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Earth and Planetary Science Letters xx (2006) xxx – xxx
www.elsevier.com/locate/epsl

Constraints on the coupled thermal evolution of the Earth's core and mantle, the age of the inner core, and the origin of the $^{186}Os/^{188}Os$ "core signal" in plume-derived lavas

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Received 16 March 2006; received in revised form 25 July 2006; accepted 25 July 2006

Editor: R.W. Carlson

Abstract

The possibility that some mantle plumes may carry a geochemical signature of core/mantle interaction has rightly generated considerable interest and attention in recent years. Correlated ^{186}Os–^{187}Os enrichments in some plume-derived lavas (Hawaii, Gorgona, Kostomuksha) have been interpreted as deriving from an outer core with elevated Pt/Os and Re/Os ratios due to the solidification of the Earth's inner core (c.f., [A.D. Brandon, R.J. Walker, The debate over core–mantle interaction, Earth Planet. Sci. Lett. 232 (2005) 211–225.] and references therein). Conclusive identification of a "core signal" in plume-derived lavas would profoundly influence our understanding of mantle convection and evolution. This paper reevaluates the Os-isotope evidence for core/mantle interaction by examining other geochemical constraints on core/mantle interaction, geophysical constraints on the thermal evolution of the outer core, and geochemical and cosmochemical constraints on the abundance of heat-producing elements in the core. Additional study of metal/silicate and sulfide/silicate partitioning of K, Pb, and other trace elements is needed to more tightly constrain the likely starting composition of the Earth's core. However, available data suggest that the observed ^{186}Os enrichments in Hawaiian and other plume-derived lavas are unlikely to derive from core/mantle interaction. 1) Core/mantle interaction sufficient to produce the observed ^{186}Os enrichments would likely have significant effects on other tracers such as Pb- and W-isotopes that are not observed. 2) Significant partitioning of K or other heat-producing elements into the core would produce a "core depletion" pattern in the Silicate Earth very different from that observed. 3) In the absence of heat-producing elements in the core, core/mantle heat flow of ~6–15 TW estimated from several independent geophysical constraints suggests an inner core age (< ~2.5 Ga) too young for the outer core to have developed a significant ^{186}Os enrichment. Core/mantle thermal and chemical interaction remains an important problem that warrants future research. However, Os-isotopes may have only limited utility in this area due to the relatively young age of the Earth's inner core.

Keywords: inner core; thermal evolution; osmium; potassium; core/mantle boundary

1. Introduction

Thermal and chemical interaction between the core and mantle may play a critical role in the physical and chemical evolution of the Earth's interior. Chemical and thermal convection in the outer core, driven by core cooling and crystallization of the inner core, powers the geodynamo that generates Earth's magnetic field. Core/mantle heat transfer may also help buffer the mantle's potential temperature, resulting in slower rates of mantle

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0012-821X/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.epsl.2006.07.044

cooling than would otherwise occur. Finally, core/mantle heat transfer may generate thermal mantle plumes responsible for ocean island volcanic chains such as the Hawaiian Islands.

Several recent studies have argued that mantle plumes, in addition to transporting heat from the core/mantle boundary, may also carry a chemical signature of core/mantle interaction. Correlated $^{187}Os/^{188}Os$–$^{186}Os/^{188}Os$ enrichments in lavas from Gorgona, Hawaii, and Kostomuksha have been interpreted as reflecting core addition or core/mantle interaction [2–4]. Fractionation of the inner core may have produced an outer core with elevated Pt/Os and Re/Os, due to high solid metal/liquid metal Os K_D [5]. Provided that inner core crystallization began sufficiently early in Earth history, this would result in generation of elevated $^{186}Os/^{188}Os$ and $^{187}Os/^{188}Os$ ratios in the outer core from the decay of ^{190}Pt and ^{187}Re. If elevated $^{186}Os/^{188}Os$ ratios in some plume-related lavas do derive from the Earth's core, this finding would have profound implications for the thermal evolution of the Earth as well as for the planform of mantle convection.

In this paper I discuss the logical implications of a core origin for $^{186}Os/^{188}Os$ enrichments in plume-derived lavas (henceforth the "Walker/Brandon model") regarding the chemical composition and thermal evolution of the Earth's core and mantle. The Walker/Brandon model appears inconsistent with a number of constraints on core composition and thermal evolution. 1) Core/mantle interaction would most likely produce covariations between Os- and W-isotopes as well as Os- and Pb-isotopes. Such covariations are not observed. 2) Experimental constraints on metal/silicate and sulfide/silicate K partitioning indicate that the Earth's core is unlikely to possess significant quantities of K or other heat-producing elements for core formation scenarios consistent with other lines of geochemical evidence. 3) Geophysical constraints suggest core/mantle heat flow of ~6–15 TW. In the absence of heat-producing elements in the core, this level of heat flow is consistent with an inner core age of ~0.2–2.5 Ga, which is too young for the outer core to have developed significant ^{186}Os-enrichment as a result of the Pt/Os increase resulting from inner core growth.

2. Geochemical constraints on core/mantle interaction

Core/mantle chemical interaction may occur in a number of ways, such as physical mixing of core material into the mantle, core/mantle diffusive isotopic exchange, or core/mantle chemical reaction. Core/mantle mixing will shift mantle isotopic compositions towards core-like values for elements such as osmium that are present in the core in high concentrations [6]. In addition to osmium, the elements W and Pb may also be sensitive to core/mantle interaction. For example, the core is believed to have lower $^{182}W/^{184}W$ relative to the mantle, so core/mantle interaction should produce a negative $^{186}Os/^{188}Os$–$^{182}W/^{184}W$ correlation. Schersten et al. [7] reported constant $^{182}W/^{184}W$ ratios in Hawaiian lavas (including lavas with variable ^{186}Os enrichment) and argued this was inconsistent with core addition models for reasonable estimates of core and mantle W and Os concentrations. However, Brandon and Walker [1] suggested that addition of pelagic sediment to the Hawaiian plume could result in a mantle source with highly elevated W concentrations, reducing the W_{core}/W_{mantle} ratio and thereby making W-isotopes insensitive to modest degrees of core/mantle interaction. Although this possibility cannot be ruled out, Hawkesworth and Schersten [8] examined the limited published data for W concentrations and W/Th ratios in Hawaiian lavas and concluded that W concentrations in the Hawaiian plume are unlikely to be significantly enriched relative to primitive mantle.

The core Pb-isotope composition should be close to the solar system initial value and thus very distinct from mantle Pb. The sensitivity of Pb isotopes in the mantle to core addition depends on the concentration of Pb in the core, which is poorly constrained but strongly depends on the timing and conditions of core formation. For example, because Pb is highly chalcophile [9], core Pb concentration is expected to be high if segregation of a distinct sulfide liquid occurred during any stage of core formation (c.f., [10]). Core Pb concentration will also likely be high if the main phase of core formation preceded large-scale planetary volatile depletion; e.g., if the volatile element depletion observed for the Silicate Earth resulted from the moon-forming giant impact [11] rather than solar nebula condensation processes [12].

As with W-isotopes, core addition should produce a negative correlation between $^{186}Os/^{188}Os$ and $\Delta 7/4$ values ($\Delta 7/4 = [^{207}Pb/^{204}Pb_{sample} - ^{207}Pb/^{204}Pb_{NHRL}] * 100$, where NHRL is the Northern Hemisphere Reference Line [13]). No correlation between $^{186}Os/^{188}Os$ and $\Delta 7/4$ values is observed for Hawaiian lavas. This lack of correlation is inconsistent with core/mantle mixing unless $(Pb/Os)_{mantle}/(Pb/Os)_{core}$ is greater than ~200. Fig. 1 illustrates the effect of core addition on Pb- and Os-isotopes for three model core compositions, with $(Pb/Os)_{mantle}/(Pb/Os)_{core}$ ranging from ~14 to 200. In all three models, the mantle is assumed to have 3.3 ppb Os. Average Ce/Pb ratios in Hawaiian basalts (25±9), are indistinguishable from the global average for MORB and OIB (25±5) [14]. Therefore, a Pb concentration in the Hawaiian plume of

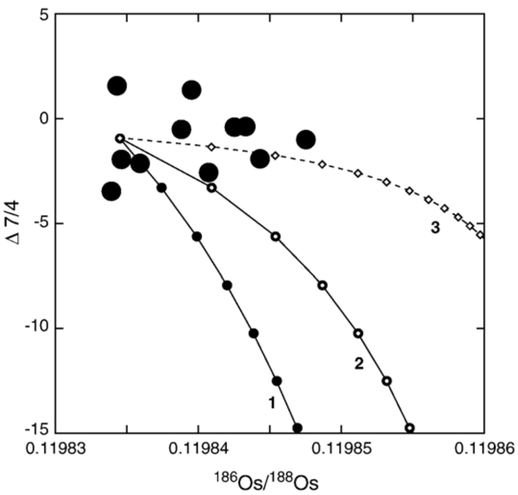

Fig. 1. Os-and Pb-isotope variations in Hawaiian picrites. $\Delta 7/4 = 100*({}^{207}Pb/{}^{204}Pb_{measured} - {}^{207}Pb/{}^{204}Pb_{NHRL})$, where ${}^{207}Pb/{}^{204}Pb_{NHRL}$ = Northern Hemisphere Reference Line ${}^{207}Pb/{}^{204}Pb$ calculated for the measured ${}^{206}Pb/{}^{204}Pb$ [13]. Hawaiian data are from [2] and references therein. The effects of core addition are shown for three core composition models. Tick marks represent 0.1% core addition to primitive mantle [34]. Core ${}^{186}Os/{}^{188}Os$ is from [3]. Core Pb-isotope composition is assumed to resemble Canyon Diablo troilite [64]. See text for other mixing parameters.

0.071 ppm Pb is estimated assuming a primitive mantle [Ce] of 1.775 ppm. Given that Nd-isotopes in the majority of Hawaiian lavas indicate a LREE-depleted source, Ce and Pb concentrations in the Hawaiian plume are likely lower than these estimates.

Mixing models 1 and 2 both assume a core Pb concentration of 0.4 ppm [15]. This estimate is consistent with ~90% volatile Pb loss prior to core formation, and is therefore a conservative estimate. In order for the outer core to develop a superchondritic Pt/Os ratio, and therefore elevated ${}^{186}Os/{}^{188}Os$, Os must partition into the inner core during inner core growth to a greater extent than Pt (or Re). The later the onset of inner core crystallization, the greater the depletion of Os in the outer core required to produce sufficient Pt/Os enrichment to generate an ${}^{186}Os$ excess in the outer core similar in magnitude to that observed in the Hawaiian and Gorgona lavas. Model 1 assumes a constant rate of inner core growth beginning at 4.4 Ga, and results in an outer core [Os] = 267 ppm [3]. Of the inner core growth models proposed by Brandon et al. [3], this model has the highest rate of present-day inner core crystallization and thus also allows the highest present-day core–mantle heat flow. Model 2 is equivalent to the early, rapid inner core growth model of Brandon et al. [3]. This model permits a much higher Os concentration in the outer core (661 ppb), but very limited inner core growth (and therefore core–mantle heat flow) after ~4.4 Ga. Neither model 1, with $(Pb/Os)_{mantle}/(Pb/Os)_{core} = 14.4$, nor model 2, which corresponds to a $(Pb/Os)_{mantle}/(Pb/Os)_{core} = 35.5$, is consistent with the Hawaiian ${}^{186}Os/{}^{188}Os$-Δ7/4 data. Instead, a much higher $(Pb/Os)_{mantle}/(Pb/Os)_{core}$ of ~200 (model 3) is required, corresponding to an outer core [Pb] of only 0.028–0.071 ppm for the continuous and early inner core crystallization models. Such low core Pb concentrations would appear to conflict with certain core formation models (e.g, sulfide segregation during core formation; core formation prior to volatile depletion of the Silicate Earth) that could produce a core with sufficient heat-producing elements to allow for early inner core crystallization despite high present-day core–mantle heat flow (see discussion in Section 4).

Quantitative evaluation of other possible mechanisms of core/mantle interaction, such as metal/silicate chemical reaction or diffusive exchange, are currently impossible because the chemical and isotopic effects of such interaction depend on physical parameters (metal/silicate K_D values, diffusivities) that are largely unconstrained at conditions relevant to the core/mantle boundary. However, special conditions are required in order for these interaction mechanisms to generate an Os-isotope signal in mantle materials without simultaneously generating observable shifts in W- or Pb-isotopes or siderophile element abundances and ratios. For example, Puchtel et al. [4,16] estimated Pt/Os and Ir/Os ratios for the Kostomuksha source within 20% of chondritic ratios, and suggested that ${}^{186}Os$ enrichment of the Kostomuksha source might have resulted from diffusive isotopic exchange between metal and silicate at the core/mantle boundary rather than simple core/mantle mixing. Because the outer core must have highly fractionated PGE abundances (i.e., high Pt/Os) in order for it to develop elevated ${}^{186}Os$, both simple core/mantle mixing and core/mantle chemical reaction would likely generate fractionated PGE patterns in the hybrid mantle material, although the type and magnitude of fractionation produced by chemical reaction depends on metal/silicate partition coefficients that are poorly constrained at elevated pressures and temperatures. Isotopic diffusion may in principle proceed faster than chemical diffusion (c.f., [17]), thereby decoupling isotopic and trace element signatures of core/mantle interaction. The extent of core/mantle diffusive isotopic exchange in this case would depend primarily on the diffusivities of the elements of interest, not the relative concentrations of these elements in the core and mantle. Therefore, in order for diffusive isotopic exchange between the core and mantle to affect Os-isotopes, but not Pb- or W-isotopes, the diffusion coefficient for Os in silicate material at the core/mantle boundary must be significantly greater than for Pb or W. In summary, although it is not possible to completely reject the possibility that core/mantle interaction could impart a core imprint on Os-isotopes without significantly affecting other isotopic or trace element systems, such selective interaction would require a number of special conditions that appear fortuitous.

3. Constraints on core/mantle heat flow

A basic prerequisite for the Walker/Brandon model is that the inner core is very old. Because the half-life of ^{190}Pt is exceedingly long ($t_{1/2} \approx 489$ Ga), development of appreciable ^{186}Os enrichment in the outer core requires either very early onset of inner core crystallization, or very large Pt/Os fractionation during inner core growth. Furthermore, generation of ^{186}Os enrichments in the 2.8 Ga Kostomuksha komatiites by core/mantle interaction would require onset of inner core growth prior to 2.8 Ga, most likely by 3.5 Ga at the latest [4]. Several models of inner core growth and accompanying outer core Pt/Os fractionation have been proposed to account for the outer core ^{186}Os enrichment required by the Walker/Brandon model (c.f., Fig. 4 of [3]). All of these models propose onset of inner core crystallization prior to 3.5 Ga.

Crystallization of the inner core results from secular cooling of the core. In the absence of heat-producing elements in the core, heat flow across the core/mantle boundary is balanced by this secular cooling, by the release of latent heat associated with inner core crystallization, and by the release of gravitational energy as light elements are sequestered into the outer core during inner core crystallization (c.f., [18]). Based on current estimates of the entropy of crystallization of the inner core, the heat capacity of the core, and the slope of the core liquidus, Labrosse [18] estimated that $\sim 29 \pm 19 \times 10^{28}$ J have been removed from the core since it first intersected its solidus at the Earth's center, consistent with other recent estimates (~ 16–36×10^{28} J; c.f., [19]). Although the uncertainty in this estimate is large, it nonetheless places an important constraint on the permissible age of the inner core for a given core/mantle heat flow. For example, using the core energy budget of Labrosse [18], constant inner core growth since 4.4 Ga (model 3 of [3]) would require an average core/mantle heat flow of $\sim 2.1 \pm 1.3$ TW. Note that other proposed models for inner core growth [3,4] all require an early phase of rapid inner core growth followed by slower rates of inner core growth today. Because the present-day rate of inner core growth is directly proportional to core/mantle heat flow, these models all require present-day core/mantle heat flow $< 2 \pm 1.3$ TW. In the following discussion, I compare various independent constraints on modern and time-averaged core/mantle heat flow with this prediction of the Walker/Brandon model.

3.1. Heat conduction along the liquid outer core adiabat

The Earth has possessed a magnetic field since at least 3.5 Ga [20,21]. Because generation of Earth's magnetic field requires rapid convection in the outer core, the presence of a magnetic field throughout most of Earth history indicates that the thermal profile of the convecting portion of outer core is and has been nearly adiabatic. Recent estimates of conductive heat flow along an outer core adiabat at the core/mantle boundary are ~ 5–7 TW [19,22,23]. Provided that the entire outer core is adiabatic, this estimate provides a minimum estimate of core/mantle heat flow, because convective power required to drive the geodynamo must be added to the conductive heat flow term.

Core/mantle heat flow is eventually controlled by the physical properties of the core/mantle boundary, not by the core itself. It is possible that mantle insulation could result in lower heat flow across the core/mantle boundary than can be transported along an outer core adiabat. Lister and Buffett [24] explored the thermal evolution of the outer core for cases where the outer core Nusselt number (the ratio of core/mantle heat flux to conductive heat flux along an outer core adiabat) is <1. This condition will result in the development of a hot upper boundary layer isolated from the convecting layer below. To first order, the thickness of this layer will grow to the point that $Q_{\mathrm{cond}}(r) = Q_{\mathrm{CMB}}$. At any depth within the outer core, $Q_{\mathrm{cond}}(r)$ is given by the expression

$$Q_{\mathrm{cond}}(r) = A_r{*}\kappa_r{*}(\mathrm{d}T/\mathrm{d}z)_r \tag{1}$$

where $Q_{\mathrm{cond}}(r)$ is the conductive heat flux at a given radius, A_r is the surface area for that radius, κ_r is the thermal conductivity, and dT/dz the adiabatic thermal gradient. $Q_{\mathrm{cond}}(r)$ decreases with increasing depth within the outer core both because the surface area over which heat is transported is reduced, and because dP/dz, and therefore dT/dz, decreases with decreasing radius. Fig. 2 illustrates the approximate conductive heat flow Q_{cond} transported along an outer core adiabat as a function of depth. If the entire outer core is actively convecting and therefore nearly adiabatic, then $Q_{\mathrm{CMB}} \geq Q_{\mathrm{cond}}$ (3480 km) ≈ 7 TW. Reduction of core/mantle heat flow to $<2 \pm 1.3$ TW (consistent with the Walker/Brandon model) would suggest a time-averaged outer core Nusselt

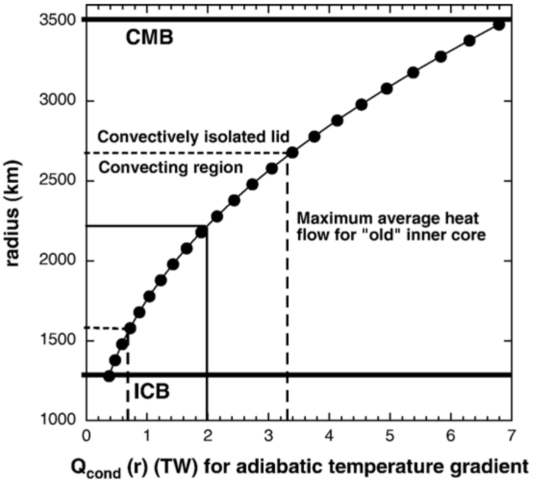

Fig. 2. Conductive heat flow along an adiabatic temperature gradient in the outer core. The adiabatic temperature gradient and thermal conductivity are assumed to vary smoothly between the outer and inner core boundaries, from 0.97 K km^{-1} to 0.27 K km^{-1} and from 46 to 63 W K^{-1} m^{-1}, respectively [22,65,66]. Solid and dashed horizontal lines indicates the approximate thickness of an upper outer core hot thermal layer for a reduced core/mantle heat flow of 2±1.3 TW. Q_{cond} (r) of 3.3 TW (the upper limit for an "old" inner core) requires an ~800 km thick upper thermal boundary layer. Reduction in the estimated thermal conductivity (e.g., to reduce estimated Q_{cond}(3480) from 7 to 5 TW) will reduce the minimum thickness of the hot upper boundary layer from ~800 km to ~500 km. See text for details.

number of ~0.3–0.5, which in turn would result in the growth of a hot, convectively isolated lid between 800 km (for Nu=0.5) and 1900 km (Nu=0.3) thick.

Although a thin (<100 km) chemically or thermally buoyant layer at the top of the outer core might be difficult to detect, a layer with a thickness >800 km would likely be readily observable both seismically and through observation of the tangent cylinder projection of the Earth's magnetic field. In a preliminary study of the seismic structure of the top of the outer core, Tanaka [25] suggested that observed S3KS wave splitting could result from a low velocity zone in the upper 50 km of the outer core (consistent with a Nusselt number of ~0.95), but there is currently no data that would support the much larger-scale chemical or thermal stratification of the outer core that a lower Nusselt number would require. Therefore, the estimated conductive heat flow along the outer core adiabat suggests a minimum core/mantle heat flow of ~5–7 TW.

3.2. Heat conduction across the core/mantle boundary (D″)

Core/mantle heat flow may also be estimated from the thermal gradient on the mantle side of the core/mantle boundary [26]. The temperature drop ΔT across the core/mantle boundary is estimated to be ~1000–1800 K [22]. This estimate derives from extrapolation of an upper mantle potential temperature of ~1340 °C along a mantle adiabat to the base of the mantle, and extrapolation of the outer core adiabat from the intersection with the core solidus at the inner core boundary (~5500 °C). For a thermal boundary layer thickness of ~200 km and $\kappa \approx 9.5$ W m^{-1} K^{-1} [22], a temperature drop of 1000–1800 K will result in Q_{CMB} of ~7–13 TW, similar to the estimate of Buffett [26].

Buffett [26,27] proposed that a chemically-dense layer at the base of the mantle rich in heat-producing elements could effectively insulate the outer core, reducing core/mantle heat flow to a level consistent with an old inner core. Several recent models have proposed that the base of the mantle may represent a significant reservoir of the Earth's heat-producing elements (c.f., [28–30]). Such a layer could provide a means of reconciling geochemical arguments for chemical stratification in the mantle with geophysical evidence for deep penetration of subducted slabs and whole mantle convection (c.f., [28]). One requirement of any such chemical layer is that it be geodynamically stable over the greater part of Earth history despite significant heat production within the layer. In principle, any basal chemical layer may be stable provided it is sufficiently dense, e.g., if this layer has a high iron content. Deep recycling of iron-rich crust or core/mantle chemical reaction are possible mechanisms that could generate a stable iron-rich silicate layer at the base of the mantle, and recent studies suggest that the post-perovskite phase can incorporate significant quantities of iron into its structure (c.f., [31]).

Fig. 3 illustrates the effect of internal heat production on the thermal profile of a 200 km thick conductive boundary layer at the base of the mantle. The rate of core/mantle heat flow is controlled by the slope of the thermal gradient at the base of this layer. In the absence of internal heat production, a 1000 °C temperature drop should result in core/mantle heat flow of ~7.8 TW. In order to reduce this heat flow today to ~2 TW, the boundary layer must contain sufficient K, U, and Th to produce ~12.4 TW of internal heat (the boundary layer is assumed to be in quasi-steady state, so that $Q_{top}=Q_{bottom}+H_{radiogenic}$). Given an estimated total heat production for the Silicate Earth of ~20 TW, this represents ~62% of the Silicate Earth's heat-producing elements. This estimate is significantly higher than the ~9 TW heat production Boyet and Carlson [30] estimated for a hidden enriched mantle reservoir based on ^{142}Nd evidence for early melt depletion of the bulk of the mantle, and would require that the entire

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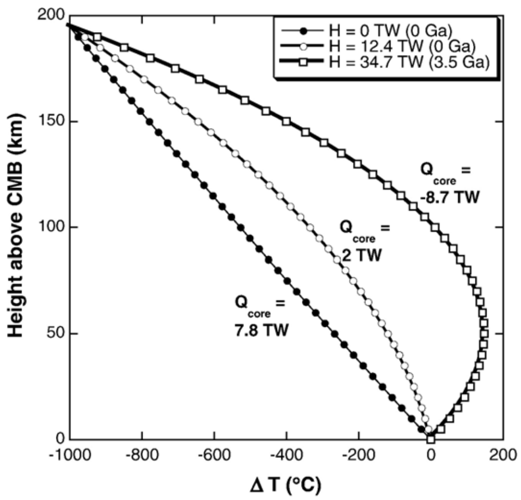

Fig. 3. Equilibrium thermal profile for a 200 km thick conductive boundary layer at the base of the mantle with variable internal heat production. Temperature contrast between the top and bottom of the layer is fixed at 1000 °C, at the low end of estimates for core/mantle temperature contrast. Temperature profiles are calculated assuming dT/dt‰0 at every depth, so that for a given thin shell with radius r, $Q_{r,\ \mathrm{out}}=Q_{r,\ \mathrm{in}}+H_r$; Q_r denotes heat flow into and out of the shell and H_r the rate of internal heat production within the shell.

mantle is as or more depleted than the source of mid-ocean ridge basalts.

Sequestration of such a large fraction of the Earth's heat-producing elements at the base of the mantle seems unlikely, but cannot be strictly excluded on geochemical grounds. However, the existence of a magnetic field early in Earth's history may place an additional limit on the amount of heat production in any primordial basal chemical layer. The Earth has possessed a magnetic field since at least 3.5 Ga [20], and although the power needed to drive the geodynamo is poorly constrained, we may safely assume that long-term preservation of the geodynamo requires $Q_{\mathrm{CMB}}>0$. However, radiogenic heat production was much greater in the past than it is today (~2.8× greater at 3.5 Ga). Thus, a chemical boundary layer that produces 12.4 TW radiogenic heat today would have produced almost 35 TW at 3.5 Ga. In addition, if we assume that inner core crystallization began early in Earth history, as required by the Walker/Brandon model, then the temperature drop across the core/mantle boundary at 3.5 Ga would have been similar to that observed today. Under these conditions, the resultant conductive thermal profile within the basal boundary layer at 3.5 Ga would have resulted in a negative heat flow across the core/mantle boundary of ~8.5 TW, because the lower ~50 km of the boundary layer would become hotter than the core itself. It is difficult to envision preservation of the geodynamo under these conditions.

Other processes, such as thermal convection within D'' or heat transport (up or down) via partial melting and melt transport, may modify the above estimates of the effects of basal heat production on core/mantle heat flow, and further geodynamic study is required on both the stability of basal chemical layers with internal heat production and the effects of such layering on the thermal evolution of the core. However, the above discussion illustrates that it may be difficult for any such chemical layer to reduce modern core/mantle heat flow by nearly a factor of 4 without reducing heat flow earlier in Earth history to a level below that required to drive the geodynamo. In summary, although considerable uncertainty exists regarding both the temperature profile and heat production at the base of the mantle, simple models of conductive heat flow across this boundary suggest ~7–13 TW of core/mantle heat flow today, consistent with the previous constraint based on consideration of heat flow along the outer core adiabat.

3.3. Secular cooling of the mantle

The rate of mantle secular cooling provides a third independent means to estimate core/mantle heat flow. The heat budget of the Silicate Earth can be written as follows:

$$Q_{\mathrm{surface,\ today}} \approx H_{\mathrm{radioactive\ decay,\ today}} + M_{\mathrm{mantle}} * C_{\mathrm{P}}(\mathrm{mantle}) * dT_{\mathrm{mantle}}/dt + Q_{\mathrm{CMB,\ today}} \tag{2}$$

For simplicity, the above expression ignores the release of gravitational energy associated with thermal contraction of the cooling Earth [32], as this is a relatively minor component of the overall heat budget. Thus, in order to estimate core/mantle heat flow, it is necessary to first constrain surface heat flow, heat from radioactive decay, and heat from mantle secular cooling.

The concentrations of the Silicate Earth's primary heat producing elements, U and Th, are well constrained at ~20 and ~80 ppb, respectively [33,34]. The concentration of K in the Silicate Earth is less well constrained, with recent estimates ranging from ~150 to 260 ppm [28,33]. However, K-decay currently accounts for only ~10–15% of radioactive heat production in the Silicate Earth, so that total radioactive heat production is constrained to be ~18.3–19.6 TW. Present day surface heat flow is also generally considered well constrained at ~44 TW (c.f., [35]; see also [36] for an alternative perspective).

Numerous studies have evaluated the rate of mantle secular cooling using constraints derived from mantle

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freeboard arguments [37], the cooling history recorded in continental lithospheric xenoliths [38], and the petrology of ancient basalts [39–41] and komatiites [42,43]. Most of these studies suggest secular cooling rates on the order of 60 °C/Ga or less. For example, calculated liquidus temperatures of ~1500 °C for MORB-like basalts from the 3.5 Ga North Pole region of the Pilbara craton suggest the mid-Archaean was at most ~150–200 °C hotter than today [39]. Liquidus temperatures of 1480 °C for basalts from the 3.8 Ga Isua Supracrustal Belt [40] and 1420 °C for the 2.04 Ga Kangamuit dikes [41] are consistent with mantle cooling rates of ~50–60 °C/Ga. These results are consistent with mantle cooling rates estimated from rates of continental uplift and erosion (~57 °C/Ga; [37]).

Earlier estimates of mantle secular cooling rates based on inferred liquidus temperatures of Archaean komatiites suggested significantly higher rates of secular cooling (>300 °C since 3.5 Ga; c.f., [42]). However, komatiites are poorly suited for constraining the potential temperature of the mantle as a whole. There is considerable debate about whether komatiites were generated from hydrous or anhydrous partial melting, and whether they derive from ancient mantle plumes or subduction zone settings (c.f., [43]). If komatiites are hydrous melts derived from subduction zone settings, then the liquidus temperatures calculated from anhydrous melting trends are too high. Alternatively, if komatiites derive from mantle plumes, then the relationship between the potential temperature of komatiitic (i.e., plume) sources and the average potential temperature of the mantle is far from straightforward. Therefore, relatively moderate rates of mantle cooling of ~60 °C/Ga appear to be better supported by both the geologic and petrologic record of Archaean terranes.

Mantle secular cooling of 60 °C/Ga can support ~9.1 TW of surface heat flow (assuming uniform cooling of the entire mantle mass and an average $C_P = 1200\ \mathrm{J\,kg^{-1}\,K^{-1}}$). If the present-day rate of cooling is similar to this geologically averaged value, then the rate of core/mantle heat flow can be estimated as:

$$
\begin{aligned}
Q_{\mathrm{CMB}} \approx\ & 44\ \mathrm{TW}(\text{surface heat flow}) \\
& -20\ \mathrm{TW}\ (\text{approximate radioactive heat production}) \\
& -9.1\ \mathrm{TW}\ (\text{secular cooling})
\end{aligned}
$$

or ~15 TW, similar to the upper end of the heat flow range predicted for conductive heat transfer across D''.

Radiogenic heat production was significantly higher earlier in Earth history than it is today. For example, average radiogenic heat production since 3 Ga (the approximate time for which estimates of mantle secular cooling exist) is ~29 TW rather than 20 TW. Surface heat flow was likely also higher in the past due to more rapid convection in a hotter, lower viscosity mantle. However, even if this effect is ignored, a lower bound for the time-averaged core/mantle heat flow since 3 Ga is:

$$Q_{\mathrm{CMB}} \approx 44\ \mathrm{TW} - 29\ \mathrm{TW} - 9.1\ \mathrm{TW} \approx 5.9\ \mathrm{TW}.$$

Thus, unless the present-day surface heat flow is anomalously high compared to average heat flow over geologic history (c.f., [44]), the inferred rate of mantle secular cooling is consistent with core/mantle heat flow of ~6–15 TW.

In summary, three very different methods can be used to constrain both present-day and time-averaged core/mantle heat flow: conduction along the outer core adiabat; conduction across D″; and the global heat balance inferred from mantle secular cooling. All three methods predict high rates of core/mantle heat flow (~6–15 TW). Each of these estimates is fraught with considerable uncertainty, due in large part to our currently poor understanding of material properties (e.g., thermal conductivity or compressibility) at the elevated pressures and temperatures relevant to the core/mantle boundary. However, for the most part the uncertainties involved in each calculation are either uncorrelated or anti-correlated with potential sources of error for the other calculations. For example, the estimated conductive heat flow across D″ depends strongly on the quantity of heat-producing elements within this layer. In contrast, the core/mantle heat flow estimate derived from the rate of mantle secular cooling depends on the estimated total quantity of heat-producing elements within the Silicate Earth, but is independent of their distribution. Given the similarity of the core/mantle heat flow estimates derived from these three methods, an average core/mantle heat flow of ~6–15 TW appears well supported. In the absence of heat-producing elements in the core and an estimated total energy of $\sim 29 \pm 19 \times 10^{28}$ J associated with core cooling and inner core crystallization since the onset of inner core formation [18], this rate of core/mantle heat flow is consistent with an inner core age of ~0.2–2.5 Ga.

4. Heat-producing elements in the core?

If the core contains heat-producing elements (e.g., U, Th, or K), then core/mantle heat flow could in part be supported by internal heat production, thus permitting slower rates of core cooling and inner core growth. Of the major heat-producing elements in the Earth, K is the most likely element to be present in appreciable quantity in the core. Uranium and Th are both extremely lithophile, even at elevated temperatures and pressures. For example, Wheeler et al. [45] reported maximum sulfide/silicate D_U of 0.001, far too low for U to be a major heat-producing element in the Earth's core. Substantial partitioning of U and Th into metallic or sulfide phases, as has been observed in some enstatite chondrites [46] requires oxygen fugacities far lower than those proposed for core/mantle equilibration.

In contrast, although K typically behaves as a lithophile element in the shallow mantle, it may become moderately chalcophile or siderophile under certain conditions. In addition, the total K content in the Bulk Earth is poorly constrained from cosmochemical data [28], so that the presence of K in the Earth's core would not require a reduction in the estimated K content in the Silicate Earth. Potassium could enter the core through high-pressure (>25 GPa) metal/silicate equilibration (c.f., [47]), or through sulfide liquid segregation during core formation [48,49]. In the following discussion I review geochemical evidence that argues against these two core formation scenarios.

4.1. Sulfide segregation during core formation

Although K is not siderophile at low pressures (<25 GPa), it is moderately chalcophile, particularly when sulfide liquids contain significant quantities of dissolved oxygen [48,50]. Gessmann and Wood [48] reported sulfide melt/silicate melt D_K up to 2.4 at 1600 °C and 2.5 GPa. Thus, segregation of a sulfide liquid during core formation could result in some K in the Earth's core. Estimated elemental abundances of lithophile elements in the Silicate Earth are strongly correlated with estimated nebula condensation temperatures, with volatile elements (including both K and S) showing strong depletions relative to CI chondrites [33,34]. If this volatile depletion pattern is the result of condensation processes predating planetary accretion and core formation [12], then the relative volatility of S suggests a maximum Bulk Earth S content of ~0.56 wt.%, equivalent to a core S content of ~1.7 wt.% [51]. Assuming a sulfide/silicate D_K of 2.4 and primitive mantle K content of ~240 ppm [34], the maximum core K content that would be produced if all of this S were removed to the core via sulfide segregation is only ~30 ppm. The modest heat production from this quantity of K (~0.2 TW today or ~1.2 TW average over Earth history) is insufficient to significantly increase the age of the inner core.

Alternatively, if core formation preceded volatile depletion of the Silicate Earth (e.g., if this volatile depletion resulted from the moon-forming giant impact; c.f., [11]), then the Earth's core could contain up to ~10% S (the approximate amount needed to account for core density assuming that S is the primary light alloying element in the core; [52]). In addition, in this scenario the Bulk Earth K content may have been close to the CI abundance of ~550 ppm at the time of sulfide segregation instead of the current estimated value of ~160 ppm. Under these conditions, sulfide segregation during core formation could result in up to 600 ppm K in the core, producing nearly 4 TW today and 25 TW averaged over Earth history. Such a high K content would clearly have a major impact on core thermal evolution.

Although extensive sulfide segregation during core formation could in principle have produced a K-rich core, mantle abundances of other strongly chalcophilic elements argue against this core formation scenario. For example, given a sulfide/silicate D_{Cu} of ~500 [53], the relatively modest depletion of Cu in primitive mantle (~30 ppm vs. ~120 ppm in CI chondrtites) is consistent with no more than ~0.5% sulfide liquid segregation during core formation (Fig. 4a). Even assuming core formation prior to volatile depletion, this amount of sulfide segregation would result in ~40 ppm K in the core at most.

A further consequence of sulfide segregation during core formation would be very high Pb abundances in the core, particularly if core formation preceded volatile depletion. Indeed, the relatively young U–Pb age of the Silicate Earth compared with Hf–W constraints on the timing of core formation may reflect minor (<1%) segregation of a sulfide liquid following giant impact formation of a magma ocean [10], resulting in a dramatic increase in the Silicate Earth μ value. Lead is believed to be highly chalcophile, although experimental data on sulfide/silicate partition coefficients are limited. Jones et al. [9] reported sulfide/metal D_{Pb} values of ~2000, and Ohtani et al. [54] determined a metal/silicate D_{Pb} of ~0.7 (albeit under different P–T conditions). Thus, sulfide/silicate D_{Pb} values > 1000 appear likely. Addition of just 1% sulfide melt to the core under these conditions would generate a core with a Pb concentration >10× that of the residual mantle. Thus, if the core contains significant quantities of K due to sulfide segregation during core formation, we would expect core/mantle interaction to produce large shifts in Pb-isotope composition. The absence of "core-like" Pb-isotopes in plume-derived lavas suggests that either sulfide segregation was not important during core formation, or that plume lavas lack a geochemical signature of core/mantle interaction.

4.2. High-pressure core formation or core/mantle equilibration

A second mechanism for incorporating potassium into the Earth's core is high-pressure core/mantle equilibration

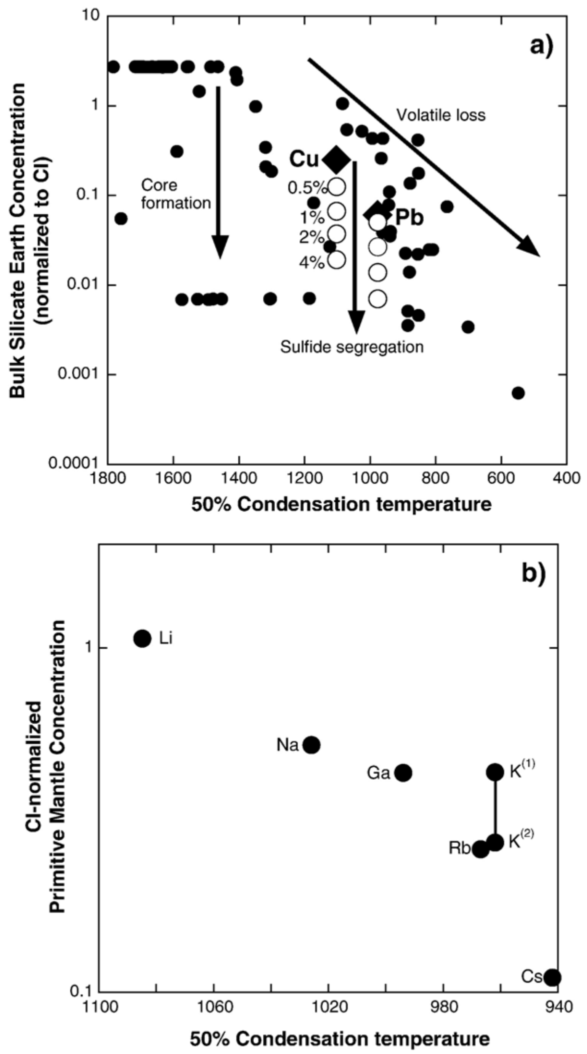

Fig. 4. (a) CI-normalized elemental abundances in the Silicate Earth [34] versus 50% condensation temperature at 10^{-4} atm [58]. Most lithophile elements display a strong correlation between normalized abundance and condensation temperature, reflecting partial volatile loss of non-refractory elements either prior to or during Earth accretion. Departures from the volatile depletion trend primarily reflect core segregation of siderophile or chalcophile elements. The effect of sulfide segregation on Cu and Pb abundances is shown (open circles), assuming sulfide/silicate D_{Cu} and D_{Pb}‰500 and 1000, respectively [10,53]. Cu and Pb abundances estimated for the Silicate Earth are consistent with <0.5% sulfide segregation during core formation. (b) Elemental abundance versus condensation temperature for the alkali metals and gallium. Two estimates of K relative abundance range from 240 ppm (1: [34]) to 150 ppm (2: [28]). The alkali metals show a smooth trend of increasing depletion in the Silicate Earth with decreasing condensation temperature, particularly if the lower K abundance estimate of [28] is considered.

either during or subsequent to core segregation. At low pressures, the 4 s outer electron orbital structure of potassium results in strongly lithophile element behavior. However, at pressures greater than ~25 GPa, K undergoes an s-to-d transition in its outer electronic orbital structure, resulting in increased transition metal-like behavior [55]. A number of experimental [47] and theoretical [56] studies suggest that up to weight percent quantities of potassium may dissolve in iron alloy liquids at pressures above the s-to-d transition. However, the solubility of potassium in iron alloys provides only a gross upper limit on the potassium content of the core if the activity of potassium in the mantle is less than one, which appears likely given an estimated K content of primitive mantle of only 150–250 ppm [28]. At present, few studies have directly measured silicate/metal partitioning of K at high pressure. However, Hirao et al. [57] reported a metal/silicate D_K of ~0.15 at 134 GPa and 3500 K. Core/mantle equilibration under these conditions would produce a core with only ~35 ppm K.

Primitive mantle abundances of moderately volatile elements such as Ga in the primitive mantle may also limit high-P partitioning of K into the Earth's core. Fig. 4b shows the relative enrichment/depletion pattern of the alkali metals Li, Na, K, and Cs, and the transition metal Ga compared to CI chondrites [34]. Elemental abundances are well correlated with condensation temperature [58], suggesting that volatile depletion rather than core segregation is the primary control on the concentrations of these elements in the Silicate Earth. High-P partitioning of K into the Earth's core would likely produce a very different depletion pattern in the Silicate Earth than is observed. For example, the partial molar volume of Ga_2O_3 favors increasing lithophile behavior with increasing pressure rather than increasing siderophile behavior [59]. If the observed depletion of alkali elements derived from core formation rather than volatile depletion, then Ga should be anomalously enriched in the Silicate Earth relative to K and Na, but such enrichment is not observed.

The relative abundances of the alkali metals provide another constraint on high-pressure K-partitioning into the core. Rubidium and Cs undergo an s-to-d transition at significantly lower pressures than K [60], and preliminary data suggest that metal/silicate D_{Rb} and D_{Cs} may be much higher than D_K. Hilgren et al. [61] report a metal/silicate D_{Rb} of 200 for an Fe–S mixture at 30–54 GPa, 20× higher than the D_K (10) determined for the same conditions (K and Rb concentrations in sulfur-free systems were below detection). Therefore, high-P partitioning of K into the Earth's core should be accompanied by much greater partitioning of Rb, resulting in a pronounced increase in the K/Rb ratio of the Silicate Earth. Given current estimates of the Silicate Earth K content (150–250 ppm; [28]), the K/Rb ratio of the Silicate Earth (~250–420) is within a factor of 2 of the CI chondrite ratio (~240; [34]).

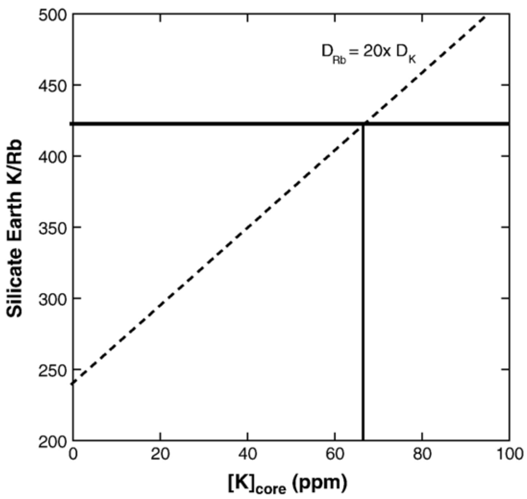

Fig. 5. Correlation of core K content and K/Rb in the residual Silicate Earth, assuming batch metal/silicate segregation, and a high-P metal/silicate $D_{Rb}=20\times D_K$ [61]. For an estimated K/Rb of ~420 for the Silicate Earth [34], core K content is limited to less than ~60 ppm, assuming a starting Bulk Earth composition similar to CI chondrites. For a Silicate Earth K content of 150 ppm [28], the resultant Rb/Sr ratio of ~250 would limit the amount of K in the core to less than 10 ppm.

The factor of 2 uncertainty in the K/Rb ratio of the Silicate Earth almost entirely reflects uncertainty in the Earth's K content; the Rb content of the Silicate Earth is well constrained from the Rb/Sr ratio inferred from the global correlation of Sr- and Nd-isotopes (c.f., [62]).

Fig. 5 shows the result of high-pressure core segregation on the Silicate Earth K/Rb ratio assuming metal/silicate $D_{Rb}=20\times D_K$ [61]. The starting composition is assumed to have CI chondrite relative abundances of Rb and K (e.g., K/Rb ≈ 240). For the upper estimate of Silicate Earth K and K/Rb (~250 ppm and ~420, respectively; [34]), the maximum core K concentration that is consistent with the Silicate Earth K/Rb ratio is ~65 ppm. Lassiter [28] argued that the K content of the Silicate Earth could be as low as 150 ppm. If this estimate were correct, the resultant nearly chondritic K/Rb ratio of the Silicate Earth (~250) would preclude more than trace quantities of K from entering the core through high-pressure metal/silicate equilibration. The upper estimate of 65 ppm K would produce ~0.4 TW of radiogenic heat in the core today, or ~2.7 TW averaged over all of Earth history. Although this quantity of K could have a significant influence on the early thermal evolution of the core, the relatively modest heat generated in more recent time would have only a minor influence on inner core age (c.f., [63]).

In conclusion, although K may theoretically partition into core-forming metal and sulfide liquids under appropriate P–T–fo_2 conditions, the mantle relative abundances of chalcophile elements such as Cu and Pb and alkali metals such as Rb do not support these core-formation scenarios. Further experimental work is required to more fully characterize metal/silicate and sulfide/silicate partition coefficients over a wide range of conditions. However, current experimental constraints suggest that the Earth's core is unlikely to contain more than ~30–65 ppm K. In the absence of heat producing elements in the core, the previous core/mantle heat flow estimates indicate a relatively young (<2.5 Ga) inner core.

5. Conclusions

The hypothesis that ^{186}Os enrichments in some plume-derived lavas reflect either direct addition of core material or indirect core/mantle chemical interaction presupposes that inner core crystallization began early in Earth history, most likely by 3.5 Ga at the latest. Inner core growth histories capable of producing early Pt/Os enrichment in the outer core sufficient to generate the ^{186}Os enrichments observed in Hawaiian and other plume lavas all predict modern core/mantle heat flow of <2 TW. This prediction is contradicted by three independent estimates of core/mantle heat flow: conductive heat flow along the outer core adiabat; conductive heat flow across D''; and global heat balance deduced from rates of mantle secular cooling. All three estimates suggest core/mantle heat flow of 6–15 TW, more than 3 times the heat flow suggested by the Walker/Brandon model.

Incorporation of heat-producing elements in the core has been proposed as a means of reconciling high core/mantle heat flow with an ancient inner core. However, the "core depletion" signal recorded in primitive-mantle trace element abundances limits the amount of K (the most likely heat-producing element to enter metallic phases) that could have been incorporated into the core either through low-pressure sulfide segregation or high-pressure core/mantle equilibration. Available metal/silicate and sulfide/silicate partitioning data suggest less than 1% sulfide segregation during core formation and a likely maximum core K content of ~30–65 ppm. This amount of K is insufficient to significantly effect the age of onset of inner core crystallization deduced from core/mantle heat flow. Inner core crystallization therefore most likely began between 0.2 and 2.5 Ga.

Identification of a geochemical "core signal" in plume-derived lavas would open up many new avenues to explore the chemical and thermal evolution of the core and core/mantle boundary. However, because the magnitude of the Os-isotope contrast between the outer core and mantle is a function of inner core age, Os-isotope variations in plume-derived lavas may have relatively little utility in the study

Please cite this article as: J.C. Lassiter, Constraints on the coupled thermal evolution of the Earth's core and mantle, the age of the inner core, and the origin of the 186O..., Earth and Planetary Science Letters (2006), doi:10.1016/j.epsl.2006.07.044.

of core/mantle interaction due to the young inner core age dictated by core/mantle thermal evolution.

Acknowledgements

This manuscript benefited from discussions with Francis Nimmo, Erik Hauri, Steve Grand, and many others. Constructive reviews from Bruce Buffett and Richard Walker and editorial comments from Richard Carlson are gratefully acknowledged. This study was supported in part by the Jackson School of Geosciences.

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