solution of which is likely to contain important information regarding planetary differentiation. In the original definition by Allègre (1969), the first terrestrial Pb-isotope paradox referred to two observations. First, the majority of rocks that occur at the Earth's surface [i.e. the accessible Earth consisting of mid-ocean ridge basalts (MORB), ocean island basalts (OIB) and upper continental crust] have significantly higher $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ than carbonaceous chondrites. Second, on average, all three reservoirs of the accessible Earth plot significantly to the right of the meteorite isochron. Later definitions have reduced the first terrestrial Pb-isotope paradox to the second observation.

The paradox requires that the rocks at the Earth's surface or their mantle source have evolved with a $^{238}U/^{204}Pb$ (μ) that is significantly higher than that of chondrites and that a hidden reservoir, whose Pb-isotope composition plots to the left of the meteorite isochron, exists in the deep Earth. Depending on the initial terrestrial Nd- and Hf-isotope compositions, there is a possibility that combined Nd- and Hf-isotope systematics might also require a hidden reservoir to complement the MORB-source mantle and continental crust (Blichert-Toft & Albarède, 1997).

There is a second terrestrial Pb-isotope paradox that adds further complexity and potential to Pb-isotope systematics. This refers to the Th/U ratio of the MORB-source mantle. Namely, the present-day Th/U ratio of the depleted mantle (2·6; Galer & O'Nions, 1985) is different from and lower than the ratio that could have produced the Pb-isotope composition of MORB-source mantle in a closed-system environment (3·75). Although the second paradox will not be addressed specifically in this paper, it is important to keep in mind that any solution to the first paradox must also be compatible with solutions to the second paradox.

The purpose of this paper is to review previous models that have attempted to explain the first terrestrial Pb-isotope paradox and to present a new solution based on expansion of a previously published model for the petrogenesis of lamproites (Murphy *et al.*, 2002) and a literature survey of the Pb-isotope compositions of lower-crustal xenoliths and continental alkaline volcanic rocks.

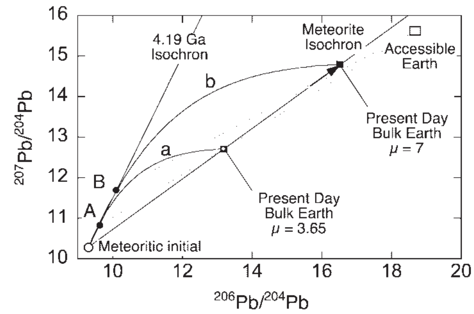

Fig. 1. A model of the $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ evolution of the Earth illustrating the timing of catastrophic core formation, assuming that the first terrestrial Pb-isotope paradox is solved by incorporation of Pb into the core [the core Pb-pumping scenario of Allègre *et al.* (1982)]. We use modern marine sediments (Hemming & McLennan, 2001) to approximate the accessible Earth (□) and a bulk Earth that evolved with a fixed μ of 3·65 (■) to calculate the timing of core formation from its Pb-isotope composition. The line connecting accessible Earth and bulk Earth (dashed line) must pass through the core and the core must plot on the bulk Earth evolution line (a). It is therefore possible to calculate the Pb-isotope composition of the core from the intersection of these two lines (A; $^{206}Pb/^{204}Pb$ 9·627 and $^{207}Pb/^{204}Pb$ 10·829). The position of the core on the bulk Earth evolution line yields the timing of core formation (4·19 Ga). For a bulk Earth with a μ of seven, catastrophic core formation at 4·19 Ga cannot explain the first terrestrial Pb paradox because the tie-line between the accessible Earth and the calculated core composition (B) does not pass through the bulk Earth value that is found at more radiogenic values (arrow) along the meteorite isochron. The unique core formation time for each μ is obtained by iteratively adjusting one parameter until bulk Earth plots along the line connecting accessible Earth and core. High bulk Earth μ requires late core formation whereas bulk Earth μ values $<3·65$ would yield shorter core formation periods.

PREVIOUS SOLUTIONS TO THE FIRST TERRESTRIAL Pb-ISOTOPE PARADOX

The core as the hidden Pb reservoir

There is no plausible process that could explain why the Pb-isotope composition of the bulk Earth should not plot along the 4·56 Ga meteorite isochron (Galer & Goldstein, 1996). In view of the observation that the accessible Earth plots significantly to the right of the meteorite isochron, Allègre *et al.* (1982) proposed that the Earth's core plots to the left of the isochron and balances the accessible Earth. Moreover, a low μ core would also be compatible with a bulk Earth of a composition similar to carbonaceous chondrites. This core Pb-pumping model (Allègre *et al.*, 1982) relies on the assumption that during core formation, Pb was partitioned into the core whereas U became enriched in the silicate Earth. With a μ of zero and no addition of radiogenic Pb after formation, the core's high $^{207}Pb/^{206}Pb$ isotope ratio was frozen to the left of the meteorite isochron, thus balancing the accessible Earth (Fig. 1). Removal of Pb but not U from the bulk Earth would also increase the silicate Earth μ (Fig. 1).

Because the core's Pb-isotope composition is unknown, the Pb-core pumping model cannot be directly tested but must be evaluated with independent constraints on maximum core formation time. For example, instantaneous accretion and core formation does not provide a solution to the first terrestrial Pb-isotope paradox, because the core would inherit a primordial Pb-isotope composition that does not plot away from and to the left of the meteorite isochron. In the absence of astrophysical and extinct radionuclide isotope constraints on accretion and core formation timing, Allègre *et al.* (1982) concluded that the first terrestrial Pb-isotope paradox indicated prolonged core formation over ~250 Myr from the beginning of accretion. Galer & Goldstein (1996) revisited the issue of core formation time on solutions for the first terrestrial Pb-isotope paradox with a more sophisticated accretion model. The basic conclusion of their model can be illustrated geometrically in a common Pb-isotope diagram (Fig. 1).

If the core were the only hidden Pb-isotope reservoir, its isotope composition would lie on a mixing line with that of the silicate Earth and the bulk Earth. The intersection of this mixing line with the meteorite isochron defines the bulk Earth Pb-isotope composition (Fig. 1). Thus, for an arbitrary intersection point (i.e. bulk Earth Pb-isotope composition) the bulk Earth Pb-isotope evolution curve can be reconstructed (Fig. 1). Projection of the silicate Earth–bulk Earth tie-line onto the bulk Earth evolution yields the core Pb-isotope composition and an estimate of catastrophic core formation time. Thus, for any given estimate of the Pb-isotope composition of the silicate Earth, catastrophic core formation time can be calculated as a function of bulk Earth μ. The concept of instantaneous catastrophic core formation is clearly unrealistic. The core formation flux is likely to have decayed exponentially in tandem with the terrestrial accretion flux. Hence, the chief limitation of using a catastrophic core formation model is to approximate a dynamic increase in the bulk silicate Earth μ with a single-stage increase. Galer & Goldstein (1996) gave a detailed discussion of a more realistic evolution of bulk silicate Earth μ during core formation. Nevertheless, the oversimplified catastrophic core formation scenario illustrates the main points in a model that can be appreciated by non-specialists and returns constraints very similar to the more sophisticated models. It is evident (Fig. 2) that irrespective of the true silicate Earth Pb-isotope composition, bulk Earth μ values higher than three yield unreasonably late core formation times. Thus, if the core is the only hidden Pb-isotope reservoir, the bulk Earth μ must be very low.

Accepting a very low bulk Earth μ, possible core formation times are calculated to between 116 and 178 Myr (Fig. 2) if the bulk silicate Earth is approximated with MORB-source mantle and upper continental crust, respectively. Because the MORB-source mantle Pb-isotope composition plots closer to the meteorite isochron, a calculation in which bulk silicate Earth is approximated by the MORB-source mantle end-member yields younger core formation ages than estimates based on average upper continental crust or sediment end-members (Fig. 2). Regardless, if bulk silicate Earth has a similar Pb-isotope composition to the accessible reservoirs at the Earth's surface, minimum core formation times must exceed 100 Myr. This constraint is very similar to the core formation ages that Galer & Goldstein (1996) obtained when approximating bulk silicate Earth with upper continental crust and MORB-source mantle. Galer & Goldstein (1996) concluded, however, that the timing of core formation was closer to 60 Myr because they used bulk silicate Earth values that plot significantly closer to the meteorite isochron than both MORB-source mantle

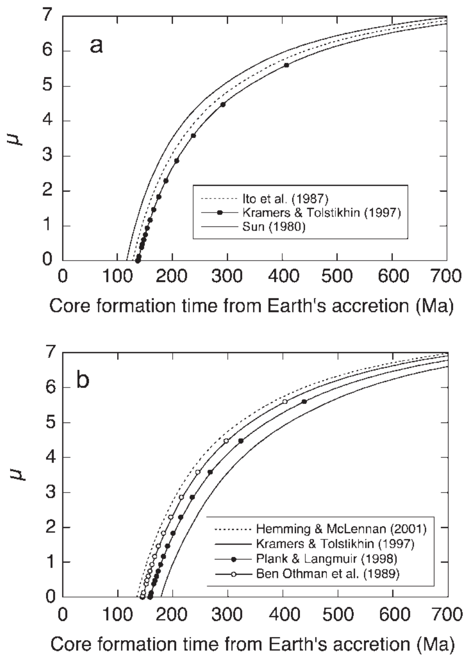

Fig. 2. Plots of the timing of catastrophic core formation vs bulk Earth μ for different approximations of the accessible Earth. (a) Plot of catastrophic core formation time (from Earth's accretion) vs μ for three approximations of MORB-source mantle Pb-isotope composition (Sun, 1980; Ito *et al.*, 1987; Kramers & Tolstikhin, 1997). In each case the calculation illustrated in Fig. 1 is iterated for a range of bulk Earth μ to calculate the timing of catastrophic core formation. For low μ there is very little variation in timing in all three curves. A minimum timing for catastrophic core formation can be calculated for each MORB-source mantle approximation as μ approaches zero. (b) Analogous to (a) but for four approximations of average upper continental crust Pb-isotope composition (Ben Othman *et al.*, 1989; Kramers & Tolstikhin, 1997; Plank & Langmuir, 1998; Hemming & McLennan, 2001). The curves are not as steep as those for the MORB approximations, but have the same shape. Estimated core formation times are longer than in (a) because continental crust plots farther off the meteorite isochron than MORB.

and continental crust (Galer & Goldstein, 1991). Although not explicitly stated, the bulk silicate Earth approximation that returned a 60 Myr core formation time implies the existence of a hidden low μ reservoir in the silicate Earth.

The problem with an average core formation time in the range of 60–120 Myr is that astrophysical models predict much more rapid accretion of planets (Safronov, 1972; Wetherill, 1990). Because metal segregation rate is limited by accretion rate, rapid accretion necessarily leads to rapid core formation. Astrophysical models are supported by terrestrial Pu–I–Xe isotope systematics, which require rapid loss of atmosphere and early establishment of the silicate Earth (Azbel & Tolstikhin, 1993; Ozima & Podosek, 1999). Even stronger support for very early core formation is the difference in Ag-isotope composition between the silicate Earth and carbonaceous chondrites, which are substantially more radiogenic, implying early loss of the short-lived parent element Pd into the terrestrial core. Hauri *et al.* (2000) interpreted their findings to reflect terrestrial core formation within <50 Myr after the collapse of the solar nebula. The only short-lived radionuclide evidence for late core formation is the similarity in W isotopes of the silicate Earth and carbonaceous chondrites determined by Lee & Halliday (1995, 1996). However, the most recent measurements by two independent research groups (Schoenberg *et al.*, 2002; Yin *et al.*, 2002) found significantly less radiogenic W-isotope compositions in carbonaceous chondrites. These new estimates are identical to that for enstatite chondrites (Lee & Halliday, 2000) and require that terrestrial core formation lasted no longer than 35 Myr.

It therefore appears that the growing consensus on early terrestrial core formation limits the potential of Pb-core pumping as an explanation of the first terrestrial Pb-isotope paradox. The core certainly is a reservoir that helps to balance the accessible silicate Earth, but one or more further hidden reservoirs are required within the silicate Earth. Irrespective of their nature, it must be stated that any explanation for the Pb paradox that argues for anomalous geochemical behaviour of Pb (i.e. chalcophile) cannot also provide a solution to the second paradox.

A solution based on subduction zone Pb enrichment

Chauvel *et al.* (1995) proposed a model for the Pb-isotope evolution of the MORB-source mantle involving a secular increase in μ by loss of Pb to the continents. In their model, Pb becomes decoupled from elements with similar partition coefficients (i.e. Ce and Nd) during hydrothermal alteration of oceanic crust in which Pb is concentrated in oxides and sulphides. Chauvel *et al.* (1995) argued that as these minerals are not stable during subduction metamorphism, Pb will dissolve into the fluid phase that escapes from the subducting slab, which ultimately leads to mantle wedge melting and formation of arc-type continental crust. Thus, the Ce/Pb ratio of the subducting slab is increased by dehydration whereas that of the continental crust is reduced. Chauvel *et al.* (1995) proposed that, by analogy with the Ce/Pb ratio, the U/Pb ratio (i.e. μ) of the subducting slab should also increase in the process of metamorphism. Therefore, recycling of subducted high μ oceanic crust (eclogite and garnetite) back into the MORB-source mantle would increase its μ over time and facilitate the production of radiogenic Pb, ultimately causing MORB to plot to the right of the meteorite isochron.

There are a number of serious problems with this model. The most prominent is that extraction of accessible continental crust, which clearly has a higher time-integrated μ than the MORB-source mantle as well as storage of high μ oceanic slabs (to act as the so-called HIMU OIB reservoir) would gradually reduce but not increase the μ of the MORB-source mantle. The only solution to this problem is found by postulating that average continental crust plots to the left of the meteorite isochron. Hence, the model proposed by Chauvel *et al.* (1995) does not actually address the first terrestrial Pb-isotope paradox but implicitly requires that the inaccessible lower continental crust be sufficiently unradiogenic for mass balance in the bulk silicate Earth.

Furthermore, Chauvel *et al.*'s (1995) proposed solution has not been subject to quantitative modelling. Our attempt at calculating a Pb-isotope evolution curve for the MORB-source mantle using Chauvel *et al.*'s (1995) hypothesis did not succeed. For example, it is impossible to derive the present-day Pb-isotope composition of MORB from the 600 Ma MORB-source mantle composition given by Kramers & Tolstikhin (1997) simply by increasing μ. In brief, any increase in μ, whether gradual or episodic, consistently produced modelled Pb-isotope ratios that plot below the observed MORB array in common Pb space. This is because an increase in MORB-mantle μ 600 Myr ago is no longer capable of boosting the $^{207}Pb/^{204}Pb$ ratio to the required level. The implication of this result is that the MORB-source mantle cannot be regarded as a reservoir that experienced unidirectional loss of Pb (i.e. depletion) but contains a significant proportion of Pb that was recycled from the upper continental crust (which has the required old, high $^{207}Pb/^{204}Pb$ memory).

Finally, because Chauvel *et al.*'s (1995) model postulates that it is the particular behaviour of Pb that solves the first paradox (like the core Pb-pumping model) it provides no mechanism for Th/U fractionation that could have caused the mismatch between measured and inferred time-integrated Th/U ratio of MORB-source mantle.

The lower continental crust as the hidden Pb reservoir

Kramers & Tolstikhin (1997) and Kramers (1998) used forward models of accretion to explore the extent to which core formation could explain the first terrestrial Pb-isotope paradox. They concluded that Pb in the core could only balance 30% of the accessible Earth Pb. Given that new Ag- and W-isotope data (Hauri *et al.*, 2000; Schoenberg *et al.*, 2002) require even earlier core formation than that modelled by Kramers (1998), the estimate of 30% must be viewed as a maximum. Consequently, an additional reservoir that has evolved with a low μ and that plots to the left of the meteorite isochron is required. Because this reservoir is not evident in the accessible Earth, Kramers & Tolstikhin (1997) suggested that it may be the lower continental crust. This lower-crustal model, originally proposed by O'Nions *et al.* (1979) and further developed by Zartman & Haines (1988), is attractive for two reasons. First, comparison between upper-crustal U, Th and K abundances with total surface heat flux requires the lower crust to be depleted in heat-producing radioactive elements. Second, although the lower crust is certainly depleted in U and Th, it may be enriched in Pb, particularly if it is rich in plagioclase (e.g. gabbroic). It is important to point out that Kramers & Tolstikhin (1997) did not envisage metamorphic U and Th loss from average crust during orogenic events, but proposed that in the process of crustal growth, the lower crust naturally inherited its low μ character from fractional crystallization of plagioclase in calc-alkaline magmas. The forward model of Kramers & Tolstikhin (1997), like earlier versions of similar concepts (e.g. Zartman & Haines, 1988) was successful at solving both terrestrial Pb-isotope paradoxes using on the one hand (first paradox) the lower crust as a low μ repository, and on the other hand (second paradox) preferential post 2 Ga U and Pb (over Th) recycling into the MORB-source mantle. The lower crust, specifically old lower crust, thus balances the low $^{207}Pb/^{206}Pb$ ratios of the upper continental crust and MORB-source mantle (Fig. 3). This hypothesis appears to be consistent with the observation that both upper continental crust and continent-derived sediment have evolved with a high $^{232}Th/^{238}U$ ratio (κ) implied from their comparatively high $^{208}Pb/^{206}Pb$ ratios because of the mobility of U in oxidized environments. Therefore, the models of Zartman & Haines (1988) and Kramers & Tolstikhin (1997) differ from all other explanations in that they propose U to be the element whose chemical behaviour changed with time, thereby providing solutions to both paradoxes.

Despite the very successful match with most input parameters, the Kramers & Tolstikhin (1997) model requires the lower crust to have an isotope composition that is very different from that observed in lower-crustal xenoliths (Fig. 4). There exists now a larger Pb-isotope database for xenoliths of different age. These include samples of mafic underplates, granulites and cumulates (see caption of Fig. 4 for references). The prevailing observation is that despite their clearly different petrogenetic origins, no xenoliths plot close to the Kramers & Tolstikhin (1997) old lower-crust value (Fig. 4). Rather, the average composition of lower-crustal xenoliths plots

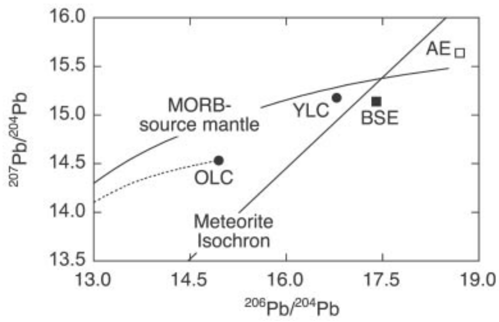

Fig. 3. Illustration of Kramers & Tolstikhin's (1997) solution to the first terrestrial Pb-isotope paradox. Present-day $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ values for the old lower continental crust (OLC) and the young lower continental crust (YLC) plot well below the Kramers & Tolstikhin (1997) MORB-source mantle evolution line and to the left of the meteorite isochron. Also shown is the Pb-isotope evolution curve for old lower continental crust (dashed line), the meteorite isochron and bulk silicate Earth (BSE) after Kramers & Tolstikhin (1997) and accessible Earth (AE) after Hemming & McLennan (2001).

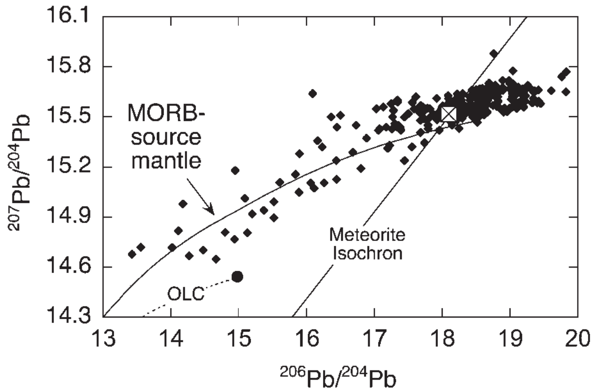

Fig. 4. Plot of $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ for a compilation of worldwide lower-crustal xenoliths (◆). Most xenoliths cluster close to and to the right of the meteorite isochron. Most xenoliths that plot to the left of the meteorite isochron must have undergone Archaean or Proterozoic metamorphic U loss (see text for details). Although some metamorphosed xenoliths plot below the MORB-source mantle evolution line (continuous line) of Kramers & Tolstikhin (1997) none plot close to the old lower-crust evolution line (dashed line). In addition, the median value for all the xenoliths (crossed square) plots slightly to the right of the meteorite isochron. Data sources: Leeman *et al.* (1985), Rudnick *et al.* (1986), Esperanca *et al.* (1988), Kempton *et al.* (1990, 1997, 2001), Rudnick & Goldstein (1990), Cameron *et al.* (1992), Halliday *et al.* (1993), Huang *et al.* (1995), Wysoczanski *et al.* (1995), Kay *et al.* (1996), Lucassen *et al.* (1999) and Downes *et al.* (2001).

close to the meteorite isochron (Fig. 4). Certain xenoliths probably derive from relatively young mafic underplated magmas that are not representative of average lower continental crust, which is on average 2–2·5 Gyr old (Nägler & Kramers, 1998). These young samples may thus not have had sufficient time to evolve to the left of the meteorite isochron. However, the important observation is that only Archaean lower-crustal granulites that have experienced metamorphism relatively early in their history plot to the left of the meteorite isochron (Fig. 4). Furthermore, more than half of those samples also plot significantly above the MORB-mantle evolution curve, unlike predictions by models that require the lower crust to have low $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$. Thus, it can either be argued that the present database is a misrepresentation of the true isotope composition of the lower crust, or that the role of the lower crust in balancing accessible Earth was overestimated by Kramers & Tolstikhin (1997). We therefore propose that in addition to the core and the lower continental crust there exists a further hidden terrestrial Pb reservoir.

An alternative low μ reservoir in the mantle

In our search for a further Pb-isotope reservoir that could plot to the left of the meteorite isochron we made three assertions. First, we argue that although a hidden reservoir is not likely to be frequently sampled, a survey of terrestrial Pb isotopes should nevertheless provide some indication of its existence. Second, because its Pb-isotope characteristics complement those of continental crust and MORB-source mantle, the processes that are involved in generating the chemical characteristics of the mantle–crust system were also responsible for the production of the hidden reservoir. Third, the reservoir can only be situated in regions of the mantle that are potentially isolated for at least 1–2 Gyr.

Because the deeper mantle is poorly represented by xenoliths recovered in volcanic rocks it is necessary to survey mantle-derived melts for Pb-isotope compositions that plot to the left of the meteorite isochron. The most abundant and voluminous mantle melts are MORB, whose Pb-isotope compositions are relatively homogeneous within the individual ocean basins. MORB from the major oceanic basins have discernibly different Pb-isotope compositions but the variability largely relates to their $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$ ratios whereas their $^{206}Pb/^{204}Pb$ ratios are fairly constant. As the average Pb-isotope compositions of MORB from all oceanic basins plot significantly to the right of the meteorite isochron the sub-oceanic asthenosphere does not seem to harbour the required low μ reservoir. The second most frequent, but much less voluminous group of oceanic mantle melts are OIB. There is a very extensive Pb-isotope database for OIB. Numerous compilations (e.g. Hofmann, 1997; Kamber & Collerson, 1999) show that with very few exceptions, OIB also plot to the right of the meteorite isochron. This is particularly true for the so-called high μ (HIMU) OIB, whereas the so-called enriched mantle type I (EM1) OIB plot at similar $^{206}Pb/^{204}Pb$ to MORB but with substantially higher $^{207}Pb/^{206}Pb$. Thus, of all MORB and OIB, EM1 OIB plot closest to the meteorite isochron. The remaining occurrences of direct mantle melts are found on the continents and there is a strong possibility that the less enriched melts could be contaminated by continental crust. Indeed, many of the voluminous flood basalt provinces show variable but significant continental contamination (e.g. Thompson *et al.*, 2001). An interesting aspect of the Pb-isotope systematics of continental flood basalts is that if their contamination is representative of the crustal columns through which they erupted, there is indeed only very limited evidence for a low μ lower crust, as the vast majority of flood basalts plot to the right of the meteorite isochron. Interpretation of isotope characteristics of uncontaminated suites of flood basalts is an issue of continuing debate. There is growing consensus that they occupy a similar field in Pb-isotope space as OIB but there might be an additional role for the continental lithospheric mantle. However, even the uncontaminated flood-basalts generally plot to the right of the meteorite isochron and therefore are not derived from a reservoir that could solve the first terrestrial Pb-isotope paradox.

The one remaining family of chemically anomalous mantle melts is volumetrically insignificant, is predominantly preserved in the continental crust, and can be classified broadly as alkaline in character. The group includes the very enriched lamprophyres, lamproites and group II kimberlites, as well as other melts with less extreme chemistries, such as basanites and alkali basalts. Although this group of rocks is chemically and isotopically very heterogeneous, there are many representatives of the various melt types, which clearly differ from all other mantle melts in their isotope composition. They define a huge range in present-day and initial Pb- and Nd-isotope ratios. For example, lamproites span a range in $^{206}Pb/^{204}Pb$ from 16 to 18·75 and in $^{207}Pb/^{204}Pb$ from 15·18 to 15·78 (Fig. 5). The most significant aspect is that all but one lamproite occurrence from southern Spain (Turner *et al.*, 1999) plot to the left of the meteorite isochron (Fig. 5). In addition to lamproites, a significant proportion of the other compiled alkaline rocks, which include alkali-basalts, basanites, leucitites, minettes, melilitites and others, plots to the left of the meteorite isochron (Fig. 5). It is beyond the scope of this study to differentiate this heterogeneous group of volcanic rocks into groups of common petrogenetic origin. Clearly, many of the rocks plotted in Fig. 5 have experienced some form of contamination, whereas others may be

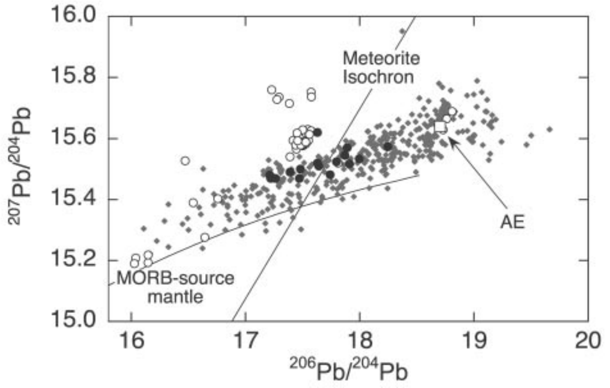

Fig. 5. Plot of initial $^{207}Pb/^{204}Pb$ vs $^{206}Pb/^{204}Pb$ for a compilation of <300 Ma continental alkaline basaltic rocks (small black diamonds). Most data points represent samples from China, mid-west USA, South America, New Guinea, southern Africa, eastern Australia and Antarctica. These rocks have highly variable Pb-isotope compositions, plotting in a broad array of $^{206}Pb/^{204}Pb$ from 16 to 19·5 and $^{207}Pb/^{204}Pb$ from 15·25 to 15·95, a significant proportion of which lies to the left of the meteorite isochron. This is a distinctive region of Pb–Pb space not normally occupied by mantle-derived melts and implies their derivation from anomalous mantle. The Pb-isotope ratios of lamproites (○) and group II kimberlites (●) are also shown. The majority of lamproites, which represent the most extreme examples of alkali volcanism, plot significantly to the left of the meteorite isochron. Only lamproites from southern Spain (Turner *et al.*, 1999) plot to the right of the meteorite isochron (see text for explanation). Also shown is accessible Earth (□) after Hemming & McLennan (2001). Data sources: Smith (1983), Fraser *et al.* (1985), Leeman *et al.* (1985), Dudas *et al.* (1986), Nelson *et al.* (1986), Meen & Eggler (1987), Cordani *et al.* (1988), Leat *et al.* (1988), Middlemost *et al.* (1988), Nelson (1989), Thompson *et al.* (1990), Basu *et al.* (1991), Mitchell & Bergman (1991), O'Brien *et al.* (1995), Zhang *et al.* (1995, 2001), Carlson *et al.* (1996), Beard & Glazner (1998), Turner *et al.* (1999), Buhlmann *et al.* (2000), Housh & McMahon (2000), Wannamaker *et al.* (2000), Yan *et al.* (2000), Zou *et al.* (2000), Hoch *et al.* (2001) and McBride *et al.* (2001).

related genetically to hotspots and could be expected to share a similar Pb-isotope signature to OIB. The point here is simply to note that of all mantle melts, some alkaline volcanic rocks are the only ones from a source whose Pb-isotope composition plots to the left of the meteorite isochron. There is a possibility that geographical distribution may have a stronger control over Pb-isotope systematics than rock type, with more samples from China, mid-west USA, South America, New Guinea, South Africa, eastern Australia and Antarctica plotting to the left of the meteorite isochron.

Historically most of the rocks used in our compilation have been interpreted as originating from enriched subcontinental lithospheric mantle and the prevailing textbook opinion is that the lithospheric mantle has played at least some part in the genesis of these magmas (e.g. Fraser *et al.*, 1985; Nelson, 1989; O'Brien *et al.*, 1995). If the anomalous Pb-isotope compositions of these rocks indeed reflect the lithospheric mantle, the implications for the terrestrial Pb-isotope paradoxes would be minimal. Namely, although those lithospheric mantle sources would have a suitable isotope composition to solve the paradox, they would be volumetrically insignificant and have Pb concentrations too low to balance the Pb contained in the continental crust and the MORB-source mantle. Furthermore, the (relatively few) available Pb-isotope measurements of lithospheric mantle xenoliths, including metasomatized samples, typically plot to the right of the meteorite isochron (Tatsumoto *et al.*, 1992; Carignan *et al.*, 1996; Viljoen *et al.*, 1996; Stern *et al.*, 1999) and there are thus no obvious lines of evidence to suggest that the low μ reservoir is situated in the lithospheric mantle.

Here we propose an alternative mantle Transition Zone (i.e. between the 400 km and 670 km seismic discontinuities in the mantle) source for at least some of the alkaline magmas, particularly those enriched in K. A detailed justification of this proposal has been given by Murphy *et al.* (2002), who showed that the isotope characteristics of lamproites can easily be reproduced with a model in which the source contains a continent-derived sediment component that was stored in the Transition Zone for 2–3 Gyr. Experiments indicate that sedimentary protoliths at Transition Zone depths metamorphose to a mineral assemblage containing majorite, K-hollandite, CaSi-perovskite, CAS-phase and stishovite (Irifune *et al.*, 1994). A source containing Na- and K-aluminosilicates of hollandite structure was seen as critical by Murphy *et al.* (2002) to explain the alkaline character of lamproites. The key feature of their model is a two-step isotope evolution. The high $^{207}Pb/^{206}Pb$ character is an inherited old feature from the continental crust. This explains why the isotope composition of all lamproites plots above the MORB-source mantle curve. During the second stage, however, the source evolves with a reduced μ, which slows the Pb-isotope evolution, particularly in $^{206}Pb/^{204}Pb$ such that the final Pb-isotope composition plots to the left of the meteorite isochron. Murphy *et al.* (2002) argued that the reduction in μ occurred, first, because sediments being subducted into the mantle could have variable but low μ as a result of the presence of carbonates and U mobility (Plank & Langmuir, 1998) and, second, that during subduction metamorphism the μ of dehydrated material is reduced. This is consistent with trace element composition of metasediments and metabasalts from ultra-high-pressure metamorphic terrains [for a detailed discussion see Murphy *et al.* (2002)] and is supported by the Pb-isotope characteristics of ancient amphibolite- and granulite-facies gneisses, which can show strong preferential loss of U over Pb (e.g. Whitehouse, 1989). Preferential loss of U (and Th) over Pb from the mantle during formation of continents by arc magmatism is also indicated by the high time-integrated μ and Th/U of the continental crust inferred from Pb-isotope compositions, particularly the fact that almost all known continental samples plot at higher $^{207}Pb/^{206}Pb$

than the MORB-source evolution. In view of the lack of low $^{207}Pb/^{206}Pb$ continental samples, it follows that subducted oceanic slabs will, on average, have a lower μ than the bulk silicate Earth. Indeed, recycling of low μ oceanic slabs back into the MORB-source mantle has led to a gradual decrease in μ so long as the terrestrial atmosphere was anoxic and continental recycling was limited. The MORB-source mantle evolution modelled by Kramers & Tolstikhin (1997) shows a secular drop in μ from 8·34 at 4·3 Ga to 6·24 at 1·7 Ga as a direct result of continent extraction, which is consistent with the requirements of Murphy *et al.*'s (2002) model. Once preferential weathering of U occurred at the Earth's surface, in response to the establishment of an oxygenated atmosphere, soluble U from the continental crust was transported to the oceans and subducted into the mantle. As the continents had already achieved a considerable volume by ∼2 Ga, recycling of a relatively small proportion of U back into the depleted MORB-source mantle had very significant effects. Thus, over the past ∼2 Gyr, the μ of the MORB-source mantle increased considerably, whereas the Th/U ratio dropped significantly from ∼3·7 to ∼2·6 [for a more detailed discussion, see Collerson & Kamber (1999)]. Increased U addition to altered oceanic crust (and eventually the MORB-source mantle) is a feature of the last 2 Gyr of the Earth's history, yet all but one of the identified lamproite occurrences (southern Spain; Turner *et al.*, 1999) require source isolation times in excess of 2 Gyr. Hence, the U addition to altered oceanic crust observed at present is not likely to have operated at the time when the lamproite sources were subducted.

The model of Murphy *et al.* (2002) appealed to subducted ancient sediment only to explain some of the most extreme lamproite Pb-isotope compositions. A solution to the first terrestrial Pb-isotope paradox, however, does not necessarily require such unradiogenic Pb-isotope composition of the low μ reservoir. The isotope composition in a particular low μ reservoir depends on its initial isotope composition, μ and the time of isolation. For example, subducted sediment or oceanic crust at present starts out with isotope ratios plotting to the right of the meteorite isochron and will take several hundred million years to evolve to the left of the meteorite isochron, if the μ is reduced during subduction. Hence, the wide array of Pb-isotope compositions seen in Fig. 6 is explained by differences in initial isotope composition at the time of isolation (i.e. metasediments vs oceanic crust), the time spent in isolation (from several billion years to <100 Myr in young subduction zones) and the extent of U/Th/Pb fractionation experienced before and during subduction.

It is interesting to note that alkaline melts from Europe and North Africa (not shown) plot significantly to the right of the meteorite isochron. This could reflect a melt contribution from relatively young recycled material (Wilson & Downes, 1991), which in our interpretation could be slabs subducted during the Phanerozoic. However, the extreme (low $^{206}Pb/^{204}Pb$ but high $^{207}Pb/^{206}Pb$) Pb-isotope character of other alkali basalts (Fig. 5) indicates that chemically anomalous regions of the mantle could have persisted for up to 2–3 Gyr.

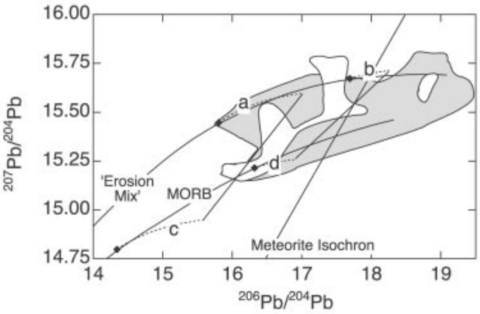

Fig. 6. Plot of the evolution curves for the MORB-source mantle and the 'erosion mix' calculated by Kramers & Tolstikhin (1997) together with the fields defined by the compilation of Pb-isotope ratios for alkaline basalts (grey field) and lamproites (white field) shown in Fig. 5. The majority of the alkaline volcanics plot between the two curves. Four additional curves are plotted representing modelled low μ mantle reservoirs. They include the Pb-isotope evolution of U-depleted 2 Ga (a) and 1 Ga (b) subducted sediment approximated by 'erosion mix' evolving with a fixed μ of 3·34; and the Pb-isotope evolution of subducted U-depleted 2 Ga (c) and 1 Ga (d) oceanic crust approximated by MORB evolving with a fixed μ of 3·34. The lamproites and alkaline basalts with the lowest $^{206}Pb/^{204}Pb$ ratios plot on or close to mixing lines (bold lines) between the two 2 Ga and 1 Ga evolution curves. Thus, the source of the alkaline volcanics could be explained as a mixture of subducted continental sediment and oceanic crust.

There is now strong geophysical evidence that a considerable proportion of subducted slabs is not returned to the MORB-source mantle but stored at the Transition Zone or even deeper mantle (e.g. Simons *et al.*, 1999). Mantle tomography has identified many regions of lateral temperature and/or composition contrast within the mantle Transition Zone (Fukao *et al.*, 2001). These areas are widely interpreted as accumulations of seismically fast material below (former) subduction zones. Our proposed solution to the first terrestrial Pb-isotope paradox requires that at least some of that material is composed of the crustal basaltic portion of subducted oceanic lithosphere and associated continental sediment (probably garnetite). Whether the mantle portion of the lithosphere delaminated and was recycled into the convecting mantle is not relevant for Pb-isotope mass balance. Thus, our model is consistent with the existence of a laterally heterogeneous Transition Zone in which recycled oceanic crust and subordinate metasediment accumulate (Ringwood, 1989). The modal proportion of stishovite is likely to play an important role in determining if thermally equilibrated slabs remain neutrally buoyant, but there is no published experimental evidence to suggest that slabs could not reside in the Transition Zone for up to billions of years, as required by our solution to the first terrestrial Pb-isotope paradox.

In addition to geophysical evidence there are claims that subduction and subsequent isolation of oceanic lithospheric slabs is also required by terrestrial Nb–Ta mass balance (Kamber & Collerson, 2000; Rudnick *et al.*, 2000). Both solutions to the terrestrial Nb–Ta imbalance logically combine the same principal reservoirs (continental crust, MORB-source mantle, and eclogite slabs) in their claim that the Nb/Ta ratio is changed during subduction processes. Thus, we conclude that, in addition to the core and lower crust, isolated slabs of oceanic crust and associated sediment are the most plausible low μ reservoir.

DISCUSSION

Pb-isotope composition of the bulk silicate Earth

Many discussions of the first terrestrial Pb-isotope paradox concerned themselves with the issue of the μ of the bulk Earth. However, the bulk Earth μ is crucial only for the core Pb-pumping model and can be treated as a variable for solutions to the paradox that seek low μ reservoirs in the silicate Earth. Interestingly, the issue of bulk silicate Earth μ has received considerably less attention. This is surprising in view of the fact that some agreement exists that the sources of certain OIB contain at least a component that is less degassed and depleted than the MORB-source mantle and must, therefore, have a Pb-isotope composition close to that of bulk silicate Earth (Kamber & Collerson, 1999; Hilton *et al.*, 2000). We next discuss the Pb-isotope composition of the bulk silicate Earth predicted by the competing solutions for the first terrestrial Pb-isotope paradox before comparing them with the OIB isotope array.

Although never explicitly stated, the core Pb-pumping model predicts bulk silicate Earth to have a Pb-isotope composition transitional between average continental crust and MORB-source mantle (Fig. 7a). Because the core in that model is the only low μ reservoir, it is reasonable to approximate average continental crust with average sediment. The exact Pb-isotope composition of bulk silicate Earth along the MORB–sediment tie-line remains unconstrained because the proportion of depleted vs undepleted mantle is unknown.

The bulk silicate Earth Pb-isotope composition of the Kramers & Tolstikhin (1997) model lies in a field defined by MORB, young and old lower crust, and upper crust. By definition, it plots much closer to the meteorite isochron than MORB or continental sediment (Fig. 7a). The deviation to the right of the meteorite isochron is a direct measure of the contribution of core Pb-isotope composition to solving the paradox. The significant point, however, is that the Kramers & Tolstikhin (1997) model cannot strictly be used to estimate the bulk silicate Earth Pb-isotope composition because that parameter was an unconstrained variable and was not specifically fitted to meet a particular target value (J. D. Kramers, personal communication, 2002). Therefore, both the modelled lower-mantle estimate and the undifferentiated mantle (which in their model are slightly different as a result of recycling of the Hadean crust into the upper mantle only) contain less radiogenic Pb than the OIB–MORB

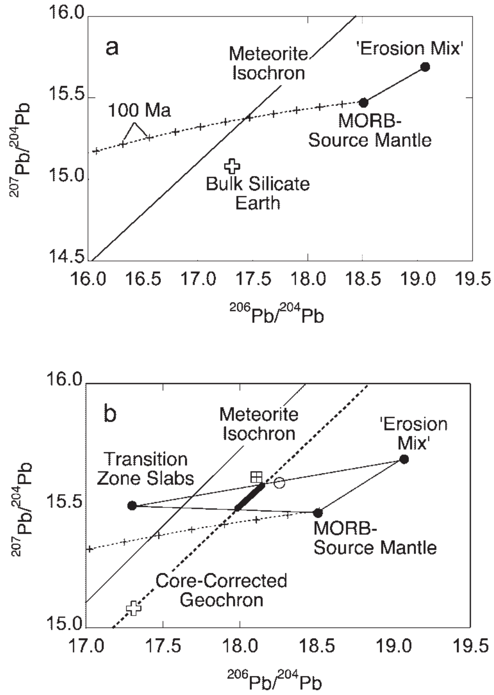

Fig. 7. Illustration of the Pb-isotope composition estimated for bulk silicate Earth by various models. (a) The core Pb-pumping model predicts bulk silicate Earth to plot between total continental crust and depleted mantle, which are here approximated by the 'erosion mix' (assuming that lower crust provides no explanation for the first terrestrial Pb paradox) and present-day MORB-source mantle (shown with its evolution curve; +, 100 Ma intervals) of Kramers & Tolstikhin (1997). Also shown for comparison is the predicted undegassed undepleted mantle estimate (open cross) of Kramers & Tolstikhin's (1997) model. (b) The bulk silicate Earth Pb-isotope composition estimated in the present study is expected to plot into a triangular field defined by MORB-source mantle, average continental crust [as in (a)] and subducted Transition Zone slabs, which plot to the left of the meteorite isochron ($^{206}Pb/^{204}Pb$ = 17·3; $^{207}Pb/^{204}Pb$ = 15·5). Mass balance dictates that the bulk silicate Earth composition must further plot along the core-corrected 'geochron', which is shown as a bold dashed line extending through the bulk silicate Earth estimate (open cross) of Kramers & Tolstikhin (1997). Thus, the likely composition of bulk silicate Earth lies at the intersection (bold segment) of the 'geochron' and the triangle. The bulk silicate Earth Pb-isotope estimate of Kamber & Collerson (1999) (large open circle) plots slightly to the right but within error of that of this study, whereas the estimate of Galer & Goldstein (1991) (crossed square) also plots within error of our prediction.

array. A more radiogenic bulk silicate Earth could be obtained with either stronger Pb loss into the core or Pb loss by volatilization, or a higher bulk Earth μ. Importantly, however, a bulk silicate Earth with more radiogenic Pb would also require lower crust with a higher $^{207}Pb/^{206}Pb$. Namely, the very retarded Pb-isotope evolution of the lower crust predicted by Kramers & Tolstikhin's (1997) model drags the point of gravity of the MORB–upper crust–lower crust triangle below the MORB field. Hence, if the Kramers & Tolstikhin (1997) model were adjusted to return a more radiogenic bulk silicate Earth similar to ours (see below), geometric relationships in common Pb space would require the lower crust to have significantly higher $^{207}Pb/^{206}Pb$ ratios. Such a composition could be achieved only by metamorphic U loss but not by plagioclase fractionation. It therefore appears that formation of the lower crust does not inherently produce a low μ.

Similarly, Galer & Goldstein's (1996) model does also not predict an independent estimate for the Pb-isotope composition of bulk silicate Earth. Their bulk silicate Earth estimate plots along a 4·50 Ga isochron (to yield a core formation time of 60 Myr) but is essentially an input parameter for the inversion model. It plots significantly to the left of both MORB-source mantle and continental crust and at higher $^{207}Pb/^{204}Pb$ than MORB. Bulk silicate Earth mass balance thus requires an inaccessible reservoir that plots to the left of the 4·50 Ga isochron.

The bulk silicate Earth Pb-isotope composition resulting from our solution to the paradox depends, apart from the core Pb-isotope composition, on the mass balance of the various silicate Earth reservoirs, especially the volume of subducted material in the Transition Zone. This results in a broad field in which bulk silicate Earth could plot. Nevertheless, if we assume, for comparative purposes, that the core contribution modelled by Kramers & Tolstikhin (1997) is approximately correct, it is possible to calculate a 'geochron', which refers to the apparent Pb-isotope age of the bulk silicate Earth, simply by connecting their bulk silicate Earth composition with primordial Pb. The slope of the calculated 'geochron' corresponds to an age of 4503 Ma, which implies catastrophic core formation within ~65 Ma. As we have stated above, core formation probably proceeded more rapidly and the true 'geochron' should thus plot closer to the meteorite isochron. In spite of this, the bulk silicate Earth Pb-isotope composition of our model must plot onto the 'geochron'. A simplified end-member scenario can be calculated if it is proposed that the lower crust provides no explanation for the paradox because on average, lower-crustal xenoliths plot to the right of the meteorite isochron. Possible bulk silicate Earth compositions would then fall into a triangle defined by MORB, average upper continental crust (here approximated by average sediment), and average recycled material in the Transition Zone. Naturally, there is great uncertainty in the last of these, as we are interested in the Pb-isotope composition of material that is not melted and transported to the surface but remains stored in the deep mantle. Using a similar value to the average lamproite composition, we obtain (Fig. 7b) a triangle, whose intercept with the 'geochron' defines the bulk silicate Earth Pb-isotope composition.

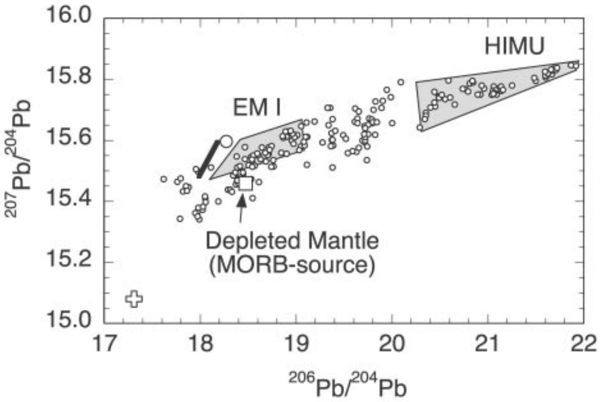

Fig. 8. Relationship between HIMU and EM1 type OIB Pb-isotope compositions and that of bulk silicate Earth determined in this study (bold continuous line), that of Kamber & Collerson (1999) (large open circle) and that of Kramers & Tolstikhin (1997) (open cross). OIB data compilation is from Kamber & Collerson (1999, fig. 2a).

Implications for interpretation of OIB Pb isotopes

Hofmann (1997) summarized the two strong arguments in favour of a mantle structure containing a significant portion of undepleted or only partly depleted material. First, the continental crust is not nearly sufficiently enriched in incompatible elements to balance a fully depleted mantle. Second, noble gas isotope ratios and inventories require the existence of a mantle portion with significant content of gas with an isotope composition that is more primordial than ambient atmosphere. The high $^{3}He/^{4}He$ ratio of many OIB is the most straightforward expression of the existence of a less degassed or undegassed terrestrial mantle reservoir. In our view, the long-standing dispute about the low He contents of those basalts [used by Anderson (2001) and others to question the notion of undegassed mantle] has been conclusively settled with the recent work by Hilton *et al.* (2000).

A comparison of OIB Pb-isotope compositions with the bulk silicate Earth estimates derived above (Fig. 8) immediately illustrates two points. First, Kramers & Tolstikhin's (1997) model would not support any involvement of primitive mantle (as approximated by bulk silicate Earth) in the OIB source because practically no samples plot below MORB, indicating that a higher bulk silicate Earth μ is required. Second, the core Pb-pumping model could explain some of the OIB as originating from undegassed mantle but it fails to represent any of the more extreme compositions reflected in the OIB Pb-isotope array.

By contrast, the bulk silicate Earth composition predicted by our model plots with the lowest $^{206}Pb/^{204}Pb$ but highest $^{207}Pb/^{204}Pb$ of the OIB Pb-isotope array (Fig. 8). This area of the array is occupied by EM1 type OIB. Some of the highest known terrestrial $^{3}He/^{4}He$ ratios have been obtained from samples with relatively low $^{206}Pb/^{204}Pb$ but high $^{207}Pb/^{204}Pb$ ratios (Eiler *et al.*, 1998). It follows that any OIB model that argues EM1 (or so-called DupAl) Pb-isotope signatures to reflect less degassed and depleted mantle (Castillo, 1988) implicitly requires that the low μ hidden Pb-isotope reservoir must plot in a similar position to that estimated here (i.e. above the MORB-source evolution line but to the left of the meteorite isochron). This is a simple geometric requirement.

The view that some OIB sources must have remained isolated for a very long time is widely accepted (e.g. Hofmann, 1997) but, as far as Pb isotopes are concerned, very different evidence is used to validate that claim. On the one (conventional) hand, it is argued that the very radiogenic Pb that characterizes HIMU OIB can only be produced over ~1–2 Gyr from isolated subducted oceanic crust (e.g. Hofmann, 1997). However, the view that the HIMU (or any other OIB) source originated from MORB-source mantle (Chase, 1981) is and has only ever been a working hypothesis, for which surprisingly little hard evidence can be found in the literature [for a discussion, see Kamber & Collerson (1999)]. Furthermore, there are now many isotopic datasets, which are very difficult to reconcile with a recycled subducted MORB-source origin for HIMU OIB (e.g. Barfod *et al.*, 1999).

In view of mounting evidence for the lower-mantle origin of major plumes, it appears equally or more justified to postulate that the long-lived OIB source is the undegassed mantle, possibly representing the lower portions of the lower mantle. In this regard it is imperative to improve our understanding of the Pb-isotope composition of the bulk silicate Earth. Here we propose that an undegassed mantle with a Pb-isotope composition similar to that obtained in this study (i.e. plotting onto the 'geochron' but above the MORB array) has a cascade of implications that remains to be fully appreciated. The most important difference to models that propose the 'plume' or 'common' Pb-isotope composition to be near the centre of gravity of the OIB array (Hanan & Graham, 1996) is that our bulk silicate Earth estimate could produce the HIMU Pb-isotope ratios over a short period of time (i.e. <150 Myr, the lifetime of large plumes). This is because our postulated undegassed lower mantle (which we equate here with bulk silicate Earth) has a much higher $^{207}Pb/^{204}Pb$ ratio than MORB-source mantle. We note that the undegassed mantle evolution line estimated by Kamber & Collerson (1999) from the Tablemount OIB, South Atlantic, fits very closely with the independent estimate for bulk silicate Earth from the present study (Fig. 7c).

The main difference between conventional OIB models (e.g. Zindler & Hart, 1986) and that of Kamber & Collerson (1999) is that the latter proposed that the large range in $^{207}Pb/^{204}Pb$ ratios of OIB does not reflect high U/Pb ratios and long isolation of the OIB sources, but a comparatively low $^{207}Pb/^{204}Pb$ ratio of MORB-source mantle, which is entrained into all plumes. The low $^{207}Pb/^{204}Pb$ ratio of MORB is readily explained by extraction of Archaean and early Proterozoic continental crust and is a simple prediction from the fact that continental crust has a higher $^{207}Pb/^{204}Pb$ ratio than MORB-source mantle. Thus, in contrast to the conventional model, we reiterate our hypothesis that it is the isolation of the MORB-source mantle from primitive mantle that is reflected in the OIB $^{207}Pb/^{204}Pb$ isotope array. Therefore, the term 'enriched mantle' to characterize the source of OIB with high $^{207}Pb/^{204}Pb$ is, strictly speaking, rather misleading.

Implications for mantle convection

Solutions to the terrestrial Pb-isotope paradoxes rest on assumptions regarding the chemical structure of the mantle. Essentially all Pb-isotope models require portions of the mantle that are less depleted than the MORB-source. This is true also for the core Pb-pumping model, which relies on a lower mantle with near-chondritic Th/U ratio to explain the second paradox (Galer & O'Nions, 1985). In our model there are only three long-lived reservoirs within the mantle: (1) the depleted portion of the mantle (the MORB-source mantle); (2) a significantly less degassed portion that has evolved to higher $^{207}Pb/^{204}Pb$ but lower $^{206}Pb/^{204}Pb$ ratios (similar to EM1 OIB); (3) deeply subducted slabs and associated metasediment in the Transition Zone (the inaccessible reservoir required by mass balance).

Of these three reservoirs, the undegassed mantle has had a simple long-term Pb-isotope evolution. After core formation, it evolved with a constant μ of ~8·9 (Kamber & Collerson, 1999). However, once material from the undegassed mantle is entrained into plumes, the short-term Pb-isotope evolution can become complex. In young plumes, large dispersion of $^{206}Pb/^{204}Pb$ (and $^{208}Pb/^{204}Pb$) but not $^{207}Pb/^{204}Pb$ ratios can develop over relatively short time (i.e. 50–150 Myr) because of the large differences in U (Th) and Pb distribution coefficients between the lower-mantle minerals CaSi-perovskite, Mg-wüstite and MgSi-perovskite (Taura *et al.*, 2001), and the possible presence of baddeleyite (Kerschhofer *et al.*, 2000). Those portions of plumes that preferentially incorporate U and Th over Pb, possibly as a result of exhaustion of residual CaSi-perovskite, quickly develop high $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios and are called the HIMU end-member. Importantly, the Sr- and Nd-isotope compositions of EM1 and HIMU OIB are limited to a narrow range between MORB and slightly super-chondritic (Sr) and sub-chondritic (Nd) ratios, easily within the confidence band of bulk silicate Earth. Thus, Pb-, Sr- and Nd-isotope systematics of these OIB do not require mantle sources of anomalous chemistry. By contrast, the isotope systematics of EM2 OIB are more complicated and reflect involvement of the lithosphere and/or the Transition Zone [as described in the model of Murphy *et al.* (2002)].

By comparison, the long-term Pb-isotope evolution of the MORB-source mantle was much more complex. It experienced a highly dynamic evolution of μ as a result of extraction and recycling of the continental crust. In addition to the dynamic evolution of the U/Pb and Th/U ratios, the MORB-source mantle Pb-isotope composition was further influenced by recycling of Pb with a very different isotope composition from the continents and possibly from the undegassed mantle. Although reconstruction of the exact Pb-isotope evolution is far from complete, it is most important to stress that the present-day Pb-isotope composition of MORB is a result of a very complex evolution. If this statement, which was explained in much more detail by Kramers & Tolstikhin (1997), is accepted it appears questionable whether we should use MORB as the point of reference for discussion of OIB Pb-isotope compositions. Indeed, by analogy with almost all other radiogenic isotope systems, it seems much more logical to use the bulk silicate Earth as a reference framework.

The third long-lived mantle reservoir in our model is that portion of the mantle Transition Zone that harbours subducted slabs. Storage of slabs in the Transition Zone is a physically plausible process that has been documented by seismic tomography. Our model requires slabs to be isolated from convection for at least 2, if not 3 Gyr. In contrast to the textbook opinion, we propose that slabs do not constitute a major OIB source component but that this 'hidden' reservoir remains virtually unsampled by mantle volcanism. There is the added possibility that slabs may penetrate to even greater depths and may be stored in the mid–lower mantle (Kellogg *et al.*, 1999). The depth of slab storage is difficult to evaluate but regardless of the true extent of mantle depletion, the large difference between the MORB-source mantle and bulk silicate Earth in $^{207}Pb/^{204}Pb$ requires long-term isolation and some form of layered mantle convection. Although there is communication between the different reservoirs, the very existence (and preservation) of the Pb paradoxes implies that convection and material exchange are evidently both slow and limited in extent.

SUMMARY AND CONCLUSIONS

Evidence for rapid terrestrial accretion and concomitant early core formation is increasing such that solutions to the first terrestrial Pb-isotope paradox appealing to a high $^{207}Pb/^{206}Pb$ core need to be refined. Kramers & Tolstikhin (1997) have previously shown that if the mean core formation time was $\sim$60 Myr, the core could only account for one-third of the paradox. An even shorter core formation interval is indicated by the latest Ag- and W-isotope work (Hauri *et al.*, 2000; Schoenberg *et al.*, 2002) such that the role of core formation for the first terrestrial Pb-isotope paradox might even be less important. Thus there is a strong requirement for the existence of one or more balancing reservoirs in the silicate Earth. We have compiled available Pb-isotope data for lower-crustal xenoliths and found that the majority of them do not plot significantly to the left of the meteorite isochron. Furthermore, most lower-crustal xenoliths plot above the MORB-source mantle evolution line, which indicates that they represent crust that has experienced U (and Th) loss long after its formation. Despite the still inadequate size of the lower-crustal xenolith database it appears that lower continental crust is probably not the sole silicate reservoir required to balance the Pb-isotope composition of the accessible Earth.

On the basis of the empirical observation that many alkaline mantle-derived magmas, particularly and unexpectedly the most enriched representatives (lamproites and certain lamprophyres), plot to the left of the meteorite isochron, we propose that their source is the missing reservoir required by Pb mass balance. The physical origin of this mantle source remains unresolved. On the basis of our previous work (Murphy *et al.*, 2002) we propose that the required low μ Pb-isotope reservoir is located in the mantle Transition Zone. Our proposal logically links the three major reservoirs (i.e. continental crust, MORB-source mantle, and subducted slabs in the Transition Zone) with the subduction process during which the slabs become depleted in all incompatible elements but more strongly in U and Th than in Pb. Thus, the fact that continental crust has a higher time-averaged μ than the MORB-source mantle is explained in our model to reflect preferential U and Th loss from the slabs, which would explain why the slabs themselves evolved with a lower μ. This solution is compatible with existing solutions to the second terrestrial Pb-isotope paradox, which relies on preferential recycling of U (over

Th) and Pb from the continents into the MORB-source mantle (Kramers & Tolstikhin, 1997; Collerson & Kamber, 1999; Elliott *et al.*, 1999).

Our model predicts bulk silicate Earth to plot at higher $^{207}Pb/^{206}Pb$ than the present-day MORB field. We note a similarity between the bulk silicate Earth Pb-isotope composition of our model and the so-called EM1 type OIB, and propose that a portion of the lower mantle remains only partly degassed and preserves radiogenic isotope ratios similar to those of bulk silicate Earth.

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