Earth and Planetary Science Letters 278 (2009) 361–369

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl

The K/U ratio of the silicate Earth: Insights into mantle composition, structure and thermal evolution

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ARTICLE INFO

Article history:
Received 30 May 2008
Received in revised form 10 December 2008
Accepted 12 December 2008
Available online 24 January 2009

Editor: R.D. van der Hilst

Keywords:
potassium
uranium
argon
degas
radiogenic
volatile

ABSTRACT

The abundance of K in the silicate Earth provides control on the composition of the Earth's interior, the dominant mode of mantle convection, the thermal evolution of the planet, and the concentration of Pb in the core. Because K acts as a volatile species during accretion, the K content of the silicate Earth is determined as a function of the terrestrial K/U ratio. A comprehensive examination of MORB from the Atlantic, Indian and Pacific oceans, including both normal- and enriched-type samples, reveals a composite MORB source K/U ratio of 19,000±2600 (2σ). In comparison, ocean island basalts and average continental crust have average K/U values of 11,900±2200 and 13,000±3000, respectively. The fractional contributions of these reservoirs establishes the K/U ratio of the silicate Earth to be 13,800±2600 (2σ), equating to 280±120 μg/g K in the silicate Earth. As a result, the planet's convective Urey ratio is verified to be ~0.34, which indicates a current mantle cooling rate of 70–130 K Gyr^{-1} after taking into account potential heat flux across the core–mantle boundary. Additionally, the Earth's balance of radiogenic heat flow and budget of ^{40}Ar necessitate a lower mantle reservoir enriched in radioactive elements. The bulk Earth Pb/U ratio, determined here to be ~85, suggests ~1200 ng/g Pb in the bulk Earth and ≥3300 ng/g Pb in the core.

1. Introduction

The dominant mode of convection in the modern mantle has been a hotly debated topic for decades. Whereas geophysical observations intimate significant material exchange across the entire mantle (e.g., Creager and Jordan, 1984; Grand, 1994; van der Hilst et al., 1997; Zhao, 2001; Montelli et al., 2004), geochemical arguments based on chemical and isotopic differences between mid-ocean ridge basalts (MORB) and ocean island basalts (OIB; e.g., Morgan, 1971; Schilling, 1973; Hofmann and Hart, 1978; Langmuir and Hanson, 1980; Sun, 1980), rare gas systematics (Kurz et al., 1982; O'Nions and Oxburgh, 1983, Allègre et al., 1983, 1996), isotope variations between continental and oceanic crust (e.g., Depaolo and Wasserburg, 1976; O'Nions et al., 1979), and the Earth's radiogenic heat budget (Albarède and van der Hilst, 2002; van Keken et al., 2002 and references cited therein) require a layered mantle structure consisting of at least two independent reservoirs: a depleted upper mantle and a chemically enriched lower mantle and/or D" layer at the core–mantle boundary. Potassium (K) plays a pivotal role in geochemical models of mantle structure, as the rate of radiogenic heat production and budget of ^{40}Ar in the modern mantle and MORB source region are contingent on the abundance and distribution of K in the silicate Earth.

Although the budgets of thorium (Th) and uranium (U) in the planet are well-established, estimates of the abundance of K in the silicate Earth are disparate and range from 130 to 280 μg/g (Wasserburg et al., 1964; Jochum et al., 1983; Allégre et al., 1987; Hofmann, 1988; McDonough et al., 1992; McDonough and Sun, 1995; Albarède, 1998; Davies, 1999; Lassiter, 2004). In addition to modeling the dominant mode of convection in the mantle, constraining the quantity of K in the silicate Earth also provides insight into: the size of the of the OIB source region, the role of K during the thermal evolution of the Earth, the degree of volatile element depletion of the Earth, and the abundance of Pb in the core.

Because potassium is a moderately volatile element during accretion, determining the K content of the silicate Earth has traditionally hinged on establishing the relatively constant K/U ratio of continental crustal rocks and MORB. Based on the chemistry of a particular type of ocean island basalt (i.e., HIMU-type) and the potential effects of eclogite in the mantle, Lassiter (2004) estimated the K/U ratio of the silicate Earth to be on the order of 7000 to 9000. This result, though consistent with several models of mantle degassing which suggest a silicate Earth K/U ratio on the order of 6000–7000 (Albarède, 1998; Davies, 1999), is significantly lower than traditional studies of terrestrial rocks (K/U≥10,000; e.g., Wasserburg et al., 1964; Jochum et al., 1983). Consequently, the terrestrial K/U ratio, and thus the abundance of K in the silicate Earth, remains a contentious issue.

In order to confidently establish the K/U ratio of the modern mantle, as well as critically test the constancy of this value among different mantle source regions, we have analyzed a comprehensive set of MORB from around the globe, including both enriched and depleted samples from the Atlantic, Indian and Pacific oceans. We

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doi:10.1016/j.epsl.2008.12.023

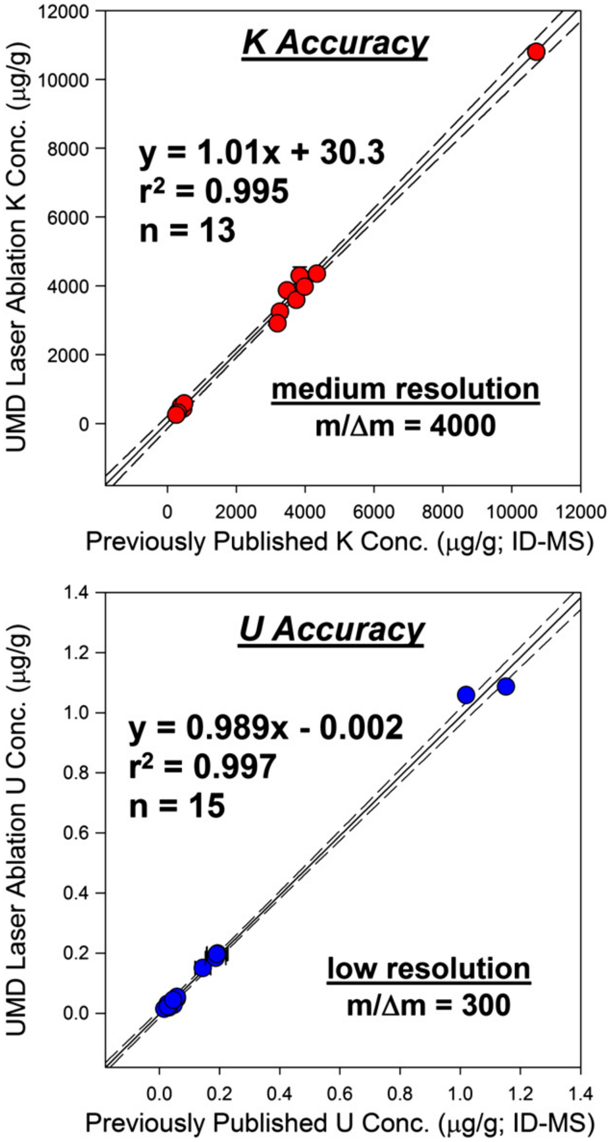


Fig. 1. Comparison of K and U concentration measurements of a subset of samples analyzed by both high-precision LA-ICP-MS (this study) and isotope dilution (various published works). Previously published data include: isotope dilution measurements of natural basaltic glasses from Loock et al. (1990) and White (1993), and synthetic basaltic standards from Raczek et al. (2001) and Jochum et al. (2006). In this study, U measurements were made using low-resolution detection ($m/\Delta m = 300$) and external calibration techniques following the protocol of Arevalo Jr. and McDonough (2008), whereas K measurements were made using medium resolution detection parameters ($m/\Delta m = 4000$) in order to discriminate the isobaric interferences from ^{38}ArH, ^{23}Na^{16}O and the tail of ^{40}Ar, and internal calibration with BIR-1G. For both K and U, typical uncertainties for our measurements are ≤3% (2σ), which are shown as error bars but are generally smaller than the size of the data points above. The dashed lines represent the 95% confidence limits of the data trends.

have also compiled literature data from the Max-Planck-Institut GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/; see Supplemental Materials) in order to more confidently estimate the K/U ratio of the OIB source region and bulk continental crust, as derivatives from these reservoirs generally have enough K (i.e., $K_2O > 1$ wt.%) to be confidently measured via common methods of major element analysis (e.g., electron probe microanalysis, EPMA, or instrumental neutron activation analysis, INAA).

2. The K/U ratio of the DMM

Mid-ocean ridge basalts (MORB), which represent melt products of a mantle that has undergone a major depletion event (i.e., crustal extraction), are typically depleted in incompatible elements ($D_i^{\mathrm{sol/liq}} < 1$, where D is approximated by the concentration ratio of element i in the solid to the liquid). Thus, trace element determinations in MORB commonly require higher-precision analytical methods than OIB and crustal analyses. Here, we report the K/U ratio of a collection of "normal-type" MORB (N-MORB; La/Sm < 1.00) and "enriched-type" MORB (E-MORB; La/Sm ≥ 1.00), as well as a limited suite of back-arc basin basalts (BABB) and several ocean island basalts (OIB). Concentration measurements were determined by high-precision laser ablation (LA-) ICP-MS; U measurements were made in low-resolution detection mode ($m/\Delta m = 300$) following the protocol of Arevalo and McDonough (2008), but K measurements required medium-resolution detection ($m/\Delta m = 4000$) in order to discriminate the ^{39}K peak from isobaric interferences, namely ^{23}Na^{16}O, ^{38}ArH and the tail-end of ^{40}Ar. The typical uncertainty on our measurements was ≤3% ($2\sigma_m$, external reproducibility of 2–4 individual measurements). A subset of samples that were previously analyzed via isotope dilution mass spectrometry coincides within 1% of our laser ablation data (Fig. 1), thus validating the accuracy of our in-situ measurements; details regarding the method, calibration and accuracy of our K measurements are reviewed in more detail in the Supplemental Materials.

A test as to the relative incompatibility of U versus K is illustrated in the log–log co-variation diagram shown in Fig. 2, where it is demonstrated that U behaves analogously to K in our spectrum of N-MORB (slope = 1.00 ± 0.10, 95% confidence), but Nb and La behave more and less incompatibly than K, respectively. Accordingly, K and U exhibit equally incompatible behavior during partial melting of upper mantle peridotite, and thus the K/U ratio of a mantle melt may provide a reliable proxy to the K/U ratio of the mantle source (e.g., Hofmann et al., 1986; Newsom et al., 1986). Accordingly, variations in the average K/U ratio of melts from different mantle reservoirs likely indicate distinct source compositions.

Because MORB are the products of passive upwelling, the MORB source represents the ambient upper mantle. As seen in Table 1 and Fig. 3, MORB can be divided into two distinct populations: N-MORB are characterized by a normal Gaussian distribution (skew = 0.0) with a mean K/U ratio of 20,000 ± 2300 (2σ), significantly higher than the N-

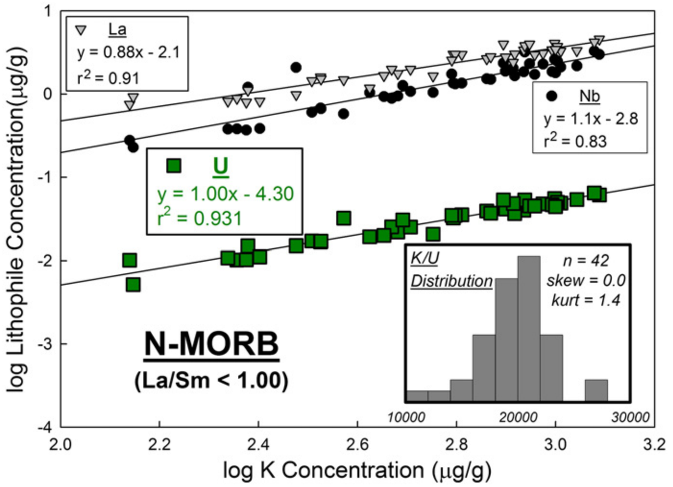


Fig. 2. Log–log co-variation diagram plotting the concentrations of Nb, La and U versus K (in μg/g) in "normal-type" MORB (N-MORB; La/Sm < 1.00). As the samples plotted here originate from the same source (upper mantle peridotite), this type of diagram reveals information regarding the effect of partial melting on the partitioning of K and U in mantle melts. A linear regression with a slope of 1.00 represents a perfectly constant element ratio. A slope of < 1.00 indicates a more incompatible element along the abscissa, and vice-versa. Whereas Nb and La are shown to be more and less incompatible than K, respectively, U behaves analogously to K during mantle melting (slope = 1.00 ± 0.10, 95% confidence). Moreover, U shows a greater correlation with K ($r^2 = 0.931$) than either Nb ($r^2 = 0.83$) or La ($r^2 = 0.91$). A statistical evaluation of the K/U ratios of the N-MORB samples examined above reveal a normal Gaussian distribution with negligible skewness.

Table 1
Representative K/U values of silicate Earth provenances

Provenance	Avg. K/U[a]	±2σ[b]
Depleted MORB Mantle (DMM)	19,000	2600
Normal-type MORB[c] (*n*=42)	20,000	2300
Enriched-type MORB[c] (*n*=33)	15,700	3100
Back-arc basin basalts[c] (*n*=12)	21,700	2000
Oceanic flood basalts	19,500	5100
Deep-source OIB (>1900 km depth)[d]	11,900	2200
Shallow-source OIB (<1900 km)[d]	12,100	2200
All OIB weighted by mass flux[e]	11,600	2000
Hawaii	13,300	400
Iceland	12,600	800
Continental crust	13,000	3000
Rudnick and Gao (2003)	12,400	4900
Global andesites	13,900	500
Continental arcs	13,000	1000
Continental flood basalts	12,600	1400
Bulk silicate Earth[f]	13,800	2600

[a] Data can be accessed in Supplemental Materials.
[b] 2 σm reported for compiled GEOROC data.
[c] Original data reported in this study.
[d] Depth of origin from Montelli et al. (2004).
[e] Flux data from Sleep (1990).
[f] DMM-OIB source interface modeled at ~1900 km depth.

MORB dataset reported by Jochum et al. (1983; K/U = 12,700 ± 400, $2\sigma_m$), whereas E-MORB have an average K/U value of 15,700 ± 3100 (2σ) and a skewed Gaussian distribution (skew = 0.5). As a result, our N-MORB and E-MORB data define two statistically distinct populations at the 99.9% confidence-level (see Supplemental Materials for details). The E-MORB source, however, provides only a fractional contribution to the composite MORB source, or depleted MORB mantle (DMM); while segments of the East Pacific Rise have been documented to produce up to 10% E-MORB (Langmuir et al., 1986), Donnelly et al. (2004) suggest the E-MORB source comprises ≤3% (by mass) of the DMM based on a two-stage E-MORB generation model and the approximate frequency of E-MORB at the Mid-Atlantic Ridge south of the Kane Fracture Zone (the MARK area). Here we consider a 5% mass contribution of the E-MORB source and a 6× enrichment relative to the N-MORB source, as determined by the log-normal mean U concentration of each reservoir according to our data (following the protocol of Ahrens, 1954); this results in a DMM K/U ratio of 19,000 ± 2600 (2σ). Interestingly, this high K/U value is corroborated by MORB data from the Lamont–Doherty PetDB database, which suggest a DMM K/U ratio of > 17,000 after low-precision measurements (e.g., via EPMA and INAA methods) have been filtered out (data available in Supplemental Materials). It should also be noted that small-degree partial melts (as low as 1%) cannot reproduce the low K/U ratios and high K concentrations seen in the most enriched E-MORB, even if K is modeled as 5× more compatible than U during upper mantle melting (see Supplemental Materials).

Additional insight into the representative K/U ratio of the DMM is provided by oceanic flood basalts, which generate as much as > 1.5 km^3 of basalt per year (Richards et al., 1989) and have been suggested to represent plume heads that have entrained a significant fraction of ambient mantle on their journey to the surface (e.g., Griffiths and Campbell, 1990). A compilation of published data from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/) illustrates a wide range in oceanic flood basalt compositions, but with an average K/U ratio of 19,500 ± 5100 ($2\sigma_m$; Fig. 4a), a value consistent with the high K/U ratio of the DMM as determined here.

3. The K/U ratio of the OIB source region

Given the abundances of K, Th and U in the continental crust (models reviewed by Rudnick and Gao, 2003), > 1/3 of the mantle was depleted by the extraction of the crust, and thus the DMM must extend below the 660 km discontinuity assuming a two-box model of mantle structure. However, the DMM and continental crust are not perfectly complimentary (e.g., Sun and McDonough, 1989), and thus another distinct reservoir must exist somewhere in the mantle. Ocean island volcanics, which are generally characterized by super-primitive U/Pb, Th/Pb and U/Th and sub–primitive Rb/Sr and Nd/Sm ratios (e.g., Zindler and Hart, 1986), and observed abundances of incompatible elements that are too enriched to be accounted for by conventional melting of a primitive source without requiring unrealistically small degrees of partial melting (e.g., Hofmann and White, 1982), likely represent an enriched mantle source in the deep mantle. However, the exact depth of the compositional transition from the depleted upper mantle to the enriched lower mantle has not been well-constrained. Tomographic images of the mantle show that not all slabs that sink across the 660 km discontinuity reach the core–mantle boundary; many downwellings lose their characteristic planar geometry across a transitional interval from 1800–2300 km depth (e.g., van der Hilst et al., 1997). Additionally, seismological observations reveal compositional heterogeneities in the bottom 1000 km of the mantle (e.g., van der Hilst and Kárason, 1999; Garnero, 2000; Trampert et al., 2004), potentially suggesting a chemical stratification at deeper depths. Here, we model a variety of potential interface depths, each with specific implications as to the enrichment of the lower mantle and the bulk modern mantle K/U value.

Some intraplate ocean islands are thought to derive from the tails of deep-rooted mantle plumes (e.g., Morgan, 1971), and studies of mantle tomography have revealed that a number of ocean island hotspots can be traced to the lowermost depths of the mantle (e.g., Zhao, 2001; Montelli et al., 2004); therefore, at least some OIB likely characterize the chemistry of the lower mantle. Compared to MORB, which typically have ≤0.5 wt.% K_2O, OIB can have up to 5.0 wt.% K_2O and thus can be readily measured via EPMA, INAA and/or other modes of traditional major element analyses. Although our sample set is small (*n* = 6), our laser ablation data suggest that ocean islands may be characterized by the lowest average K/U of the major mantle source regions.

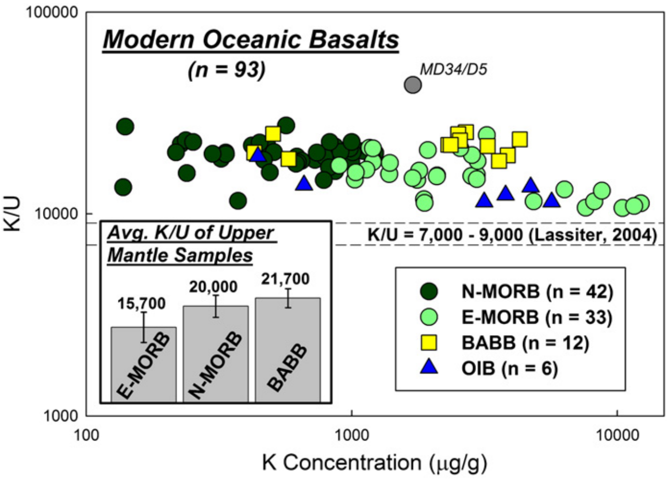


Fig. 3. K/U ratios of modern oceanic basalts examined here versus K concentration (in μg/g). Relative to a silicate Earth K/U ratio of 7000–9000, as preferred by Lassiter (2004), all of our oceanic basalts plot at higher K/U values. Amongst the mantle reservoirs examined here, back-arc basin basalts (BABB) have the highest average K/U ratio, whereas ocean island basalts (OIB) show the lowest values, though both sample sets are relatively small. Mid-ocean ridge basalts can be separated into two statistically distinct (at 99.9% confidence) populations; depleted N-MORB have an average K/U ratio of 20,000 ± 2300 (2σ), while "enriched-type" samples (E-MORB; La/Sm ≥ 1.00) display an average K/U ratio of 15,700 ± 3100 (2σ). The varying K/U ratios seen between different mantle reservoirs represent source differences rather than effects from partial melting, as K and U exhibit equally incompatible behavior during upper mantle melting (see Fig. 2). The anomalous MD34/D5 sample (K/U > 40,000) was not included in the calculations in this study.

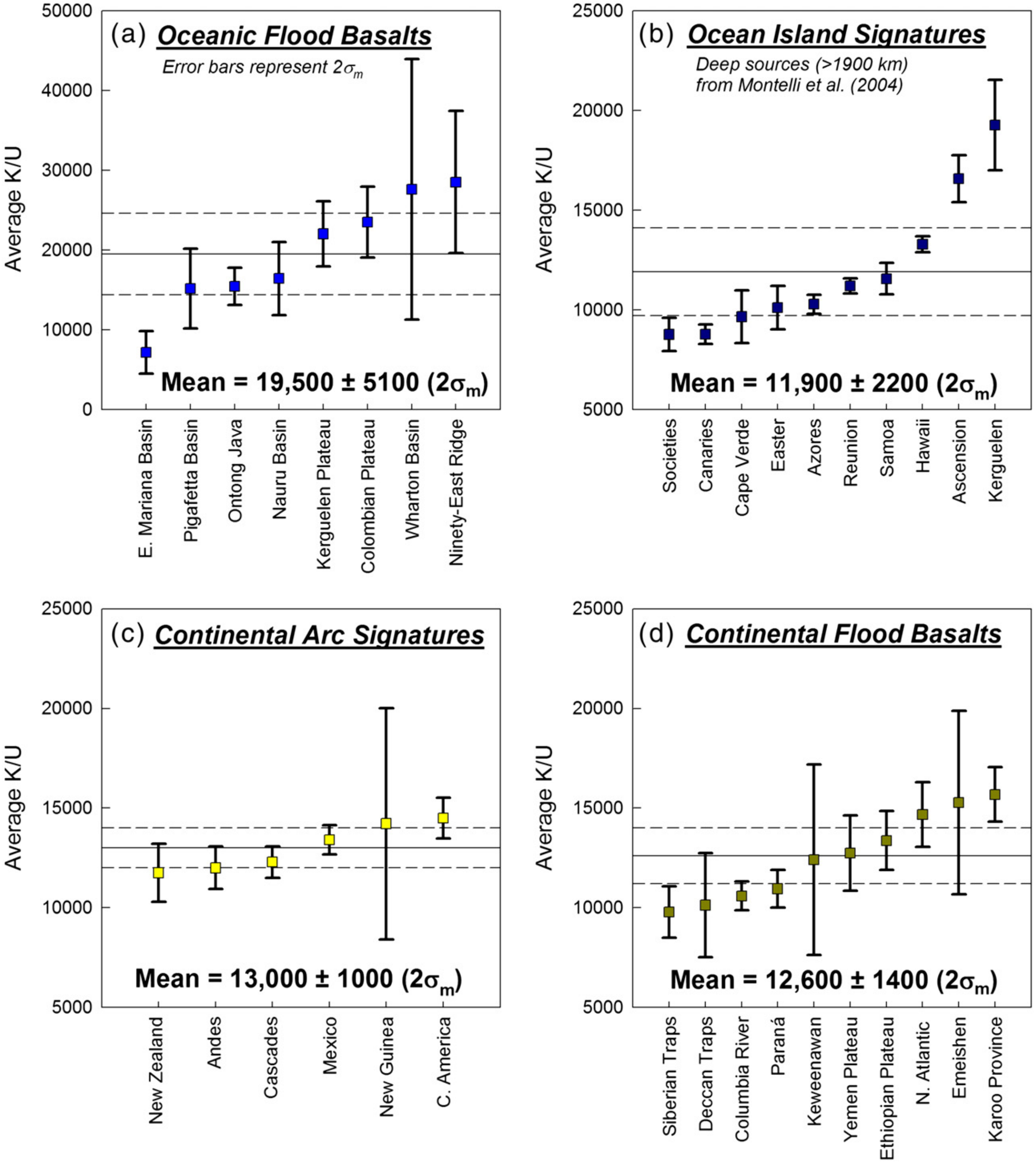


Fig. 4. Literature data for global oceanic and continental flood basalts, ocean island volcanics and continental arc rocks compiled from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/). Sample data were filtered for major element totals >98.0 wt.% and MgO contents between 4.0–16.0 wt.%. The reported mean of the OIB source represents the average K/U ratio of ocean islands with evidence for a deep origin (>1900 km; Montelli et al., 2004); this value is statistically indistinguishable from the average of OIB with shallower origins (K/U ≈ 12,100) as well as the average of all ocean islands weighted according to mass flux (K/U ≈ 11,600; flux data from Sleep, 1990). The compiled data files from GEOROC are available in the Supplemental Materials.

The Hawaiian plume, which transfers a higher mass flux than any other ocean island hotspot (Sleep, 1990), has been demonstrated to originate in the deep portion of the mantle (e.g., Russell et al., 1998; Zhao, 2001; Montelli et al., 2004), and thus provides a window into the lower mantle. A survey of the GEOROC database reveals that Hawaiian picrites and tholeiitic basalts are defined by an average K/U value of ~13,300. However, if we consider other ocean islands that are interpreted to have deep-mantle origins (>1900 km depth; Montelli et al., 2004) in addition to Hawaii, the OIB source is approximated by a mean K/U ratio of 11,900 ± 2200 ($2\sigma_m$; Fig. 4b); it should be noted that this K/U value is statistically indistinguishable from the average K/U ratio of OIB without evidence for deep-rooted sources (K/U ≈ 12,100) as well as the average of *all* ocean islands weighted according to mass flux (K/U ≈ 11,600; flux data from Sleep, 1990), as shown in Table 1 (data available in Supplemental Materials).

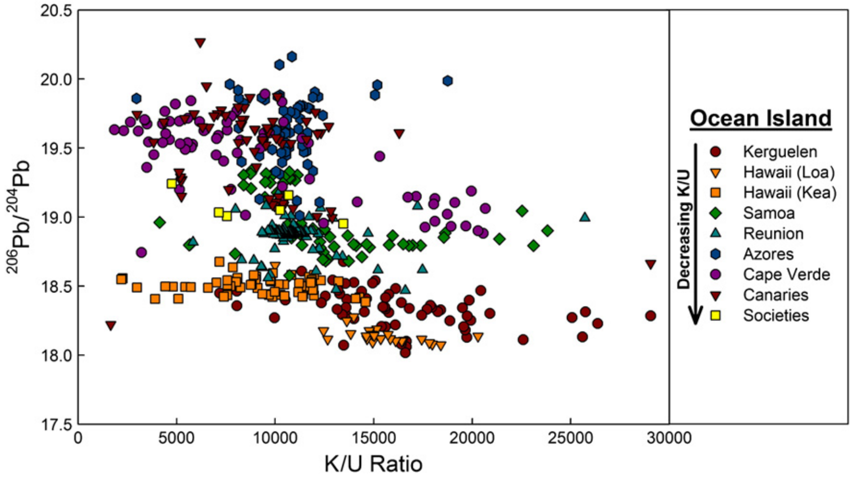


Fig. 5. ^{206}Pb/^{204}Pb versus K/U ratios in ocean island basalts with evidence for deep-rooted sources (Montelli et al., 2004). Different volcanic centers appear to show sub-parallel, linear trends with large ranges in K/U (up to a factor of 2–3) over a relatively small range in ^{206}Pb/^{204}Pb. This apparent decoupling between radiogenic Pb and K/U signatures suggests that a different process is responsible for the variable K/U values seen in OIB, as opposed to representing long-term source features or the effects of variable degrees of partial melting.

The ocean islands examined here show a significant spread in K/U values across relatively narrow ranges in ^{206}Pb/^{204}Pb (Fig. 5). These sub-parallel trends imply a diversity in K/U ratios (spanning a factor of 2–3) that is independent of radiogenic Pb and melt fraction, and thus likely not a coupled long-term source feature as argued by Lassiter (2004). Lassiter (2004) also asserted that eclogitic material in the mantle could significantly lower the K/U ratio of both the OIB source and silicate Earth. However, as suggested by primitive olivine compositions in Hawaiian lavas (Sobolev et al., 2005, 2007), the Hawaiian source region may contain as much as 20–30% recycled ocean crust (present as eclogite), yet still exhibits an average K/U ratio >13,000. The Iceland source (K/U = 12,600, not shown in Fig. 4) and DMM (K/U = 19,000) also show evidence for an eclogitic component (Sobolev et al., 2007), though both fail to produce low K/U ratios. Therefore, recycled eclogite in OIB sources does not appear to be responsible for low K/U values, and thus it is unlikely that the K/U ratio of the modern mantle, and therefore the K/U ratio of the silicate Earth, is significantly lowered by the role of eclogitic material.

4. The K/U ratio of the modern mantle

In order to establish the K/U ratio of the modern mantle, we need to consider the mass fraction of K and U in, and the relative sizes of, both the MORB and OIB source regions. In a comprehensive examination of global MORB ridge segments, Su (2002) established that typical MORB, located away from known hotspots, contain 1000 ± 100 ($2\sigma_m$) μg/g K; assuming average MORB represent 8–12% partial melting (e.g., Hofmann, 1988) and a nominal K partition coefficient similar to that of U ($D_U^{sol/liq} = 0.001$–0.0001; www.germ.com), the mean MORB source is predicted to have a composition with 100 ± 10 μg/g K. Thus, based on the K/U ratio of the DMM, defined here as 19,000 ± 2600 (2σ), the DMM has 5.4 ± 1.4 ng/g U, representing a ~4× depletion relative to the silicate Earth (20.3 ng/g U; McDonough and Sun, 1995). This MORB source composition is consistent with independent estimates of U in the DMM (Sun and McDonough, 1989) as well as chondritic and non-chondritic DMM models based on parent-daughter ratios of radiogenic isotopes (e.g., Salters and Stracke, 2004; Boyet and Carlson, 2006).

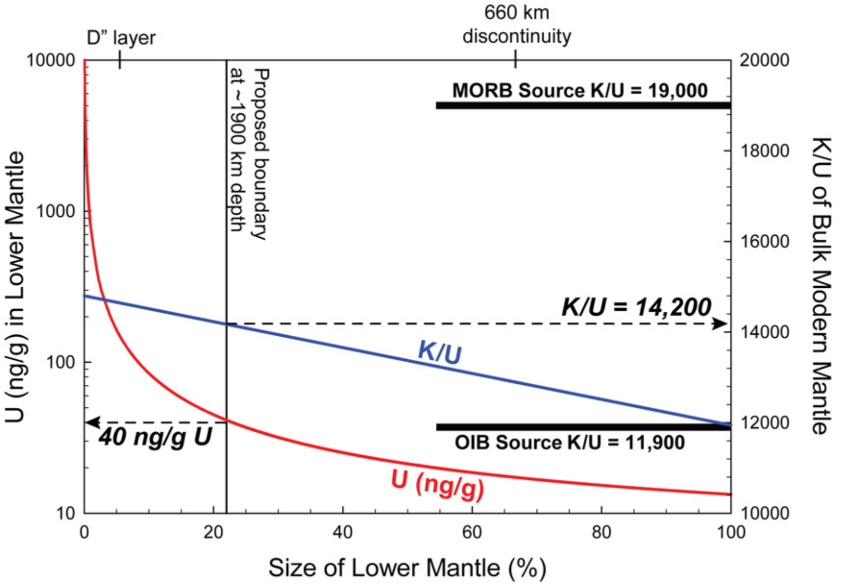


Fig. 6. Size of the lower mantle and K/U ratio of the bulk modern mantle modeled as a function of the enrichment of the lower mantle, as sampled by OIB. Assuming a composition with 40 ng/g U, as suggested by Hawaiian volcanics (see text), the lower mantle must constitute ~20% of the bulk modern mantle, resulting in a bulk mantle K/U ratio of 14,200 ± 2400 (2σ) and implicating a potential chemical layering at an average depth of ~1900 km in an incompressible mantle. Considering only a 300 km thick D" layer, this reservoir would need to contain ≥160 ng/g U (≥8× the silicate Earth), which would be difficult to maintain convectively isolated due to radiogenic heat. Figure modified from Lassiter (2004).

Assuming the DMM represents the ambient upper mantle and deep-rooted mantle plumes represent a lower mantle reservoir, we can model the size of the lower mantle and the K/U ratio of the bulk modern mantle as a function of the enrichment of the OIB source region (Fig. 6). Modeling ~40 ng/g U in the OIB source (or 2× the concentration of the silicate Earth), as suggested by the maximum enrichment of U observed in our Hawaiian tholeiites and following 5–15% partial melting for Hawaiian lavas as suggested by picritic trace element signatures (Norman and Garcia, 1999) and tholeiite Th–U disequilibria (Sims et al., 1999), the modern mantle is defined by a K/U ratio of 14,200 ± 2400 (2σ). Given this model composition, the OIB source must constitute ~20% of the mantle, which is in accord with the mass balance calculations of Workman and Hart (2005). Additionally, if the chemical distinction between the OIB and MORB source regions is preserved by a thermochemical boundary layer, the depth of this interface would need to have an average depth of ~1900 km, assuming an incompressible mantle. This proposed boundary, which provides support for the mid-mantle stratification proposed by Kellogg et al. (1999), may correlate with the loss of resolution of downwelling material in tomographic studies (e.g., van der Hilst et al., 1997) as well as the identification of chemical heterogeneities in the lowermost 1000 km of the mantle (e.g., van der Hilst and Kárason, 1999; Garnero, 2000; Trampert et al., 2004). Alternatively, a less enriched OIB source region would necessitate a shallower chemical layering and a lower modern mantle K/U ratio, and a more enriched OIB source would require a deeper layering and higher mantle K/U.

We may further consider the effect of a chemically heterogeneous 200–300 km thick D" layer at the core–mantle boundary, which has been suggested by seismological (e.g., Lay et al., 1998; Wen et al., 2001), experimental (Murakami et al., 2004), and geochemical observations (Boyet and Carlson, 2005, 2006; Tolstikhin and Hofmann, 2005). A 300 km thick enriched reservoir at the base of the mantle would indicate a modern mantle K/U value >14,700 and need to contain ≥160 ng/g U (or ≥8× the silicate Earth). However, such an enriched reservoir would be thermally unstable and difficult to isolate for several Ga, and the limited size of this reservoir likely could not serve as the source for deep-rooted OIB.

5. The K/U ratio of the continental crust and silicate Earth

Although the modern mantle comprises >99% of the silicate Earth by mass, ~35% of the highly incompatible element budget (e.g., K, Th and U) of the silicate Earth resides in the continental crust (Rudnick and Gao, 2003). The composition of the bulk continental crust, though, is a significant variable; as an example, geochemical estimates of K_2O in the crust vary by a factor >2 (Rudnick, 1995 and references cited therein). A comprehensive examination of the bulk continental crust by Rudnick and Gao (2003) suggests a mean crustal K/U ratio of ~12,400, but with an associated uncertainty of >40% (2σ). We attempt here to evaluate the bulk crustal K/U value by considering the role of continental arc rocks, global andesites and continental flood basalts.

Convergent margin tectonism has been linked to the formation of the continental crust through the recycling of crust back into the mantle and the production of arc magmatism. Trace element patterns of typical arc rocks, particularly continental arc lavas, are similar to those of continental crustal rocks (e.g., high La/Nb and low Ce/Pb relative to the silicate Earth; Rudnick, 1995). Island arc basalts are typically characterized by high K/U ratios (Lassiter, 2004), comparable to our back-arc basin dataset (K/U ≈ 21,700; Table 1), and thus likely record an upper mantle signature. Continental arc rocks, on the other hand, are more commonly andesitic in composition, analogous to the composition of average continental crust (Rudnick, 1995). Published data for a number of continental arcs from the GEOROC database show a narrow variation with an average K/U ratio of 13,000 ± 1000 ($2\sigma_m$; Fig. 4c). This value is also broadly consistent with global andesitic lavas, which have a mean K/U value of ~13,900 ($n > 1400$; data available in Supplemental Materials).

Continental flood basalts may also provide a guide to the representative K/U ratio of the continental crust, as these massive lava flows travel through thick sequences of incompatible element-rich crust before they erupt at the surface, resulting in chemical and isotopic overprinting by the continental crust (Carlson, 1984; McDonough, 1990). A compilation of flood basalt data from the most prominent large igneous provinces around the globe indicates that continental flood basalts have an average K/U ratio of 12,600 ± 1400 ($2\sigma_m$; Fig. 4d).

Considering the crustal model of Rudnick and Gao (2003), as well as the average K/U ratio of continental arcs, global andesites and continental flood basalts, we propose a K/U value for the bulk continental crust of 13,000 ± 3000 (2σ; Table 1). As might be expected, the average K/U ratio of the continental crust is in between those of the enriched OIB and depleted MORB sources, indicating the complementary relationship of these three reservoirs and the bulk silicate Earth.

Taking into account the fractional contributions and K/U signatures of the modern mantle (modeled to included the DMM and OIB source regions stratified at an average depth of ~1900 km) and continental crust, as illustrated in Fig. 7, the silicate Earth is hereby defined by a K/U ratio of 13,800 ± 2600 (2σ), consistent with the original estimate of Jochum et al. (1983; K/U ≈ 12,700), though for different reasons. All of the above observations are at odds with arguments for a lower K/U ratio in the silicate Earth, as advocated by Lassiter (2004) on the basis of eclogite in the mantle, as well as the degassing models of Albarède (1998) and Davies (1999). Further, a high K/U ratio for the silicate Earth: i) implies a greater role for K during the thermal evolution of the Earth, ii) exacerbates the need for a lower mantle reservoir enriched in radioactive elements and ^{40}Ar, and iii) suggests a less severe volatile element depletion in the bulk Earth, implying a significant fraction of Pb in the core.

6. Discussion

6.1. Radiogenic heat and Earth's heat flux

The heat flow from the Earth's interior, which serves to drive mantle convection and global plate tectonics, derives primarily from two major components: energy from planetary accretion and differentiation (e.g., gravitational collapse, core formation, inner core crystallization, and secular cooling), as well as radiogenic heat from

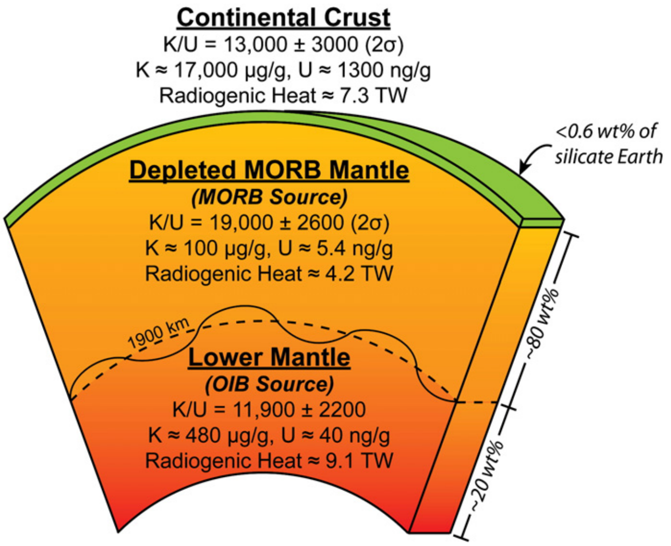


Fig. 7. Composition of and radiogenic heat flow from the continental crust, DMM and OIB source. The estimates of K and U in the continental crust do not take into account the role of the continental lithosphere, though its contribution is considered negligible. The continental crust is assumed to have 5.6 μg/g Th, following the model of Rudnick and Gao (2003), and the DMM 16 ng/g Th, following a mantle Th/U ratio of 3.0.

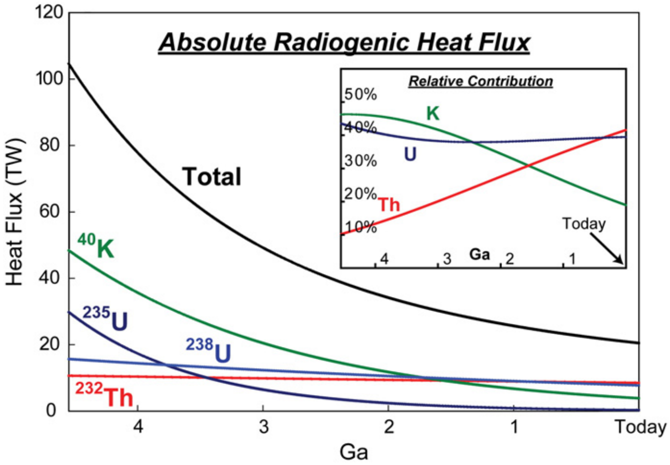


Fig. 8. Earth's radiogenic heat production from the decay of long-lived radionuclides through time. Prior to 2.5 Ga, K acted as the dominant radiogenic heat source within the planet. The exponential increase in radiogenic heat in the geologic past likely resulted in a higher convective Urey number in the ancient mantle.

the decay of long-lived radionuclides, namely ^{40}K, ^{232}Th and ^{235,238}U. Although primordial energy from secular cooling contributes a significant portion of the planet's current global heat loss, geochemical and geophysical models underline the role of radioactive isotopes in powering mantle convection, particularly early in the Earth's history when radiogenic heat generated more than 5× the energy than produced today (Fig. 8).

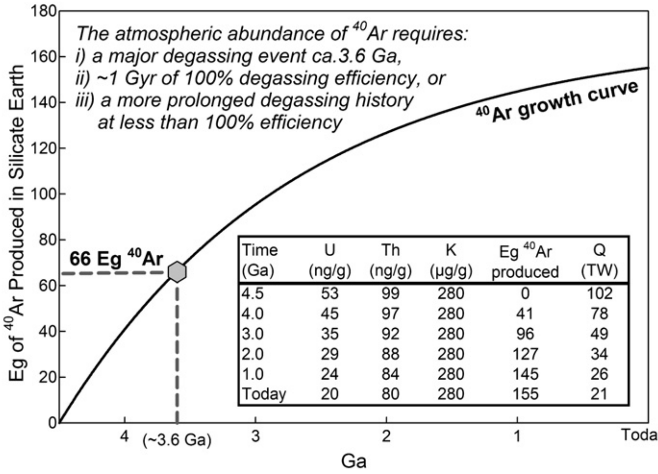
The Urey ratio (Ur), which serves to relate the radiogenic heat production within a body to its total heat output, can be defined in two distinct ways: geochemical studies often refer to a bulk Earth Ur, defined as the ratio of the planet's radiogenic heat production to total surface heat loss, whereas geophysical models focus on a convective Ur, or the ratio of radiogenic heat generation in the modern mantle to the total mantle heat flux (e.g., Korenaga, 2008). The convective Ur can provide information regarding the thermal evolution of the planet and the driving forces behind a variety of global dynamic processes, including mantle convection, plate tectonics, secular cooling, the geodynamo, and inner core crystallization.

The value of the bulk Earth Urey ratio inherently depends on the terrestrial abundances of the long-lived radioactive isotopes of K, Th and U. Because the half-life of ^{40}K ($t_{1/2}$ ~ 1.25 Gyr) is short relative to the age of the planet, the abundance of K in the silicate Earth is not only vital to the understanding of radiogenic heat production today, but even more so to evaluating the radiogenic heat budget of the early Earth, as more than 12 times more ^{40}K was extant ca. 4.5 Ga than today (Fig. 8). A silicate Earth composition with 20 ± 8 (2σ) ng/g U, which is consistent with both geochemical models (e.g., McDonough and Sun, 1995) and measured geoneutrino fluxes (Araki et al., 2005), implies 280 ± 120 (2σ) µg/g K in the silicate Earth, following a K/U value of 13,800 ± 2600 (2σ). Considering the silicate Earth also has 80 ± 25 (2σ) ng/g Th (McDonough and Sun, 1995) and assuming negligible K, Th or U in the core (e.g., Chabot and Drake, 1999; Wheeler et al., 2006; Corgne et al., 2007), the Earth currently emits 21 ± 4 (2σ) TW of radiogenic heat. Relative to the Earth's total surface heat loss of 46 ± 6 TW (Jaupart et al., 2007 and references therein), this represents a bulk Earth Ur of ~0.45.

More relevant to geophysical models is the convective Urey ratio, an essential variable for parameterized models of mantle convection that also provides a strong case for a stratified mantle structure. Subtracting the 7.3 ± 2.3 (2σ) TW of radiogenic heat produced within the continents today (Rudnick and Gao, 2003, with a crustal K/U = 13,000 ± 3000) from the total surface heat flow, we arrive at ~39 TW of heat currently being emitted by the modern mantle, with ~13 TW due to radiogenic heat. A DMM composition with 100 µg/g K, 5.4 ng/g U and ~16 ng/g Th (assuming a MORB Th/U ratio of 3.0), however, could only produce some ~5 TW of radiogenic heat assuming whole-mantle convection, leaving ~8 TW of radiogenic heat unaccounted for and suggesting a convective Ur of <0.15. Taking into account the potential for a layered mantle structure with an enriched lower mantle reservoir, such as the source region of OIB, the budget of radioactive elements in the modern mantle can be reconciled to produce 13 TW of radiogenic heat, which is indicative of a more realistic convective Ur of 0.34, a value which is significantly lower than that preferred by parameterized convection models (Ur ≥ 0.65; e.g., Davies, 1980; Schubert et al., 1980; Turcotte et al., 2001; Schubert et al., 2001), but consistent with the findings of Jaupart et al. (2007) and Korenaga (2008), and suggestive of a current mantle cooling rate on the order of ~170 K Gyr^{-1} (assuming a constant mantle heat capacity of 1.2 J g^{-1} K^{-1}). If we also consider the potential for 5–15 TW of heat flow across the core–mantle boundary (Lay et al., 2008 and references cited therein), only 10–20 TW of the mantle's heat output represents secular cooling, implying a more probable modern mantle cooling rate somewhere between 70–130 K Gyr^{-1}; this indicates a hotter ancient mantle than previous estimates based on wet Archean komatiite formation (e.g., Grove and Parman, 2004 and references cited therein), studies of MORB-like Archean greenstones (Abbott et al., 1994) and required conditions for subsolidus mantle convection (Jaupart et al., 2007).

6.2. The terrestrial budget of ^{40}Ar and bulk Earth Pb/U ratio

Noble gas systematics in mantle-derived materials have traditionally been interpreted as robust evidence for a chemically layered mantle. At the forefront of such arguments is the balance of ^{40}Ar in the planet, as originally described by Allègre et al. (1996). Considering a silicate Earth composition with 280 ± 120 (2σ) µg/g K, 155 ± 70 (2σ) Eg (or 10^{18} g) of ^{40}Ar has been produced by the decay of ^{40}K over the past 4.5 Gyr (Fig. 9). Turekian (1959) determined that approximately ~66 Eg of ^{40}Ar currently resides in the atmosphere, and an additional ~14 Eg of ^{40}Ar may reside in the continents, assuming no degassing and a bulk continental crustal composition with 1.3 µg/g U (Rudnick and Gao, 2003), a K/U ratio of 13,000 (and thus 17,000 µg/g K, or 2.0 wt.% K_2O), and a mean crustal age of ~2.5 Ga. As such, ≥75 Eg of ^{40}Ar may reside in the mantle. However, considering whole-mantle convection with a DMM composition, ≤55 Eg of ^{40}Ar could be produced over



The atmospheric abundance of ^{40}Ar requires:
i) a major degassing event ca.3.6 Ga,
ii) ~1 Gyr of 100% degassing efficiency, or
iii) a more prolonged degassing history at less than 100% efficiency

Time (Ga)	U (ng/g)	Th (ng/g)	K (µg/g)	Eg ^{40}Ar produced	Q (TW)
4.5	53	99	280	0	102
4.0	45	97	280	41	78
3.0	35	92	280	96	49
2.0	29	88	280	127	34
1.0	24	84	280	145	26
Today	20	80	280	155	21

Fig. 9. Silicate Earth evolution and production of ^{40}Ar through time, and three different scenarios that could theoretically explain the abundance of ^{40}Ar in the atmosphere. Only the first two scenarios are compatible with recent measurements on the solubility and diffusivity of Ar in upper mantle minerals, which suggest that Ar behaves as a compatible element during modern mantle melting (Watson et al., 2007). The abundance of ^{40}K, which comprises ~0.012% of K today, was more than 12× higher ca. 4.5 Ga, resulting in the higher production rates of ^{40}Ar in the geologic past.

4.5 Ga. Therefore, a chemically enriched layer (i.e., the OIB source) with excess ^{40}Ar likely resides somewhere in the deep mantle, providing further evidence for a stratified mantle structure.

As an additional observation, Pb/U and K/U ratios of carbonaceous chondrites are correlated (Allègre et al., 1995) and suggest that the Pb/U ratio of the bulk Earth is on the order of ~85. Considering a bulk Earth composition with ~14 ng/g U, this ratio indicates ~1200 ng/g Pb in the bulk Earth. According to geochemical models which estimate between 150 and 180 ng/g Pb in the silicate portion of the Earth (e.g., Hofmann, 1988; McDonough and Sun, 1995), the core must contain ≥3300 ng/g Pb, which is 10 times higher than previous estimates (e.g., McDonough, 2003).

7. Conclusions

We have analyzed an extensive, global suite of MORB glasses, including both normal- and enriched-type samples, and determined the K/U ratio of the DMM to be 19,000±2600 (2σ), consistent with the average K/U ratio of oceanic flood basalts and back-arc basin basalts. The lower mantle, as represented by deep-rooted OIB, and the continental crust, which is characterized by continental arc rocks, global andesites and continental flood basalts, have mean K/U ratios of 11,900±2200 and 13,000±3000, respectively. Taking into account the mass fraction of K and U in each of theses reservoirs, the silicate Earth is modeled to have a K/U ratio of 13,800±2600 (2σ).

Assuming a composition with 20±8 (2σ) ng/g U, the silicate Earth has 280±120 μg/g K. As a result: i) the planet's convective Urey ratio is confirmed to be ~0.34, which indicates a present-day mantle cooling rate on the order of 70–130 K Gyr^{-1} after taking into account potential heat flux across the core–mantle boundary; ii) the Earth's balance of radiogenic heat and budget of ^{40}Ar require a layered mantle structure; and iii) the Pb/U ratio of the bulk Earth, established here to be ~85, indicates ~1200 ng/g Pb in the bulk Earth and ≥3300 ng/g Pb in the core.

Acknowledgements

We would like to thank Leslie Hale, Sorena Sorenson, Timothy O'Hearn, the late Jim Luhr, and the Division of Petrology and Volcanology, Department of Mineral Sciences, Smithsonian Institute, as well as Michael Garcia, Emily Klein, Charles Langmuir, Gaby Loock, Yaoling Niu, Marc Norman, and Michael Perfit for sample donations. We appreciate reviews from Rhea Workman, Francis Albaréde, Albrecht Hofmann, Roberta Rudnick, Thomas Ireland, Kathleen Scheiderich, and an anonymous reviewer, as well as helpful discussions with Saswata Hier-Majumder, Cin-Ty Lee and Jeremy Bellucci. A special thanks to Richard Ash for troubleshooting and helping us to develop our analytical methods, Barry Reno for his statistical expertise, Rob van der Hilst for editing our manuscript, and Mark Chen for inspiring this work during the first Neutrino Geophysics meeting in Hawaii. This study was funded by NSF grants #0337621 and #0739006.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.12.023.

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