Part 1
Contribution of Geochemistry to the Study of the Earth

1 Geochemistry and Secular Geochemical Evolution of the Earth's Mantle and Lower Crust

BALZ S. KAMBER

Laurentian University, Sudbury, Ontario, Canada

The incompatible elements U and Th are related to Pb via radioactive decay. Extraction, modification and storage of continental crust have, over time, left an isotopic record in the continental crust itself and in the depleted portion of the mantle. Ancient lower crustal xenoliths require that crust has matured by upward transport of radioactive heat-producing elements; hundreds of millions of years after formation.

Recycling of continental material has contributed in at least three ways to the generation of enriched mantle-melt sources. First, this has occurred by delamination of lower crustal segments back into the mantle. Second, sediment has been recycled back into the mantle in subduction zones, and third, since the oxygenation of the atmosphere, seawater U, weathered from the continents, has been incorporated into hydrated oceanic crust with which it has ultimately been recycled back into the mantle.

The joint treatment of the lower continental crust and the mantle in terms of their geochemistry and their isotopic evolution may seem, at first, a less than obvious choice. They are, however, related in the sense that the evidence for their evolution is largely of indirect nature, either inferred from rare xenoliths or via products of partial melting. Any joint treatment of these two geochemical reservoirs also inherently carries with it the assumption that they have, at least in part, mutually influenced each other's temporal evolution. Before attempting to condense into an opening book chapter the relevant aspects of the exhaustive body of knowledge about the geochemistry of the mantle and the much sparser information regarding the lower crust, it is necessary to remind ourselves of the evidence for their mutually related evolutions.

INTRODUCTION

The view that the Earth has suffered some form of early global, planetary-scale depletion event is deeply rooted in classic geochemical texts, including those focusing on plumbotectonics, i.e. the reconstruction of planetary differentiation from a Pb-isotope perspective (e.g. Stacey and Kramers 1975). Most early attempts at modelling the isotopic evolution of the mantle postulated one or

Frontiers in Geochemistry: Contribution of Geochemistry to the Study of the Earth, First edition. Edited by Russell S. Harmon and Andrew Parker.

two pervasive differentiation steps, resulting, for example, in the increase of the U/Pb ratio of the silicate portion of the Earth (the bulk silicate Earth). The notion of an early depletion event was further cemented with the observation that Archaean komatiites and high-Mg basalts, in terms of their trace-element chemistry, appeared to resemble modern ocean-island picrites, yet their radiogenic isotope character was much more depleted (e.g. Campbell and Griffiths 1993). This finding seemed to suggest an early depletion event that imparted the long-term isotopic effect with superimposed much more recent (relative to 2.7 Ga) re-enrichment of the mantle, which explains the trace-element systematics but which had not yet translated into long-term isotopic evidence. More recently, the observation has been made that the bulk silicate Earth has a $^{142}Nd/^{144}Nd$ ratio different from the most common chondritic meteorites (Boyet and Carlson 2005). This has added new momentum to the idea of a very early silicate differentiation event that must have occurred within less than 1 half-life (103 Ma) of the short-lived parent of ^{142}Nd.

While the evidence for such an event appears as strong as ever, the critical question for this present treatment is whether that event was the principal cause for establishing the chemistry of the depleted mantle as it is sampled at most ocean ridges via the normal mid-ocean-ridge basalt (N-MORB). Namely, if the early depletion event imparted such a fundamental geochemical signal, which over time also was manifest as a long-lived radiogenic isotope signature, then the subsequent extraction, maturing and recycling of continental crust would only have played a secondary role in modifying the chemistry of the depleted mantle. Hence, the chemistry and radiogenic isotope composition of the depleted mantle would largely tell us about the early planetary depletion event and not about the history of extraction and recycling of continental crust.

In order to address this question, it is necessary to consider elemental systematics and the radiogenic isotope evolution of those elements that are most strongly enriched in continental crust, for their extraction will be most strongly reflected by the residual depleted mantle. While average continental-crustal absolute abundances are difficult to estimate on account of the sparse occurrence of *bona fide* lower crustal rocks, there is nonetheless wide agreement regarding the relative enrichment of elements. The elements most strongly enriched in continental crust are largely those that behave most incompatibly during mantle melting, plus an assortment of elements that are particularly soluble in hydrous fluids, and were therefore preferentially moved into the melt-source regions of the magmas that eventually differentiated to give rise to continental crust. The best studied of these is Pb (e.g. Miller et al. 1994) but other fluid mobile elements, such as B (e.g. Ryan and Langmuir 1993), W (e.g. Kamber et al. 2005; König et al. 2008), Li (e.g. Chan et al. 1999) and As (Mohan et al. 2008) have also been documented. The extended trace-element diagram for average upper-continental crustal rocks, in which elements are arranged in order of incompatibility during mantle-decompression melting, illustrates not only the extraordinary enrichment of the most incompatible elements but also the strong deviations of the fluid-mobile elements from an otherwise predicable, smoothly decaying trend. Regardless of the particular significance of the elements that deviate from this trend, it is intuitively appreciable that the geoscientist interested in that aspect of mantle depletion potentially caused by the extraction of continental crust is best served by working with the elements that plot toward the left side of the abscissa of Fig. 1.1. From an isotopic point of view, it is therefore not surprising that the extent of variability in the U/Pb and Th/Pb isotope systems in crustal and mantle rocks is of the order of several tens of percent and has formed the very basis of the mantle-rock nomenclature.

Indeed, one of the strongest pieces of evidence for the mutual chemical interaction between mantle and crust is found in the Pb-isotope composition and U-Th-Pb systematics of the source of N-MORB basalts. The present-day Pb-isotope composition of N-MORB firmly shows that, on the billion-year timescale, the time-averaged Th/U ratio of the depleted mantle source was

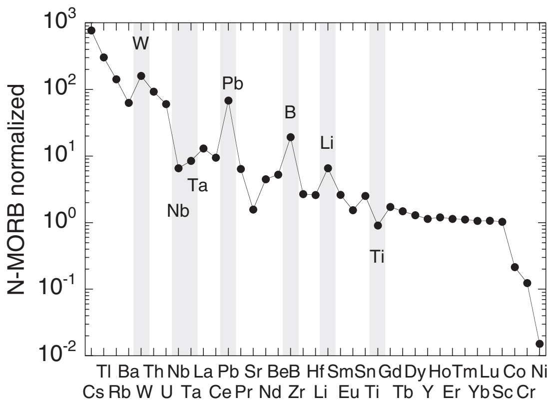

Fig. 1.1 Extended trace-element diagram in which elements are arranged, from left to right, in order of decreasing incompatibility during anhydrous mantle decompression melting. Shown is an average upper crustal river sediment composite, normalized to N-MORB (modified after Kamber et al. 2005). Boron value is an estimate, using the B/Be ratio 11 for arc rocks from Mohan et al. (2008). Grey bars highlight elements discussed in text.

ca. 3.6. This can be inferred from the $^{208}Pb/^{206}Pb$ ratio (Kramers and Tolstikhin 1997), which represents the decay products of the long-lived ^{232}Th and ^{238}U, respectively. Rather surprisingly, then, the measured elemental Th/U ratio of N-MORB is much lower, somewhere between 2.4 and 2.6. This observation is often termed the second terrestrial Pb-isotope paradox (e.g. Kramers and Tolstikhin 1997) or the kappa (as in $^{232}Th/^{238}U$) conundrum (e.g. Elliott et al 1999). This discrepancy is not an artefact of preferential U over Th partitioning into the N-MORB parental melt because the intermediate decay product systematics of the U and Th chains support a low Th/U ratio of the source rocks, i.e. the depleted mantle itself (Galer and O'Nions 1985). The solution to this paradox is now widely believed (e.g. McCulloch 1993; Elliott et al. 1999; Collerson and Kamber 1999) to be the preferential recycling of continental U under an oxidized atmosphere since the great oxygenation event at ca. 2.3 Ga (Bekker et al. 2004). This observation alone provides very robust evidence that the depleted mantle has not remained chemically inert and unchanged since an early depletion event.

The high-field-strength elements Th, U, Nb, and Ta offer further insight into the interaction between the depleted mantle and continental crust. These elements are all very incompatible and have very similar bulk partition coefficients during mantle-decompression melting. This is reflected in their close grouping in the extended trace-element diagram (Fig. 1.1). Yet the chemistry of upper continental crust shows a very distinctive deficit in Nb (and to a lesser extent Ta) relative to Th and U. This finding is very widely attributed to the preferential sequestering of Nb and Ta into a Ti-phase (e.g. rutile) in subducting slabs (e.g. Hofmann 1988). Extraction of continental crust, to the extent of its present mass of ca. 2.09×10^{25} g, has severely depleted the entire mantle in Th and U. It is estimated that between 30–50% of terrestrial Th and U are harboured by continental crust. By contrast, enrichment in the equally incompatible Nb is much lower, and, hence the mantle is proportionally less depleted in this element by a factor of at least three. It should come as no surprise then that the modern N-MORB Nb/Th ratio of ca. 18 is much higher than that of chondrites of ca. 8. If this greater-than-100% difference in a ratio that can be analysed to within 2–5% precision was caused by the early depletion event, it follows that ancient melting products of the depleted mantle should also have a ratio of ca. 18; but this is not in fact the case. For example, it is found that regardless of locality, high-Mg basalts and komatiites of the widespread 2.7 Ga mantle melting event have a Nb/Th of only 12 (e.g. Sylvester et al. 1997; Collerson and Kamber 1999), much lower than modern depleted mantle melts and much closer to the chondritic value. This observation shows that, at least for the very incompatible elements, the mantle has become more depleted as a function of how much continental crust was extracted. For these elements, the early depletion event played a less important role and, therefore, they are the tools with which to most effectively reconstruct the depletion history of the mantle.

TEMPORAL EVOLUTION OF THE DEPLETED MANTLE RESERVOIR

There are two principal methods to reconstruct the depletion history of the N-MORB mantle source. The first is to search for well-preserved N-MORB-like rocks of as large an age range as possible and to study their chemical and radiogenic isotope systematics. The second is to use forward modelling to approximate the isotopic contrast displayed by modern N-MORB and average continental crust. Examples of both approaches are reviewed here.

The reconstruction approach has the obvious advantage that each temporal observation from ancient N-MORB samples provides a time capsule for the evolution from the primitive to the present-day depleted mantle. In practice, it turns out that finding well-preserved N-MORB comparable basalts is difficult. The densest array of observations is, surprisingly, from the Archean eon. Many well-preserved greenstone belts exist, ranging in age from 3.7 to 2.6 Ga, and while some are clearly ensialic in origin (e.g. Blenkinsop et al. 1993), a sufficient number of uncontaminated mafic to ultra-mafic volcanic rocks are preserved. The situation for the Proterozoic is much less satisfactory. Apart from two ophiolites (Zimmer et al. 1995; Peltonen et al. 1996), the majority of other Proterozoic greenstones either formed in an arc or back-arc environment (e.g. Leybourne et al. 1997), were variably contaminated during magmatic ascent through pre-existing continental crust, or are not sufficiently well-preserved. For the Phanerozoic, the number of ophiolites and accreted ocean-floor assemblages is adequate. It must be stressed here that N-MORB of any age is particularly sensitive to continental contamination in those elemental systematics of most interest to this discussion, the systematics of those elements for which there is the most divergence between the mantle and continental crust.

In terms of suitable element systematics for reconstruction, any pair of elemental neighbours with sharply deviating behaviour on Fig. 1.1 are candidates. Namely, for elements with near-identical bulk partition coefficients during mantle melting, a suitably large-degree melt (such as the parental melt of N-MORB) will truthfully reflect the relative concentrations in the source. Subsequent fractional crystallization (up to ca. 6% MgO) will also not greatly affect the ratio of the elements of interest. Theoretically at least, it should be possible to track mantle depletion by study of the following ratios: Th/W, Nb/Th, Ta/U, Be/B, Pr/Pb, and Zr/Li. Note that, in all these examples, the element more enriched in continental crust is the denominator and hence all ratios are expected to have increased in the depleted mantle with increasing extraction of continental crust.

In reality, a number of factors conspire to render most of these ratios less than useful for the intended purpose. Insufficient data are available for Th/W, Be/B and Zr/Li. Post-emplacement elemental mobility may affect Pr/Pb and Be/B, and the redox-sensitivity of U has affected the mantle Ta/U ratio. At present, then, the only viable ratio is Nb/Th, which was used earlier to illustrate the fact that the N-MORB source mantle has become depleted by extraction of continental crust. Jochum et al. (1991) first proposed that the reconstruction of this ratio in the depleted mantle should be a reliable monitor of the mass of continental crust that had been extracted from the mantle through time, but their limited dataset and, by modern standards, insufficient analytical precision prevented these authors from drawing a conclusion. Collerson and Kamber (1999) applied a three-fold filter to the by then much improved literature database for Nb/Th in greenstones. They eliminated most rocks that had less than 6% MgO, excluded rocks with negative slopes in CI-normalized rare earth element (REE) patterns (to screen against ocean island basalts; OIB) and rejected rocks that had lower radiogenic $^{143}Nd/^{144}Nd$ ratios than widely accepted depleted-mantle evolution curves, (such as dePaolo and Wasserburg 1976) to avoid contaminated samples.

The Nb/Th curve for the depleted mantle, depicted on Fig. 1.2(a), was converted into the continental crust mass-versus age, curve (shown on Fig. 1.2(b)), that uses a primitive mantle Nb/Th starting value lower than in chondrites to

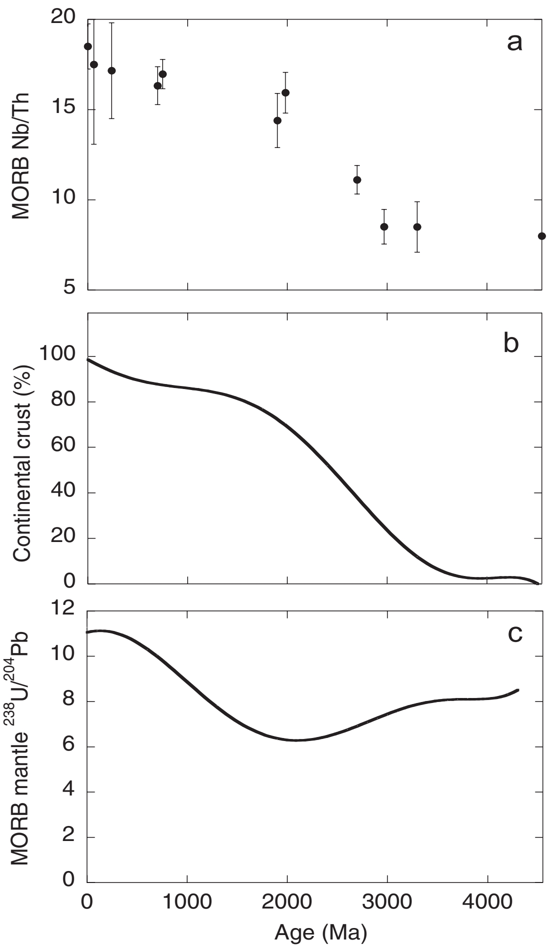

Fig. 1.2 Temporal evolution trends for (a) Nb/Th ratio in the depleted mantle; (b) continental crust mass estimated from Nb/Th ratio and Pb-isotope systematics; (c) modelled U/Pb ratio evolution in the depleted mantle. Modified from Kamber et al. (2003) and Kramers and Tolstikhin (1997).

allow for sequestration of ca. 15% Nb into the core (following Kamber et al. 2003) because Nb can become siderophile under very reducing conditions prevailing during metal removal into the core (Wade and Wood 2001). The curve suggests a sigmoidal evolution for Nb/Th in the depleted mantle, starting with relatively low ratios until 3.5 Ga, then increasing strongly between 3.0 and 2.0 Ga, and a slow increase ever since.

The second approach to track mantle depletion is to study the time-integrated effect of continental extraction and recycling on depleted mantle isotope systematics. Most readers are probably familiar with the long-lived $^{147}Sm/^{143}Nd$ system. Owing to the slightly higher incompatibility of Nd, continental crust has a lower Sm/Nd ratio than its mantle source and as a result, over time, will develop a lower $^{143}Nd/^{144}Nd$ ratio. The contrary situation is, of course, true for the depleted portion of the mantle. However, because neither Sm nor Nd are nearly as concentrated in continental crust as Th, and because Sm/Nd fractionation is much more modest than Nb/Th, it turns out that the present-day mantle $^{143}Nd/^{144}Nd$ ratio is not very sensitive to the extraction history and recycling rate of continental crust. Nägler and Kramers (1998) explained, in detail, that Nd-isotope systematics cannot easily discriminate between models with linear net growth of the continents or that producing the sigmoidal curve shown in Fig. 1.2(b). However, Nd-isotope systematics do argue against very early formation of voluminous continents and subsequent recycling (to lower the average continental age to ca. 2 Ga).

The only isotopic system that is truly sensitive to the mantle depletion history is U/Pb, because the mantle is so depleted in both these elements. Kramers and Tolstikhin (1997) explored the effects of a variety of mantle-depletion scenarios on the difference in predicted Pb-isotope compositions of the depleted mantle and average continental sediment. While their preferred solution for a continental-crust volume-versus-age curve is not unique, they identified a few key parameters. First, the strongest control over the position of the modelled Pb-isotope composition of the depleted mantle is exerted by the continental crust-extraction versus recycling balance, which must satisfy an average continental age of ca. 2 Ga. Second, the timing of preferential U-recycling is important. This is tied to the age of the great oxygenation event, because under an atmosphere devoid of free O, U remained immobile. Once free O accumulated in the atmosphere, U but not Th was transferred into the ocean, and from there into hydrated oceanic lithosphere and sediment. A proportion of this U became recycled into the mantle. The timing of the onset of this process is critical for modelling of the mantle Pb isotope curves and this marker has since been confirmed to have occurred between 2.4 and 2.2 Ga (Bekker et al. 2004). Finally, the timing of Pb loss to space (volatility) and to the core is also important. The preferred solution of Kramers and Tolstikhin (1997) is sensitive to relatively late Pb loss to the core, but this is not supported by W-isotope systematics (e.g. Yin et al. 2002). The information available at present supports the conclusion of Kramers and Tolstikhin (1997) that the U/Pb ratio of the depleted mantle was dynamic (Fig. 1.2c). The most important outcome concerns the significant difference in the position of the depleted mantle Pb-isotope evolution modelled with a dynamic U/Pb compared to that of a static U/Pb, such as could have been set by a single early depletion event. Figure 1.3 illustrates that the differences are greatest for the late Archaean and Palaeoproterozic as well as for the modern mantle. We will return to this important point when discussing the Pb-isotope systematics of OIB.

Remembering that because this type of forward model only uses modern isotope-compositions as input parameters, it can be tested by comparing predicted ancient Pb-isotope compositions with those actually observed. The most meaningful such comparison is for late Archaean rocks, as it is for this particular time period that the dynamic U/Pb model predicts a rather different composition from that of the static U/Pb model (Fig. 1.3). The greenstones of the Abitibi greenstone belt of Ontario and Quebec are widely regarded to have formed from largely juvenile mantle sources. They have the most radiogenic initial Nd-isotope compositions for rocks of that age and, undoubtedly, have come from the depleted mantle (Ayer et al. 2002). Thus, Abitibi and Wabigoon greenstone belt initial Pb (conveniently preserved in ores and feldspars) can be used to test the accuracy of the dynamic U/Pb model. As is seen in Fig. 1.3, the observed Pb-isotope composition plots almost exactly on the depleted mantle-

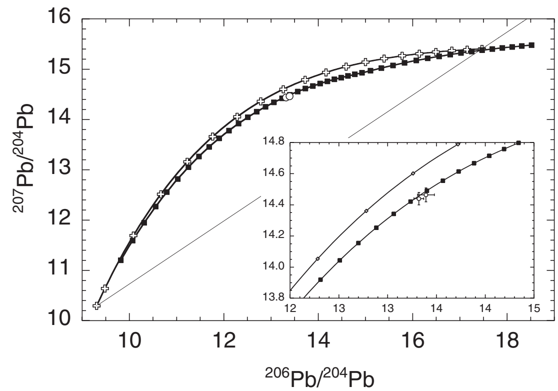

Fig. 1.3 Common Pb-isotope diagram contrasting the curve of the depleted mantle source (solid curve with black square markers) consistent with the sigmoidal continental crust volume-versus-age curve shown in Fig. 1.2(b) and a single-stage growth curve (solid curve with open-cross symbols) with a $^{238}U/^{204}Pb$ ratio of 7.91. Modified from Kramers and Tolstikhin (1997) and Kamber and Collerson (1999). Also shown for reference and in the inset are the observed initial Pb-isotope compositions of 2.72 Ga Wabigoon and 2.68 Ga Abitibi greenstone belts. Data sources: Tilton (1983); Gariépy and Allègre (1985); and Carignan et al. (1993, 1995).

evolution curve between 2.7 and 2.8 Ga, and has a much lower $^{207}Pb/^{204}Pb$ ratio than predicted by a static single-stage model for the depleted mantle.

In summary, it is not currently possible to quantify the relative contributions of a very early planet-scale depletion event versus the depletion effects of continental extraction for the mildly incompatible elements, such as the middle rare-earth elements (REE). However, for the very incompatible elements, it is clear that their inventories in the depleted mantle have changed as a function of continental extraction and recycling.

THE LOWER CRUST AS A PARTLY HIDDEN RESERVOIR OF INCOMPATIBLE ELEMENTS

The formation of the chemically-evolved continental crust, which is on average andesitic in composition, from an essentially basaltic parental melt continues to pose major mass-balance problems. The bulk density of continental crust is not permissive of the presence of ultramafic cumulates at the base of the seismically defined lower crust. Therefore, models that attempt to explain the mass imbalance resort to either placing the seismic Moho shallower than the igneous crust, or invoke the delamination of dense lower crustal cumulates, such as eclogite (e.g. Arndt and Goldstein 1989; Ellis and Maboko 1992). In the former case, lower-crustal igneous cumulates could reside below the seismic Moho where they cannot be distinguished (seismically) from residual depleted peridotite (e.g. Muentener et al. 2001). Alternatively, delaminated crustal eclogite may have foundered through the lithosphere and left the average crust with a more evolved bulk composition than the parental melt.

Regardless of this petrological issue, it is clear that the seismically-defined crust is chemically and mineralogically heterogeneous. While the composition of the upper continental crust is very well studied (e.g. Taylor and McLennan 1985), there are surprisingly few genuine lower-crustal rock sections exposed, and most of the relatively sparse information about the composition of the lower crust is actually derived from xenoliths. It is important to stress that orogenic granulites exposed in exhumed collisional mountain belt roots cannot, in most cases, be used to approximate the composition of 'typical' lower continental crust.

The key observations regarding distribution of highly incompatible elements in the lower continental crust are heat-flow measurements and determinations of geothermal gradients. The former reflect the total heat flow from a particular area of continental crust, while the latter tell us about the vertical distribution of the three main radioactive heat-producing elements – K, Th and U – which are all highly incompatible. Estimates of thermal gradients and heat flow (from deep mines and boreholes) firmly show that the heat-producing elements are strongly concentrated in the upper continental crust (e.g. Rudnick and Fountain 1995; Perry et al. 2006). The observed mechanical strength of continents also requires a relatively stiff middle crust, which implies that temperatures there cannot exceed the brittle/plastic transition of feldspar at ca. 550°C (e.g. Pryer 1993).

There are two principal ways in which the lower crust could have ended up depleted in heat-producing elements. First, magmatic compositional stratification would necessarily lead to a feldspar-pyroxene dominated lower continental crust inherently poor in heat-producing elements. Alternatively, the lowermost continental crust originally could have harboured some heat-producing elements. The resulting build-up of heat could have led to crustal melting (e.g. Michaut et al. 2009), during the course of which the highly incompatible elements would have been removed into granitoid melts and relocated much higher in the crustal column (e.g. O'Nions et al. 1979; Whitehouse 1989).

Lead isotope compositions of lower crustal xenoliths, particularly for those that contain plagioclase, can be used to distinguish between these two scenarios. Figure 1.4(a) illustrates a theoretical model of how Pb-isotope ratios can be used to infer the U/Pb history of lower crust. Two end-member model crusts are modelled. Both are calculated to have formed at 2.50 Ga with the same isotopic composition as coeval mantle. The first curve shows the Pb-isotope evolution of an inherently low U/Pb crust and the second illustrates the curve of a crust that initially had a U/Pb ratio similar to upper continental crust, but lost 90% of its U some 500 million years later. The models show that, in the latter case, the composition plots above the depleted mantle evolution curve, but far to the left of modern continental sediment. From the Pb-isotope compositions of lower crustal xenoliths shown in Fig. 1.4(b) it is observed that almost all plot well above the mantle evolution curve and that almost none plot below. This firmly argues against an inherently U (and by analogy Th and K) -poor lower continental crust.

The distribution of observed lower crustal feldspar Pb-isotope compositions is also insightful. On account of its low (U+Th)/Pb ratio, feldspar preserves the Pb-isotope composition of the last

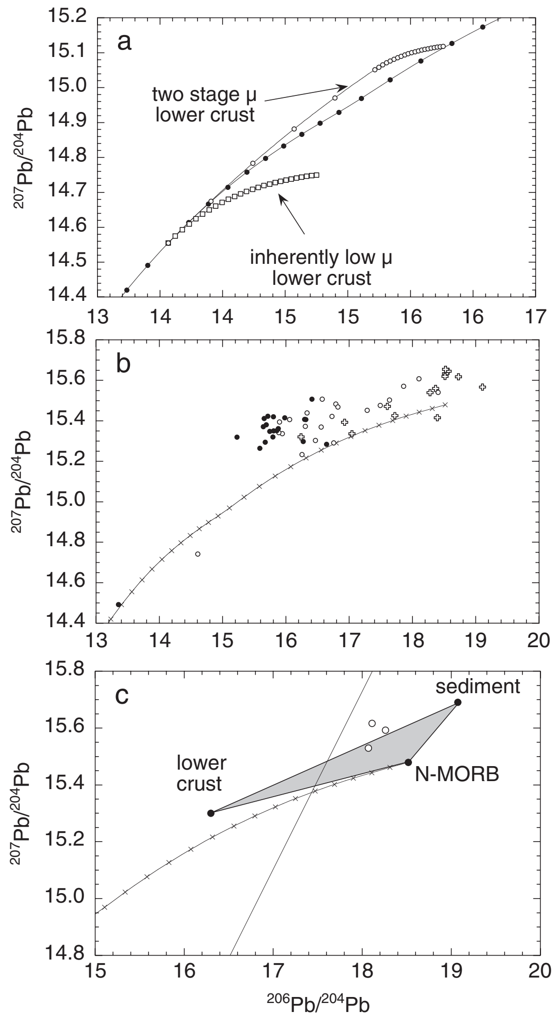

Fig. 1.4 Lead isotope models and compositions of lower crustal rocks. (a) Two contrasting models illustrating the difference in Pb-isotope evolution of an inherently low U/Pb crust (μ = 2.5) and that of a crust that initially had a U/Pb ratio (15) identical to upper continental crust but, 500 million years later, lost 90% of its U. The latter plots above the depleted mantle evolution curve (solid line connecting solid circles) but the former below; (b) compilation of average Pb-isotope compositions of world-wide lower crustal xenoliths (open crosses) after Bolhar et al. (2007). Also shown are individual Wyoming craton xenolith whole-rock (open circles) and feldspar (solid circles) compositions; (c) Positions of lower continental-crust average (from Bolhar et al. 2007), continental sediment and N-MORB (after Kramers and Tolstikhin 1997) relative to the 4568 Ma meteorite isochron. Three estimates of bulk silicate-earth Pb-isotope composition are shown as open circles. That of Galer and Goldstein (1996) plots above the triangle defined by N-MORB, upper and lower continental crust while those of Kamber and Collerson (1999) and Murphy et al. (2003) plot near and into the triangle, respectively.

time of recystallization, at which time it will have exchanged Pb with the whole rock (Fig. 1.4b). By comparing whole-rock and feldspar Pb-isotope compositions, it is possible to get a rough idea of when U was lost and, furthermore, by approximately how much the U/Pb ratio of the whole rock was lowered. This approach was explained by Bolhar et al. (2007) using Precambrian lower crustal xenoliths from the northern Wyoming province. These authors showed that U-loss from Neoarchean lower crust occurred ca. 500 million years after igneous crystallization. Uranium loss was driven by partial melting that lowered the U/Pb ratio between 50% and 90%. Similar reductions in U/Pb were calculated for granulites from Fyfe Hills in Antarctia (dePaolo et al. 1982).

In the vertical direction, the chemical self-reorganization of the continents is driven by the geothermal gradient (e.g. Michaut et al. 2009). In the typical case of geological terrains, where only upper crustal levels are exposed, lower crustal melting is inferred from abundant late (with respect to deformation) K-rich granitoids (e.g. Sandiford and McLaren 2002). In Archaean terrains, the intrusion of these granitoids is often seen as the critical step for cratonization. The most important factors that determine the geotherm are basal heatflow, crustal thickness, and the concentration and vertical distribution of the three main heat-producing radioactive elements K, U and Th. These factors remaining equal, the delicate thermal stability of continental crust is also a strong function of time, because of the decrease in heat output, mainly from ^{235}U (Kramers et al. 2001).

Although it is difficult to predict the time period for which lower crust of a given age might have remained thermally stable before reaching the granitoid solidus, it can nonetheless be qualitatively appreciated that as radioactive heat production decays with time, the lag between crust formation and lower crustal melting will become longer. For the Neoarchean and Palaeoproterozoic examples that have been studied, a 500 million year time lag seems typical (e.g. Whitehouse 1989; Bolhar et al. 2007). Younger, Phanerozoic crust may therefore not yet have reached its final vertical chemical stratification. This probably explains why the well-studied lower crustal xenoliths from northeastern Australia (Rudnick and Goldstein 1990) have Pb-isotope compositions similar to continental sediment. Namely, insufficient time has yet elapsed for their host lower crust to lose enough K, U and Th to eventually reach thermal stability, and for the lower (U+Th)/Pb ratio to be expressed in Pb-isotope compositions.

Partial melting of lower continental crust not only distils U, Th and K into the upper crust but also affects a host of other incompatible trace elements. Therefore, to accurately estimate the composition of the lower continental crust, it is necessary to study xenoliths from crust that have undergone the full reorganization, because average continental crust has an age in excess of 2 Ga. However, the most widely used estimate of the composition of the lower crust relies predominantly on xenoliths from Phanerozoic crust (e.g. Rudnick and Fountain 1995). Further studies are required to determine the chemistry of older xenoliths to refine current understanding of typical lower crustal composition, and, by inference, the average composition of continental crust (e.g. Taylor and McLennan 1985).

Radiogenic isotope studies of the lower continental crust demonstrate that the transfer of heat-producing elements via partial melting strengthens primary vertical chemical stratification. In the simplest case, this is achieved by a single partial melting event, but, at least for old crustal sections, multiple melting events are more plausible. The net result for Pb-isotope composition is the multi-stage lowering of the U/Pb ratio and the retardation of Pb-isotope evolution. This has an important implication for global mass balance. Figure 1.4(c) illustrates that both continental sediment and N-MORB both plot well to the right of the 4568 Ma meteorite isochron. This forms part of the first terrestrial Pb-isotope paradox (Allègre 1969) and implies the existence of hidden or rarely tapped Pb-reservoirs at depth that plot to the left of the meteorite isochron. Estimates for the bulk silicate-earth Pb-isotope composition that take into account the effect of core formation and volatility related Pb-loss are shown in Fig. 1.4(c). It is obvious in common Pb-isotope space that old lower crust (as sampled by xenoliths) could help to pull the combined compositions of upper crustal sediment and N-MORB closer towards bulk-silicate Earth estimates.

ENRICHED MANTLE RESERVOIRS AND THEIR CONNECTION TO CONTINENTAL CRUST AND THE DEPLETED MANTLE

The study of the geochemistry and radiogenic isotope systematics of basaltic rocks from enriched mantle sources has yielded a vast body of evidence that cannot be summarized here, not least because fundamental controversies about the meaning of isotopic signatures remain. Thus, only those aspects of enriched mantle reservoirs that are directly relevant to the two reservoirs already discussed – the depleted mantle and the lower continental crust are considered.

Of all possible mechanisms that could have led to mantle enrichment, as sampled by modern mantle melts, the early silicate differentiation event can be excluded on present evidence. Regardless of whether this differentiation, which apparently increased the Sm/Nd of the accessible mantle, was caused by formation and subsequent deep recycling of a protocrust (e.g. Tolstikhin and Hofmann 2005; Boyet and Carlson 2005) or by cumulates from an early magma ocean, it appears that none of the modern mantle melts is tapping into it. The lack of low $^{142}Nd/^{144}Nd$ mantle melts on Earth (Boyet et al. 2005) complementary to the widely accessible reservoirs could also imply a terrestrial Sm/Nd ratio of the terrestrial planets (e.g. Caro et al. 2008) that is different from that of typical chondrites, such as might be caused by incomplete mixing of products of different nucleosynthetic processes in the feeding zone of the early Solar nebula (e.g. Ranen and Jacobsen 2006). This possibility may question altogether whether a very early silicate differentiation event occurred on Earth. Alternatively, the early reservoir could be completely hidden. Regardless, neither solution offers insight into the significance of the enriched reservoirs actually observed.

A second generally valid observation is that the nomenclature of the enriched mantle reservoirs (e.g. Zindler and Hart 1986) was developed largely on the basis of Pb-isotope compositions, for they show by far the largest dispersion compared to Sr-, Nd-, Hf- and Os- radiogenic isotope systems. The term 'enriched' in this context is somewhat ambiguous. Namely, the principal three enriched reservoirs, enriched mantle 1 (EM-1), enriched mantle 2 (EM-2) and the 'high μ' reservoir (HIMU) are enriched in U/Pb relative to depleted mantle. But by analogy with all other isotope systems, enrichment should ideally be defined relative to bulk-silicate Earth. It is noted that since the seminal work by Zindler and Hart (1986), estimates of the Pb-isotope composition of the bulk-silicate Earth have evolved (Fig. 1.4(c)) and the idea needs to be entertained that there may be two principal ways of arriving at the $^{207}Pb/^{206}Pb$ composition of EM-1. This issue will be discussed next, before commenting on the possible significance of the HIMU reservoir and the OIB Pb-isotope array as a whole.

Figure 1.5(a) shows the position of OIB of EM-1 character in common Pb-isotope space alongside the bulk-silicate Earth estimates already discussed in Fig. 1.4(c). It can be seen that, with the exception of Kerguelen, most EM-1 basalts have $^{207}Pb/^{204}Pb$ ratios no higher than estimates of undepleted (primitive) but not enriched mantle. This illustrates the point that the term 'enriched', with regard to elevated $^{207}Pb/^{204}Pb$ relative to depleted mantle, is not necessarily accurate. Melts from the undepleted mantle would, of course, be expected also to have high $^{3}He/^{4}He$ ratios, such as those found in certain Hawaiian (Loihi) and early Iceland plume picrites (e.g. Hilton et al. 2000). The alternative explanation for the Pb-isotope composition of EM-1 is that its mantle source contains a component of recycled continental material. The possibility of continental sediment recycling was proposed to account for the peculiarly high $^{208}Pb/^{206}Pb$ ratios (Fig. 1.5b) of seamounts of the Pitcairn chain (Woodhead and

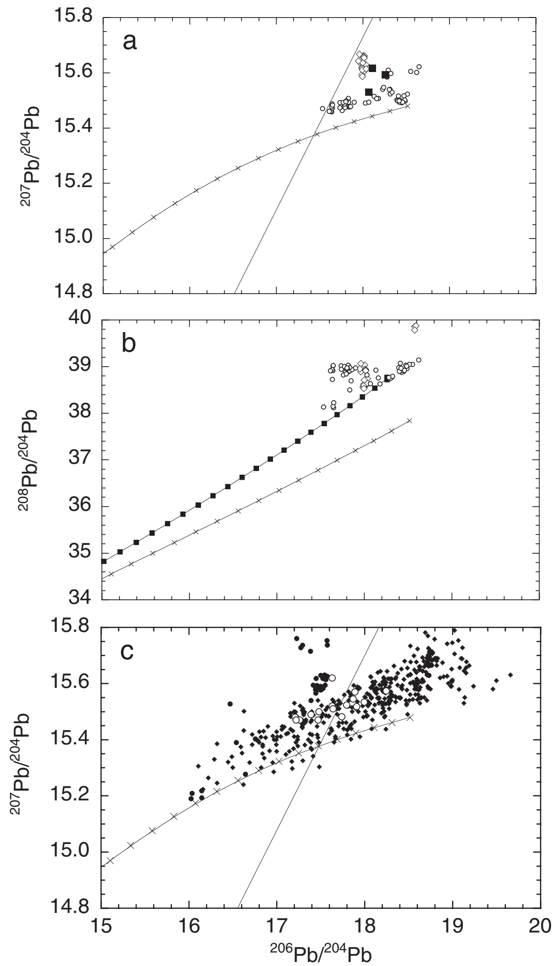

Fig. 1.5 Pb-isotope systematics of enriched mantle sources. (a) Common Pb-isotope diagram showing a selection of EM-1 type ocean-island basalts from Walvis Ridge, Pitcairn, Gough and South Atlantic Ridge seamounts (all as open small circles) and Kerguelen (open diamond symbols) compared to bulk-silicate Earth estimates from Fig. 1.4(c) (solid squares), meteorite isochron and depleted mantle curve (Kramers and Tolstikhin, 1997). Basalt data are from Eiler et al. (1995); Eisele et al. (2002); Gast et al. (1964); Ingle et al. (2002); Regelous et al. (2009); Richardson et al. (1982); Weis et al. (2001) and Woodhead and McCulloch (1989). (b) The same data in thorogenic Pb-isotope space. Note that this comparison only shows one bulk silicate-earth evolution (after Kamber and Collerson (1999), in 100 Ma time steps). (c) Common Pb-isotope diagram with lamproite (solid circles), selected kimberlite (open circles) and alkali basalt (solid small diamonds) data relative to 4568 Ma meteorite isochron (adapted from Murphy et al. 2003) and depleted mantle curve.

Devey 1993). These authors argued that preferential loss of U>Pb>Th during subduction dehydration of pelagic sediment leads to relatively low U/Pb and high Th/U ratios, which, over time, express as low $^{206}Pb/^{204}Pb$ and high $^{208}Pb/^{206}Pb$ ratios. The similarity between lower continental crust and certain EM-1 ocean island basalts in Pb-isotope composition and pertinent trace element geochemical signatures also has led to the proposal that there might be recycled lower continental crust in the shallow astenosphere (e.g. Weis et al. 2001) and that it might be the source of at least the South Atlantic EM-1 signature (e.g. Willbold and Stracke 2006; Regelous et al. 2009). It can be seen from Fig. 1.5(b) that EM-1 type OIB define a considerable spread in $^{208}Pb/^{204}Pb$ at any given $^{206}Pb/^{204}Pb$. Those samples with the lowest $^{208}Pb/^{204}Pb$ ratios plot exactly onto the undepleted mantle curve of Kamber and Collerson (1999). That curve was modelled using single-stage evolution, with $^{238}U/^{204}Pb$ and $^{232}Th/^{238}U$ ratios of 8.9 and 4.21, respectively. A $^{232}Th/^{238}U$ ratio of 4.21 is at the upper end of chondritic estimates (e.g. Kramers and Tolstikhin 1997) and it appears unlikely that those EM-1 type ocean island basalts (OIB) with the highest $^{208}Pb/^{204}Pb$ ratios could be generated in undepleted mantle. In summary, combined Th-U-Pb isotope systematics can be used to subdivide EM-1 basalts into two possible origins. Those with modestly high $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios could come from the least U- and Th-depleted mantle, while those with much higher $^{208}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios, as well as a very low $^{206}Pb/^{204}Pb$ ratio, would have continental material in their source. The continental material can either be subduction zone-modified sediment with low $^{238}U/^{204}Pb$ and high $^{232}Th/^{238}U$ ratios, owing to preferential loss of U over Pb and Pb over Th, or delaminated segments of old lower continental crust that preferentially had lost U>Th>Pb during earlier episodes of intracrustal differentiation. Proterozoic granulite xenoliths have been recovered in Kerguelen Plateau boreholes (e.g. Weis et al. 2001), proving that entrainment of granulite facies continental crust is feasible, at least in that particular setting. It was further suggested that such crust could have affected the radiogenic isotope, and particularly the Pb-isotope, systematics of the entire Indian Ocean basin mantle (e.g. Weis et al. 2001).

Experimental studies of element behavior during sediment dehydration (Rapp et al. 2008) have confirmed that the proposal of a sediment component in the high $^{208}Pb/^{206}Pb$ EM-1 type source is compatible with trace-element systematics. The experimental findings by Rapp et al. (2008) further showed that lamproites (i.e. ultrapotassic magnesian volcanic rocks) could represent a more extreme approximation to melt from subducted continental sediment as originally proposed by Nelson (1992) and further elaborated by Murphy et al. (2002). It is interesting to note that many examples of highly alkaline magnesian volcanic rocks – such as lamproites, minettes, carbonatites, and lamprophyres – plot well above the depleted mantle evolution curve but to the left of the meteorite isochron (Fig. 1.5(c)). Murphy et al. (2003) suggested that their mantle source (subduction modified recycled continental sediment) could help to solve the first terrestrial Pb-isotope paradox, alongside the lower continental crust.

Another widely advocated mechanism for mantle enrichment is via recycling of oceanic crust. Again, this idea has its origin in Pb-isotope systematics. In his highly influential paper on Pb-isotope systematics of OIB, Chase (1981) noted that the OIB Pb-isotope array as a whole (Fig. 1.6a) defines a slope of ca. 1.7 Ga. Further noting that the linear regression line intersected a single stage Pb-isotope curve also at ca. 1.7 Ga, he proposed that isolation of recycled oceanic crust with a 10–20% higher U/Pb ratio than typical mantle could, over time, evolve to the array of Pb-isotope compositions displayed by OIB (other than EM-1). Thus, the increase in U/Pb relative to contemporary mantle could be inherent in oceanic crust formation (as originally proposed by Chase, 1981) and caused by U-addition during sea-floor alteration (e.g. Jochum and Verma 1996) or have its origin during preferential removal of Pb during subduction dehydration (Chauvel et al. 1995). The latter process would ultimately lead to the characteristic over-enrichment in Pb of continental crust (see Fig. 1.1).

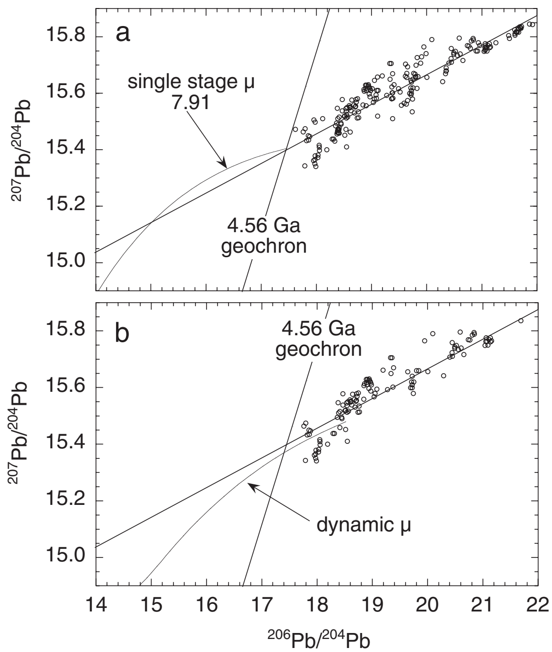

Fig. 1.6 Common Pb-isotope array of world-wide OIB modified from Kamber and Collerson (1999). In (a) a linear regression line is shown (with a slope corresponding to ca. 1.7 Ga) relative to the single stage (μ = 7.91) mantle evolution curve of Chase (1981), which is intersected at approximately 1.7 Ga; in (b) the same regression line is shown relative to the depleted mantle evolution curve of Kramers and Tolstikhin (1997), which is not intersected by the OIB linear regression line. See text for explanation.

The idea of initially increasing the U/Pb of oceanic crust via U-addition during seafloor metamorphism is attractive from the point of view of also linking this explanation to the solution to the second terrestrial Pb-paradox, as explained in the opening section of this chapter. Thus, the low Th/U ratio of N-MORB; and its position to the right of the meteorite isochron would be related to the more extreme position of the HIMU source, in particular, and the OIB Pb-isotope array, in general. The proposal that the OIB Pb-isotope systematics could have been influenced additionally by preferential (relative to Th and U) Pb-loss from oceanic crust during prograde subduction dehydration (Chauvel et al. 1995) is also attractive, as it could explain the surprisingly low continental U/Pb ratio. Compared to typical lunar rocks (e.g. Premo et al. 1999), terrestrial arc rocks have much lower U/Pb ratios, clearly demonstrating the role of aqueous fluids in shaping terrestrial geochemical reservoirs.

Despite the pleasing internal consistency emerging from these models, new observations challenge the simplicity (and elegance) of the elemental cycles described above. The key problem is the highly dynamic U/Pb evolution of the depleted mantle that was discussed earlier. It has led to a Pb-isotope curve very different from that produced by a single stage, constant U/Pb model (Fig. 1.3). This has significant ramifications for the idea proposed by Chase (1981). While a regression line through the general OIB array (with a slope corresponding to ca. 1.7 Ga) indeed intersects the constant U/Pb growth curve at roughly 1.7 Ga, it does not intersect the depleted mantle curve of Kramers and Tolstikhin (1997) at all (Fig. 1.6(b)), plotting instead at too high a $^{207}Pb/^{204}Pb$ ratio for a given $^{206}Pb/^{204}Pb$ ratio. Since the dynamic U/Pb model is successful at predicting not only modern N-MORB Pb-isotope compositions but also juvenile Pb of late Archaean age, it seems difficult to derive OIB Pb-isotope ratios via storage of oceanic slabs in the mantle. This problem was originally discussed by Kamber and Collerson (1999) and has not yet been satisfactorily solved.

The second potential problem arises from considerations of Nb/Th and Nb/U ratios. If, as is widely thought, the continental Nb/Th ratio is low because Nb is preferentially retained in the metamorphosed oceanic slab, then it follows that partial melts from such slabs should have higher Nb/Th ratios than contemporaneous N-MORB, but most modern OIB have Nb/Th ratios of ca. 16. This is lower than modern N-MORB with Nb/Th of 18. However, a solution is still possible, if these OIB were derived from ancient oceanic lithosphere. For example, the observed Nb/Th ratio for N-MORB at 2.0 Ga is about 14 (Fig. 1.2(a)). Subducted oceanic crust of that age would be expected to have lost more Th than Nb, and therefore its Nb/Th ratio would be expected to be higher than 14. Modern OIB do indeed show a somewhat higher ratio, but only marginally so (Hofmann 1997).

It is now well established that continental crust has a lower Nb/Ta ratio (11–12) than chondrites (18) and N-MORB (14), leading to an unresolved mass imbalance that requires a missing high Nb/Ta reservoir (e.g. Rudnick et al. 2000). If the low continental Nb/Ta ratio is acquired during the modification of oceanic crust to eclogite that also imprints the low continental Nb/Th, it follows that melts from subducted oceanic slabs (i.e. OIB) should have high Nb/Ta ratios (Kamber and Collerson 2000). However, they do not (e.g. Pfander et al. 2007). These observations could be used to argue that most OIB are not the melting products of ancient recycled oceanic crust (e.g. Kamber and Collerson 2000; Pilet et al. 2005; Niu and O'Hara 2009) or that oceanic slabs do not have a high Nb/Ta ratio (Pfander et al. 2007).

SUMMARY

The origin of the chemical enrichment that characterizes the mantle source regions that generate OIB is still a major area of on-going research. It is not possible at present to satisfy all mass-balance constraints with a single model of mantle depletion, continent formation and recycling, and evolution of OIB source regions in the mantle. The idea of metasomatic enrichment of the deep lithosphere (e.g. Pilet et al. 2005) is gaining momentum as an alternative source for many OIB, but this proposal carries a large number of implications that fundamentally challenge widely accepted ideas regarding formation of the continents. Some of these have been discussed by Niu and O'Hara (2009). Compared to the first generation models for large-scale differentiation of the planet, current ideas place even more emphasis on the highly dynamic nature of elemental and isotopic evolution within the major terrestrial geochemical reservoirs. The extraction history of continental crust and its recycling into the mantle, modified and possibly influenced by the change in the composition of the atmosphere, remain as very significant controls over mantle evolution. The successful combination of information from radiogenic isotopes with highly incompatible trace elements will be key in further refining our understanding of the fascinating history of terrestrial differentiation.

REFERENCES

Allègre, CJ. (1969) Comportement des systemes U-Th-Pb dans le manteau superieur et modele d èvolution de ce dernier au cours des temps geologiques. *Earth and Planetary Science Letters*, **5**: 261–9.

Arndt, NT and Goldstein, SL. (1989) An Open Boundary between Lower Continental-Crust and Mantle – Its Role in Crust Formation and Crustal Recycling. *Tectonophysics*, **161**: 201–12.

Ayer, J, Amelin, Y, Corfu, F, Kamo, S, Ketchum, J, Kwok, K and Trowell, N. (2002) Evolution of the southern Abitibi greenstone belt based on U-Pb geochronology: autochthonous volcanic construction followed by plutonism, regional deformation and sedimentation. *Precambrian Research*, **115**: 63–95.

Bekker, A, Holland, HD, Wang, PL, Rumble, DI, Stein, HJ, Hannah, JL, Coetzee, LL and Beukes, NJ. (2004) Dating the rise of atmospheric oxygen. *Nature*, **427**: 117–120.

Blenkinsop, TG, Fedo, CM, Eriksson, KA, Martin, A, Nisbet, GE and Wilson, JF. (1993) Ensialic origin for the Ngezi Group, Belingwe greenstone belt, Zimbabwe. *Geology*, **21**: 1135–8.

Bolhar, R, Kamber, BS and Collerson, KD. (2007) U-Th-Pb fractionation in Archaean lower continental crust: Implications for terrestrial Pb isotope systematics. *Earth and Planetary Science Letters*, **254**: 127–45.

Boyet, M and Carlson, RW. (2005) 142Nd isotope evidence for early (>4.53 Ga) global differentiation of the silicate Earth. *Science*, **309**: 576–8.

Boyet, M, Garcia, MO, Pik, R and Albarede, F. (2005) A search for Nd-142 evidence of primordial mantle heterogeneities in plume basalts. *Geophysical Research Letters*, **32** (4).

Campbell, IH and Griffiths, RW. (1993) The evolution of the mantle's chemical-structure. *Lithos*, **30**: 389–99.

Carignan, J, Gariepy, C, Machado, N and Rive, M. (1993) Pb isotopic geochemistry of granitoids and gneisses from the late Archean Pontiac and Abitibi Subprovinces of Canada. *Chemical Geology*, **106**: 299–316.

Carignan, J, Machado, N and Gariépy, C. (1995) Initial lead composition of silicate minerals from the Mulcahy layered intrusion: Implications for the nature of the Archean mantle and the evolution of greenstone belts in the Superior Province, Canada. *Geochim. Cosmochim. Acta*, **59**: 97–105.

Caro, G, Bourdon, B, Halliday, AN and Quitte, G. (2008)Super-chondritic Sm/Nd ratios in Mars, the Earth and the Moon. *Nature*, **452**: 336–9.

Chan, LH, Leeman, WP and You, CF. (1999) Lithium isotopic composition of Central American volcnic arc lavas: Implications for modification of the sub-arc mantle by slab-derived fluids. *Chemical Geology*, **160**: 255–80.

Chase, CG. (1981) Oceanic island Pb: two-stage histories and mantle evolution. *Earth and Planetary Science Letters*, **52**: 277–84.

Chauvel, C, Goldstein, SL and Hofmann, AW. (1995) Hydration and dehydration of oceanic crust controls Pb evolution of the mantle. *Chemical Geology*, **126**: 65–75.

Collerson, KD and Kamber, BS. (1999) Evolution of the continents and the atmosphere inferred from Th-U-Nb systematics of the depleted mantle. *Science*, **283**: 1519–22.

DePaolo, DJ, Manton, WI, Grew, ES and Halpern, M. (1982) Sm-Nd, Rb-Sr and U-Th-Pb Systematics of Granulite Facies Rocks from Fyfe-Hills, Enderby Land, Antarctica. *Nature*, **298**: 614–18.

DePaolo, DJ and Wasserburg, GJ. (1976) Nd Isotopic Variations and Petrogenetic Models. *Geophysical Research Letters*, **3**: 249–52.

Eiler, JM, Farley, KA, Valley, JW, Stolper, EM, Hauri, EH and Craig, H. (1995) Oxygen-Isotope Evidence against Bulk Recycled Sediment in the Mantle Sources of Pitcairn Island Lavas. *Nature*, **377**: 138–41.

Eisele, J, Sharma, M, Galer, SJG, Blichert-Toft, J, Devey, CW and Hofmann, AW. (2002) The role of sediment recycling in EM-1 inferred from Os, Pb, Hf, Nd, Sr isotope and trace element systematics of the Pitcairn hotspot. *Earth and Planetary Science Letters*, **196**: 197–212.

Elliott, T, Zindler, A and Bourdon, B. (1999) Exploring the kappa conundrum: the role of recycling in the lead isotope evolution of the mantle. *Earth and Planetary Science Letters*, **169**: 129–45.

Ellis, DJ and Maboko, MAH. (1992) Precambrian tectonics and the physicochemical evolution of the continental crust. I. The gabbro-eclogite transition revisited. *Precambrian Research*, **55**: 491–506.

Galer, SJG and O'Nions, RK. (1985) Residence time of uranium, thorium and lead in the mantle with implications for mantle convection. *Nature*, **316**: 778–82.

Galer, SJG and Goldstein, SL. (1996) Influence of accretion on lead in the Earth. In: A. Basu and S. Hart (Editors), *Earth processes: Reading the isotopic code*. AGU, Washington, pp. 75–98.

Gariepy, C and Allegre , CJ. (1985) The lead isotope geochemistry and geochronology of late-kinematic intrusives from the Abitibi Greenstone-Belt, and the implications for late Archean crustal evolution. *Geochimica Et Cosmochimica Acta*, **49**: 2371–83.

Gast, PW, Hedge, C and Tilton, GR. (1964) Isotopic Composition of Lead + Strontium from Ascension + Gough Islands. *Science*, **145**: 1181–5.

Hilton, DR, Thirlwall, MF, Taylor, RN, Murton, BJ and Nichols, A. (2000) Controls on magmatic degassing along the Reykjanes Ridge with implications for the helium paradox. *Earth and Planetary Science Letters*, **183**: 43–50.

Hofmann, AW. (1988) Chemical differentiation of the Earth: the relationship between mantle, continental crust, and oceanic crust. *Earth and Planetary Science Letters*, **90**: 297–314.

Hofmann, AW. (1997) Mantle geochemistry: the message from oceanic volcanism. *Nature*, **385**: 219–29.

Ingle, S, Weis, D, Scoates, JS and Frey, FA. (2002) Relationship between the early Kerguelen plume and continental flood basalts of the paleo-Eastern Gondwanan margins. *Earth and Planetary Science Letters*, **197**: 35–50.

Jochum, KP, Arndt, NT and Hofmann, AW. (1991) Nb-Th-La in komatiites and basalts: constraints on komatiite petrogenesis and mantle evolution. *Earth and Planetary Science Letters*, **107**: 272–89.

Jochum, KP and Verma, SP. (1996) Extreme enrichment of Sb, Tl and other trace elements in altered MORB. *Chemical Geology*, **130**: 289–99.

Kamber, BS and Collerson, KD. (1999) Origin of ocean-island basalts: A new model based on lead and helium isotope systematics. *J. Geophys. Res.*, **104**: 25'479–25'491.

Kamber, BS and Collerson, KD. (2000) Role of 'hidden' deeply subducted slabs in mantle depletion. *Chemical Geology*, **166**: 241–54.

Kamber, BS, Greig, A and Collerson, KD. (2005) A new estimate for the composition of weathered young upper continental crust from alluvial sediments, Queensland, Australia. *Geochim. Cosmochim. Acta*, **69**: 1041–58.

Kamber, BS, Greig, A, Schoenberg, R and Collerson, KD. (2003) A refined solution to Earth's hidden niobium: Implications for evolution of continental crust and depth of core formation. *Precambrian Research*, **126**: 289–308.

König, S, Münker, C, Schuth, S and Garbe-Schönberg, D. (2008) Mobility of tungsten in subduction zones. *Earth and Planetary Science Letters*, **274**: 82–92.

Kramers, JD, Kreissig, K and Jones, MQW. (2001) Crustal heat production and style of metamorphism: a comparison between two Archaean high grade provinces in the Limpopo Belt, southern Africa. *Precambrian Research*, **112**: 149–63.

Kramers, JD and Tolstikhin, IN. (1997) Two terrestrial lead isotope paradoxes, forward transport modelling, core formation and the history of the continental crust. *Chemical Geology*, **139**: 75–110.

Leybourne, MI, van Wagoner, NA and Ayres, LD. (1997) Chemical stratigraphy and petrogenesis of the Early Proterozoic Amisk Lake Volcanic Sequence, Flin-Flon-Snow Lake Greenstone Belt, Canada. *J. Petrol.*, **38**: 1541–64.

McCulloch, MT, 1993. The role of subducted slabs in an evolving earth. *Earth and Planetary Science Letters*, **115**: 89–100.

Michaut, C, Jaupart, C and Mareschal, JC. (2009) Thermal evolution of cratonic roots. *Lithos*, **109**: 47–60.

Miller, DM, Goldstein, SL and Langmuir, CH. (1994) Cerium/lead and lead isotope ratios in arc magmas and the enrichment of lead in the continents. *Nature*, **368**: 514–20.

Mohan, MR, Kamber, BS and Piercey, SJ. (2008) Boron and arsenic in highly evolved Archean felsic rocks: Implications for Archean subduction processes. *Earth and Planetary Science Letters*, **274**: 479–88.

Muentener, O, Keleman, PB and Grove, TL. (2001) The role of H_2O during crytsallization of primitive arc magmas under uppermost mantle conditions and genesis of igneous pyroxenites: an experimental study. *Contrib. Mineral. Petrol.*, **141**: 643–58.

Murphy, DT, Collerson, KD and Kamber, BS. (2002) Lamproites from Gaussberg: Possible transition zone melts of Archaean subducted sediments. *J. Petrol.*, **43**: 981–1001.

Murphy, DT, Kamber, BS and Collerson, KD. (2003) A refined solution to the first terrestrial Pb-isotope paradox. *J. Petrol*, **44**: 39–53.

Nägler, TF and Kramers, JD. (1998) Nd isotopic evolution of the upper mantle during the Precambrian: Models, data and the uncertainty of both. *Precambrian Research*, **91**: 233–52.

Nelson, DR. (1992) Isotopic Characteristics of Potassic Rocks – Evidence for the Involvement of Subducted Sediments in Magma Genesis. *Lithos*, **28**: 403–20.

Niu, YL and O'Hara, MJ. (2009) MORB mantle hosts the missing Eu (Sr, Nb, Ta and Ti) in the continental crust: New perspectives on crustal growth, crust-mantle differentiation and chemical structure of oceanic upper mantle. *Lithos*, **112**: 1–17.

O'Nions, RK, Evenson, NM and Hamilton, PJ. (1979) Geochemical modeling of mantle differentiation and crustal growth. *J. Geophys. Res.*, **84**: 6091–6101.

Peltonen, P, Kontinen, A and Huhma, H. (1996) Petrology and geochemistry of metabasalts from the 1.95 Ga Jormua Ophiolite, Northeastern Finland. *J. Petrol*, **37**: 1359–83.

Perry, HKC, Jaupart, C, Mareschal, JC and Bienfait, G. (2006) Crustal heat production in the Superior Province, Canadian Shield, and in North America inferred from heat flow data. *Journal of Geophysical Research-Solid Earth*, **111** (B4).

Pfander, JA, Münker, C, Stracke, A and Mezger, K. (2007) Nb/Ta and Zr/Hf in ocean island basalts – Implications for crust-mantle differentiation and the fate of Niobium. *Earth and Planetary Science Letters*, **254**: 158–72.

Pilet, S, Hernandez, J, Sylvester, P and Poujol, M. (2005) The metasomatic alternative for ocean island basalt chemical heterogeneity. *Earth and Planetary Science Letters*, **236**: 148–66.

Premo, WR, Tatsumoto, M, Misawa, K, Nakamura, N and Kita, NI. (1999) Pb-isotopic systematics of lunar highland rocks (>3.9 Ga): Constraints on early lunar evolution. In: GA Snyder, CR Neal and WG Ernst (Editors), *Planetary petrology and geochemistry*. GSA, Bellwether Publishing Ltd.

Pryer, LL. (1993) Microstructures in feldspars from a major crustal thrust zone: the Grenville Front, Ontario, *Canada J. of Structural Geology*, **15**: 21–36.

Ranen, MC and Jacobsen, SB. (2006) Barium isotopes in chondritic meteorites: Implications for planetary reservoir models. *Science*, **314**: 809–12.

Rapp, RP, Irifune, T, Shimizu, N, Nishiyama, N, Norman, MD and Inoue, J. (2008) Subduction recycling of continental sediments and the origin of geochemically enriched reservoirs in the deep mantle. *Earth and Planetary Science Letters*, **271**: 14–23.

Regelous, M, Niu, YL, Abouchami, W and Castillo, PR. (2009) Shallow origin for South Atlantic Dupal Anomaly from lower continental crust: Geochemical evidence from the Mid-Atlantic Ridge at 26 degrees S. *Lithos*, **112**: 57–72.

Richardson, SH, Erlank, AJ, Reid, DL and Duncan, AR. (1982) Major and trace element and Nd and Sr isotope geochemistry of basalts from the DSDP Leg 74 Walvis Ridge transsect. In: TC Moore (ed.), *Initial Reports on the Deep Sea Drilling Project 74*. US Government Printing Office, Washington DC, pp. 739–54.

Rudnick, RL, Barth, M, Horn, I and McDonough, WF. (2000) Rutile-bearing refractory eclogites: missing link between continents and depleted mantle. *Science*, **287**: 278–81.

Rudnick, RL and Fountain, DM. (1995) Nature and composition of the continental crust: a lower crustal perspective. *Rev. Geophys.*, **33**: 267–309.

Rudnick, RL and Goldstein, SL. (1990) The Pb Isotopic Compositions of Lower Crustal Xenoliths and the Evolution of Lower Crustal Pb. *Earth and Planetary Science Letters*, **98**: 192–207.

Ryan, JG and Langmuir, CH. (1993) The systematics of boron abundances in young volcanic rocks. *Geochim. Cosmochim. Acta*, **57**: 1489–98.

Sandiford, M and McLaren, S. (2002) Tectonic feedback and the ordering of heat producing elements within the continental lithosphere. *Earth and Planetary Science Letters*, **204**: 133–50.

Stacey, JS and Kramers, JD. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and Planetary Science Letters*, **26**: 207–21.

Sylvester, PJ, Campbell, IH and Bowyer, DA. (1997) Niobium/uranium evidence for early formation of the continental crust. *Science*, **275**: 521–3.

Taylor, SR and McLennan, SM. (1985) The continental crust: its composition and evolution. *Geoscience Texts*. Blackwell, Oxford.

Tilton, GR. (1983) Evolution of depleted mantle – the lead perspective. *Geochimica Et Cosmochimica Acta*, **47**: 1191–1197.

Tolstikhin, I and Hofmann, AW. (2005) Early crust on top of the Earth's core. *Physics of the Earth and Planetary Interiors*, **148**: 109–30.

Wade, J and Wood, BJ. (2001) The Earth's 'missing' niobium may be in the core. *Nature*, **409**: 75–8.

Weis, D, Ingle, S, Damasceno, D, Frey, FA, Nicolaysen, K and Barling, J. (2001) Origin of continental components in Indian Ocean basalts: Evidence from Elan Bank (Kerguelen Plateau, ODP Leg 183, Site 1137). *Geology*, **29**: 147–50.

Whitehouse, MJ. (1989) Pb-Isotopic Evidence for U-Th-Pb Behavior in a Prograde Amphibolite to Granulite Facies Transition from the Lewisian Complex of Northwest Scotland – Implications for Pb-Pb Dating. *Geochimica Et Cosmochimica Acta*, **53**: 717–24.

Willbold, M and Stracke, A. (2006) Trace element composition of mantle end-members: Implications for recycling of oceanic and upper and lower continental crust. *Geochemistry Geophysics Geosystems*, **7**.

Woodhead, JD and McCulloch, MT. (1989) Ancient seafloor signals in Pitcairn island lavas and evidence for large amplitude, small-scale mantle heterogeneities. *Earth and Planetary Science Letters*, **94**: 257–73.

Woodhead, JD and Devey, CW. (1993) Geochemistry of the Pitcairn seamounts, I: source character and temporal trends. *Earth and Planetary Science Letters*, **116**: 81–99.

Yin, Q, Jacobsen, S.B, Yamashita, K, Blichert-Toft, J, Télouk, P and Albarede, F. (2002) A short timescale for terrestrial planet formation from Hf-W chronometry of meteorites. *Nature*, **418**: 949–52.

Zimmer, M, Kröner, A, Jochum, KP, Reischmann, T and Todt, W. (1995) The Gabal Gerf complex: A Precambrian N-MORB ophiolite in the Nubian Shield, NE Africa. *Chemical Geology*, **123**: 29–51.

Zindler, A and Hart, S. (1986) Chemical geodynamics. *Annu. Rev. Earth Planet. Sci.*, **14**: 493–571.