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Lead isotopes and the age of the Earth – a geochemical accident

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Abstract: The assumptions underlying the models used in the literature for obtaining the age of the Earth from terrestrial lead isotopes are severely violated by the complex evolution of the Earth, particularly the extreme chemical fractionation occurring during crust–mantle differentiation. Young conformable lead deposits are isotopically very similar to young sediments, the erosion products derived from the Earth's most highly fractionated large-scale reservoir, the upper continental crust. Therefore, ancient conformable lead deposits are also likely to track continental compositions rather than the composition of any truly primitive reservoir.

Although the specific enrichment mechanisms during crust formation are both extreme and quite different for U and Pb, the net enrichments in the crust, as well as the corresponding depletions in the residual mantle, are on average very similar for the two elements. It is because of this geochemical coincidence that the time-integrated U/Pb ratios of conformable lead deposits, which integrate and average large volumes of crustal lead, are very close to average mantle values. For the same reason, the isotopic evolution of these conformable lead deposits follows an apparently (nearly) closed system evolution path of a 4.4 to 4.5 Ga-old U–Pb system rather closely, even though that system was actually very far from remaining chemically closed during its history. From these considerations I conclude that terrestrial Pb isotopes do not furnish a suitable tool for determining a refined estimate of the age of the Earth within the broad bounds of 4.4 and 4.56 Ga limits, which are given by other types of evidence, such as the ages of meteorites, the Moon, and the formation intervals of the Earth's core and atmosphere derived from the decay products of short-lived, now-extinct nuclides.

All the king's horses and all the king's men
Couldn't put Humpty together again.
(English nursery rhyme)

The scientific breakthroughs achieved by Holmes, Gerling, Houtermans and Patterson in using lead isotopes to determine the ages of meteorites and the Earth, which culminated with Patterson's classic paper published in 1956 'Age of meteorites and the Earth' (Patterson 1956), have led to the persistent and widely held belief, even today, that lead isotopes provide the best means for determining the age of the Earth. The scientific story of this approach has been traced in the superb, scholarly treatise of Dalrymple (1991; see also Dalrymple 2001).

The original idea of the Holmes–Houtermans approach was that the Earth was, at the time of its formation, permanently differentiated into different reservoirs characterized by different U/Pb ratios. This reflected a general view of the Earth that was essentially static, with no plate tectonics, no mantle convection, and no sea-floor spreading. A sampling of these different reser-

voirs at the present time would yield lead isotope systematics that could be described by straight-line isochrons on a diagram (referred to as the 'Holmes–Houtermans diagram') showing $^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$, which is still seen in present-day textbooks on isotope geology (Faure 1986). Indeed, the combined data for meteorites and terrestrial oceanic sediments conformed to such an isochron (see figs 2 and 3 in Dalrymple 2001). However, subsequent sampling of terrestrial lead sulphide ores of a given age showed that they did not yield any purely terrestrial isochrons. Instead, most of them appeared to follow a single isotopic growth curve (see fig. 4 in Dalrymple 2001), which could be explained if the ores were derived from a single reservoir with a single U/Pb ratio. This reservoir was thought to be the Earth's mantle, then believed to be chemically and isotopically homogeneous. Crustal rocks were thought to be extracted more or less directly from this reservoir at various times, without significantly affecting the composition of the (residual) mantle. In this case, the growth curve of lead

ores could be used to date the ages not only of the ore deposits, but also that of their source reservoir, the Earth's mantle.

Given this general view of the Earth, much of the older literature concerning lead isotopes and their relationship to the age of the Earth was centred on the concepts of 'ordinary' and 'anomalous' lead and 'conformable' lead ores (Stanton & Russell 1959; Russell & Farquhar 1960). A review of these concepts is beyond the scope of this paper, and the reader is referred to Dalrymple (2001). For the present purpose, it is sufficient to say that the central idea developed by Stanton, Russell and others was that the isotopic compositions of 'ordinary' leads follow a single, unique growth curve which defines the age of the Earth. 'Anomalous' leads, on the other hand, deviated significantly from this growth curve. These authors were aware of the dangers of circularity in defining what is ordinary and what is anomalous. They argued, however, that 'ordinary' leads could be identified on geological grounds. Thus, geologically 'conformable' sulphide ores occurring in volcanic-sedimentary associations, and usually forming geologically conformable lenses or layers in the sediments, were found to have remarkably homogeneous ('ordinary') lead isotopic compositions, whereas vein-type, discordant deposits are isotopically much more heterogeneous and thus 'anomalous'. The observations of local isotopic uniformity and the remarkable uniqueness of the isotopic evolution curve with geological time led these workers to infer that conformable leads are derived from a chemically and isotopically primitive uniform reservoir beneath the crust, namely the mantle. Although the concept of 'conformable leads' is no longer particularly fashionable, the notion that common lead isotopes in lead ores and in other rocks derived from the crust or the mantle can define the age of the Earth is by no means dead. For example, a standard set of lead isotope data from conformable ores has been used by Stacey & Kramers (1975) to propose a two-stage model for the evolution of the Earth, which is still widely used today. A nearly identical set of data was used by Albarède & Juteau (1984) and by Galer & Goldstein (1996) to throw light on the earliest history (namely the first 100 million years) of the Earth. Tera (1980, 1981) used lead isotope data from Archaean crustal rocks to put closer constraints on the age of the Earth, and Allègre *et al.* (1995) attempted to use the isotopic composition of Recent mid-ocean ridge basalts to establish an upper limit of the age of the Earth of <4.45 Ga.

In this paper, I will argue that lead isotopes, by defining the ages of meteorites, do indeed pro-

vide a firm limit for the age of the Earth of about 4.56 Ga. However, the Earth is very likely significantly younger than 4.56 Ga, and lead isotopes cannot provide a definitive 'best estimate' of the actual age of the Earth and only a very approximate lower limit for this age. The reason for this is simple: the original assumptions for both the Gerling-Holmes-Houtermans method and the conformable-lead method are fundamentally inconsistent with our current knowledge of the Earth's evolution. The assumptions of both models were that one could sample at least one primitive reservoir within the Earth, whose U/Pb ratio has not changed since the formation of the Earth, and which has not exchanged lead or uranium with other, less primitive reservoirs. The developments in geochemistry since the advent of plate tectonics have led to a new understanding of crust-mantle evolution, which effectively rules out the possibility that a truly primitive reservoir is available for sampling anywhere on the Earth's surface. It is conceivable that nearly primitive reservoirs did exist during Archaean time and were sampled by lead deposits (Tera 1980, 1981), but the early Archaean crust-mantle evolution is far from being completely understood, and most workers argue, on the basis of Nd isotopes, that even the oldest continental crust was formed from a mantle reservoir that was already at least slightly fractionated with respect to Sm and Nd, for example (see, however, Nägler & Kramers 1998). Given this situation, it seems unlikely, and in any case it cannot be demonstrated by any kind of independent evidence, that any early Archaean lead deposit was formed from a reservoir that was truly primitive with respect to U and Pb.

Although the emphasis of this paper is somewhat different from that of Galer & Goldstein (1996) and of Kramers & Tolstikhin (1997), its conclusions are entirely consistent with the results of their thorough and elaborate analyses of Pb isotope data from several present-day and ancient Pb reservoirs and individual samples. The 'age' of the Earth, as measured by lead isotopes, is essentially the time when the present-day U/Pb ratio was established in the silicate portion of the Earth. This ratio was lowered relative to its value in the primitive solar nebula and stony meteorites, the Earth's basic building material, by factors of 10 to 100. This dramatic change was caused by a combination of loss of the relatively volatile lead to space and transfer of lead from the silicate mantle to the liquid metallic core. Thus, slow accretion of the Earth, lasting perhaps up to 100 Ma (Wetherill 1986), and relatively late core formation will yield lead

isotope 'ages' for the Earth significantly younger than the ages of the oldest, most primitive meteorites.

Galer & Goldstein (1996) emphasized that *all* of the accessible present-day lead isotope 'reservoirs' (continental crust estimates, depleted mantle estimates, and bulk Earth estimates based on the combination of the former two reservoirs), as well as individual samples from Archaean rocks, yield accretion times lasting longer than about 40 Ma (and less than about 250 Ma). Kramers & Tolstikhin (1997) constructed a sophisticated (forward) Earth evolution model, in which they reconciled estimates of lead isotopic compositions of several mantle and crustal reservoirs of various ages with Earth accretion scenarios constrained by other information such as the age of the Moon and core segregation models (see also Halliday 2000). Thus, these investigations aimed to explain the composition of observed terrestrial lead isotope reservoirs in terms of independent information on the age and history of accretion, rather than determining an 'age of the Earth.' My aim in the present paper is consistent with their approach, but emphasizes the point that none of the lead samples or reservoirs used in connection with Gerling–Holmes–Houtermans models is likely to have remained a closed U–Th–Pb system since the end of accretion, so that none of these reservoirs is suitable for a detailed analysis of the age of the Earth. The observation that both the average present-day upper continental crust and the average oceanic crust (and upper mantle) have similar mean isotopic Pb compositions is a 'geochemical accident'. Far from actually being primitive, these reservoirs nevertheless yield apparent Pb isotope ages that are roughly consistent with what we do know about the age of the Earth.

Present-day lead

Patterson's initial, ingenious idea was that marine sediments might yield a well-mixed, representative terrestrial lead reservoir. By showing that lead isotopes of such sediments essentially fall on the 4.5 Ga isochron defined by meteorite samples, he had good reasons to think that this provides powerful confirmation for the hypothesis that the sediments are indeed representative of the whole Earth, and, equally important, that the age of the Earth is identical to that of the meteorites.

Sediments and conformable lead

Our present understanding is that marine sediments are derived from the upper continental

crust. This crust has a mean age of about 2 Ga, far younger than the primary ages of meteorites. In addition, we know that the crust is the product of an extreme fractionation process of the mantle. Highly incompatible elements such as U, Th, Ba and Rb are enriched in the crust by factors of 50 to 100 relative to the initial ('primitive') mantle values (Rudnick & Fountain 1995). Consequently, the continental crust now contains (very roughly) 50% of the total terrestrial inventory of these elements, even though it constitutes only about 0.5% of the mass of the total silicate portion of the Earth. Moreover, this enrichment process has separated ('fractionated') these elements from one another. For example, the Th/U ratios of the continental crust and the oceanic crust differ by about a factor of two. To complicate matters further, the continental crust has become differentiated internally, and much of the uranium has been transported from the lower to the upper half of the crust, so that U/Pb ratios in these reservoirs differ considerably (Rudnick & Goldstein 1990). Finally, U is oxidized in near-surface environments to its rather soluble hexavalent oxidation state. As a result, this element becomes mobile and is partly removed from the bulk crust by dissolution during weathering and erosion. In summary, the continental crust represents a chemical reservoir that is as different from any primitive Earth reservoir as one can imagine. Given this knowledge, probably no geochemist would today choose the erosion product of this most highly differentiated of all terrestrial reservoirs, namely marine sediments, to represent the lead isotopes of the Earth system (or any primordial subreservoir of that system).

In spite of the overwhelming geological and geochemical evidence for their 'non-primitiveness', marine sediments do come amazingly close to falling on the meteorite isochron (although they are actually displaced to the right-hand side by a small amount). This is illustrated in Figure 1 which shows data for young conformable lead sulphide ores, oceanic and river sediments, and Pacific and Atlantic mid-ocean-ridge basalts (MORB). Also shown are the 4.566 Ga meteorite isochron, and two zero-age isochrons ('geochrons') for hypothetical primary Earth reservoirs of ages 4.50 and 4.43 Ga. (These younger isochrons are, strictly speaking, valid only for the case where the initial lead isotopic composition of the accreting material did not change between the time of meteorite formation, 4.56 Ga ago, and the time of instantaneous formation of the Earth, 4.50 or 4.43 Ga ago (see also Galer & Goldstein 1996).) Two primary growth curves are given for a 4.43 Ga

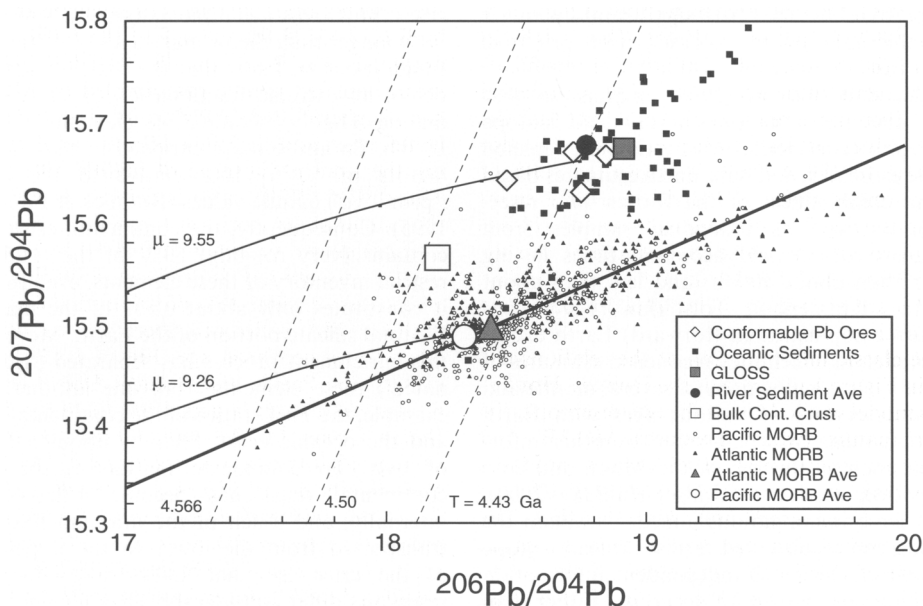


Fig. 1. Holmes–Houtermans-type lead isotope diagram ($^{207}\text{Pb}/^{204}\text{Pb}$ versus $^{206}\text{Pb}/^{204}\text{Pb}$) showing oceanic sediments (Ben Othman *et al.* 1989; Plank & Langmuir 1998), the global average of subducting sediments (GLOSS) estimated by Plank & Langmuir (1998), average river sediments (Asmerom & Jacobsen 1993), present-day values of conformable ore leads (large open diamonds) (Cumming & Richards 1975; Stacey & Kramers 1975; Albarède & Juteau 1984; Davies 1984), an estimated composition of the bulk continental crust (Rudnick & Goldstein 1990), mid-ocean ridge basalts (MORB) from the Pacific (small circles) and Atlantic (small triangles) oceans (for references see Hofmann 1997), as well as their respective average values (large open circle and large shaded triangle). The heavy, low-angle line is a linear regression through the Pacific MORB. The dashed lines are zero-age isochrons ('geochrons') for 4.566, 4.50 and 4.43 Ga old U–Pb systems, starting from the primordial Pb isotopic composition of the Canyon Diablo meteorite (see Dalrymple 2001). Also shown are two isotopic growth curves, starting 4.43 Ga ago with Canyon Diablo lead, and corresponding to U/Pb ratios described by μ ($\equiv (^{238}\text{U}/^{204}\text{Pb})_{t=0}$) = 9.26 and 9.55.

old Earth, corresponding to two slightly different U/Pb ratios. Because U/Pb ratios necessarily change with time as a result of radioactive decay, they are conventionally expressed in terms of present-day values as a common reference frame. By this convention, a parameter expressing the U/Pb ratio is defined as $\mu \equiv (^{238}\text{U}/^{204}\text{Pb})_{\text{today}}$. The two growth curves in Figure 1 are for $\mu = 9.55$ for conformable lead and average recent sediments, and $\mu = 9.26$ for average Pacific and Atlantic MORB.

Figure 1 shows that young conformable lead ores are essentially identical in Pb isotopes to average marine and river sediments, and subtly but significantly different from MORB. This figure also demonstrates that the inference of Stanton, Russell and others, namely that conformable leads are derived directly from the mantle, cannot be correct. The isotopic composition of the upper mantle is best represented by MORB, and it has systematically lower $^{207}\text{Pb}/^{204}\text{Pb}$ values than conformable lead ores

(and sediments). In the 1950s, MORB had not been sampled, and there was no independent way to know the isotopic composition of the upper mantle. Today, we know that oceanic sediments have lead concentrations roughly 50 times higher than those of MORB. It is therefore not so surprising that the lead found in the volcanic-hosted ores is primarily derived from the sediments, not the upper mantle. None of this could have been anticipated by Stanton and co-workers. Derivation from sediments also helps to explain the uniformity of lead isotopes in conformable ores. Oceanic sediments have lead isotopic compositions that are far more uniform than those of MORB (or 'unprocessed' crustal rocks). This must be the result of extensive mixing during erosion, transport and deposition of these sediments.

Figure 1 also shows that marine and river sediments actually cluster around a 4.43 Ga geochron of the Holmes–Houtermans type, not identical but remarkably close to the measured

age (4.56 Ga) of primitive meteorites (Lugmair & Galer 1992; Göpel *et al.* 1994). This is true in spite of the extreme differentiation of incompatible elements into, and within, the continental crust. Even more remarkable is the fact that the mean values of lead isotopes of MORB also lie close to the 4.43 Ga isochron, in spite of the enormous range of individual sample compositions. (Fig. 1 shows lead isotopes for MORB from two of the three major ocean basins, the Atlantic and Pacific oceans; Indian Ocean MORB are even more heterogeneous and have been omitted for clarity.)

The classic interpretation of the relationships seen in Figure 1 in terms of the Holmes–Houtermans model would be that the two reservoirs, the upper mantle (which produces MORB) and the upper continental crust (which produces sediments), were separated about 4.43 Ga ago and have evolved separately since that time. The primary separation age would then be called the ‘age of the Earth’. The slope of the correlation lines, shown here for Pacific MORB as an example, would simply reflect the mean age of internal differentiation of the Pacific MORB source (in this case about 1.9 Ga). From the record of crustal ages, we know that this simple interpretation cannot be correct, not only because the mean age of the crust is much younger than 4.43 Ga, but also because crust and mantle have not been closed systems but have been exchanging some material throughout traceable geological history. The distribution of formation ages of the continental crust, recently reviewed by Condie (1998) (see also Kamber *et al.* 2001), shows no continental masses older than 4 Ga, and even the advocates of constant-continental-volume models (e.g. Armstrong 1991) do not argue that the present-day continental crust is as old as the Earth, but is newly formed and destroyed through plate tectonic processes throughout Earth history. Thus, irrespective of whether the crust grew progressively in time or existed in a steady state of growth and destruction, the continental crust is not a reservoir that can be used to date the formation of the Earth.

Upper mantle and mid-ocean ridge basalts (MORB)

The mantle region that produces MORB is the depleted residue of the continental crust. It is internally quite heterogeneous in terms of lead isotopes (see Fig. 1) because of internal differentiation and exchange with the crust. Nevertheless, Allègre *et al.* (1995) attempted to use the mean isotopic composition of MORB from

the three major ocean basins to calculate an *upper* limit of 4.45 Ga for the age of the Earth. Their argument was based on the assertion that the mean depleted mantle (as sampled by MORB) has a higher $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio¹ than the continental crust and the ‘bulk silicate Earth’ (meaning the total assemblage of mantle and crust). This $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio is defined as the slope of a single-stage isochron (or ‘geochron’), such as those shown on Figure 1 formed by connecting the present-day isotopic composition of a given reservoir with that of primordial lead. The $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratio can therefore be directly related to a geochron age. Figure 1 shows that present-day Pacific and Atlantic Ocean MORB lie close to a 4.43 Ga geochron. Inclusion of the Indian Ocean MORB would raise the overall average slightly to approximately 4.45 Ga. However, this is by no means a generally accepted maximum geochron age obtained for the major present-day terrestrial reservoirs. For example, the geochron age of the bulk continental crust as calculated by Allègre & Lewin (1989) is 4.43 Ga, but the corresponding age of the bulk crust estimated by Rudnick & Goldstein (1990) is 4.50 Ga. Even the bulk-silicate Earth age of Allègre *et al.* (1988) and Allègre & Lewin (1989) of 4.46 Ga is slightly higher than the upper limit claimed by Allègre *et al.* (1995). Clearly, this type of model calculation is no more applicable to the depleted mantle than it is to the crust, because there are good reasons to believe that the depleted mantle is strongly coupled, and largely complementary, to the continental crust (e.g. Hofmann 1988).

Bulk silicate Earth

If we knew the present-day lead isotopic composition of the bulk silicate Earth (BSE) (total mantle and crust) and its initial value (essentially from meteorites), we could determine the age of this silicate portion of the Earth directly according to the Holmes–Houtermans method. Galer & Goldstein (1996) have compiled eight published estimates of the lead isotopic composition of BSE. They are all rather similar, mostly because of the remarkable similarity between sediments, conformable lead ores and MORB, as discussed above. They have $^{207}\text{Pb}^*/^{206}\text{Pb}^*$

¹ The asterisks signify an abbreviated notation for the ‘radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ ratio’. It is defined as follows:

$$\begin{aligned} &^{208}\text{Pb}^*/^{206}\text{Pb}^* \\ &= ((^{208}\text{Pb}/^{204}\text{Pb})_{\text{today}} - (^{208}\text{Pb}/^{204}\text{Pb})_{\text{primordial}}) / \\ &((^{206}\text{Pb}/^{204}\text{Pb})_{\text{today}} - (^{206}\text{Pb}/^{204}\text{Pb})_{\text{primordial}}). \end{aligned}$$

values ranging from 0.566 to 0.606, corresponding to single-stage ages of 4.42 to 4.52 Ga. These BSE estimates (rather than just conformable leads) constitute the main reason why many workers would agree today that lead isotope data require a 'young' age of the Earth. The apparent strength of this argument is that it is in rough agreement with the estimates derived from both the upper continental crust and the depleted mantle. In other words, it appears that all the accessible reservoirs point in the same direction.

One weakness of this argument is that it still leaves an uncertainty of about 100 Ma. Another, perhaps more serious weakness lies in the fact that the above BSE estimates are heavily dependent on the type of data shown in Figure 1 which represent a depleted mantle reservoir and the upper continental crust as sampled by sediments. Depending on the general geochemical Earth model one uses, the lower mantle may or may not be isotopically rather different from the MORB data shown in Figure 1 (see, for example Hofmann 1997).

A probably even larger element of uncertainty is introduced by our poor knowledge of the composition of the lower continental crust, which is generally not sampled by erosion and sediment production. Thus, while we do have outcrops of lower-crustal granulites as well as xenoliths from regions where there is no outcrop, crustal rocks are notoriously heterogeneous. In general, the lower crust is variably depleted in uranium relative to lead, and, depending on the age of the particular crustal province, this causes the lower crust to be less radiogenic than the upper crust. On diagrams of the type shown in Figure 1 the lower crust lies to the left of the upper crust, and this causes the estimate of the BSE composition to shift in the same direction, and therefore to older values. Rudnick & Goldstein (1990) have taken this into account in estimating the composition of the bulk continental crust, by using data from lower-crustal xenoliths in conjunction with a specific crustal growth model. Their effort is probably the best that is available in the literature, but it is still model-dependent and it is based on only nine xenolith localities worldwide, in which the observed Pb isotopic compositions scatter widely, ranging from $^{206}\text{Pb}/^{204}\text{Pb} = <16$ to >19 . In comparison, the much more extensive data for oceanic sediments have a total range from 18.3 to 19.3 (see Fig. 1), less than one-third of the xenolith range. Additional uncertainties are added by the largely unknown composition of the subcontinental lithosphere, for which very few lead isotope data exist, and which is also part of the required bulk silicate Earth budget.

All in all, substantial uncertainties remain about the total inventory of the bulk silicate Earth. Present indications are that BSE does lie to the right of, and is therefore younger than, the 4.56 Ga meteorite isochron. Indications are further that BSE is older than about 4.4 Ga, but the extreme internal heterogeneity of the accessible terrestrial reservoirs and the partial to complete inaccessibility (to sampling) of some reservoirs make it impossible to use these isotope data to narrow this range significantly. No individual, demonstrably primitive, geochemical reservoir is available today to which we could apply the Holmes–Houtermans model, and no amount of averaging, conducted by nature or on a computer, is likely to reconstruct reliably the composition of the present-day bulk silicate Earth reservoir from rock samples. As the nursery rhyme from *Mother Goose's Tales* quoted at the beginning of the paper suggests, no matter how hard we try, we cannot put Humpty together again.

Ancient lead

If present-day lead reservoirs are too evolved and fractionated with respect to U and Pb, as I have argued above, it is still conceivable, at least in principle, that examination of ancient rocks might reveal the existence of primitive reservoirs that have undergone only single-stage U-Pb evolution, and from these it might be possible to infer an 'age of the Earth'. This is the idea behind using ancient conformable lead deposits to obtain a unique growth curve, which would also define its initial starting time. In particular, Tera (1981) has investigated the systematics of Archaean lead with this objective in mind (see also Dalrymple 2001). However, any such effort must necessarily contain a circular element, as long as the choice of samples is made on the basis of the lead isotopic relationships themselves. If, on the other hand, evidence for a geochemically primitive mantle source reservoir could be found in some suite of Archaean rocks, then we could use initial isotopic compositions of these rocks to infer the age of this primitive reservoir (for an explanation of initial isotope ratios, see Lewis 2001).

Figure 2 shows the evolution of lead isotopes in conformable lead deposits as a function of age. For this purpose, it is useful to follow the approach of Albarède & Juteau (1984), which replaces the somewhat complex three-isotope plots used in the Holmes–Houtermans models and its more recent derivatives (e.g. Tera 1980, 1981), by a diagram plotting the evolution of a single isotope ratio directly as a function of age.

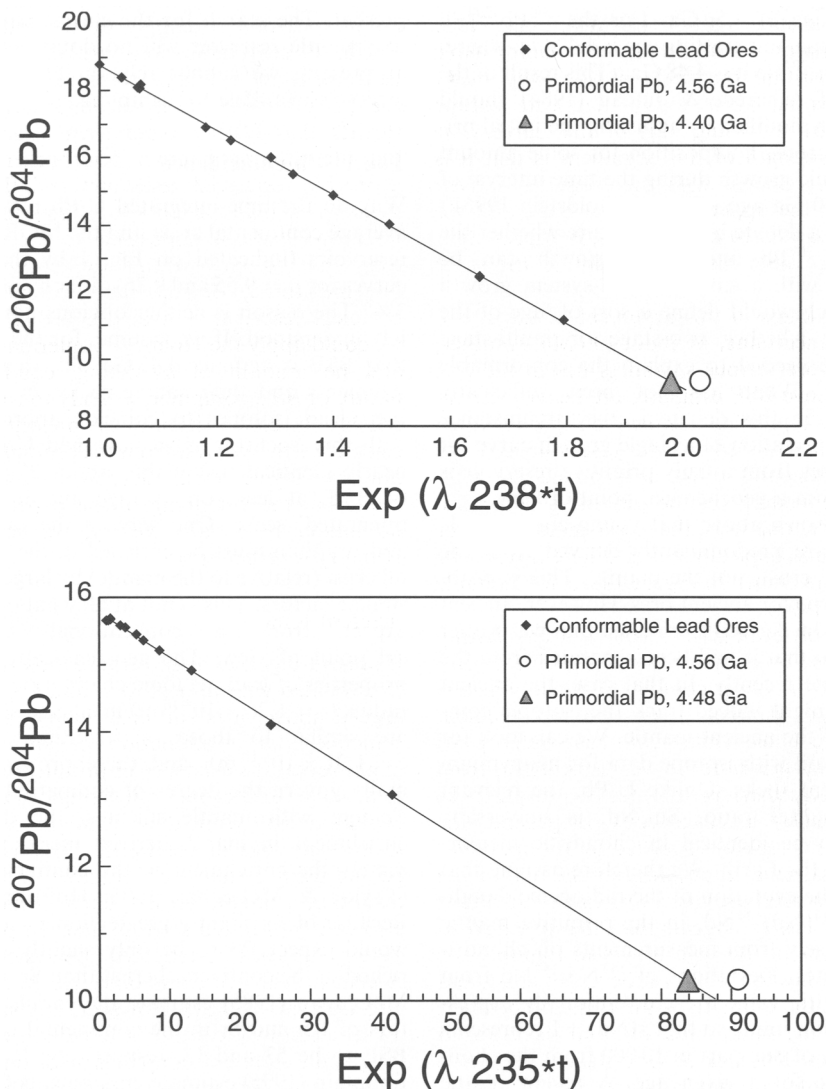


Fig. 2. Linearized evolution plots for radiogenic $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ in conformable lead ores as functions of $\text{exp}(\lambda t)$, following the approach of Albarède & Juteau (1984). Extrapolation to the composition of primordial lead from the Canyon Diablo meteorite (Tatsumoto 1973) would yield 'ages' of 4.40 Ga for $^{206}\text{Pb}/^{204}\text{Pb}$ and 4.48 Ga for $^{207}\text{Pb}/^{204}\text{Pb}$ (Albarède & Juteau 1984).

The only complication here is that the half-lives of ^{238}U and ^{235}U (4.5 and 0.7 Ga respectively) are similar to and less than the age of the Earth, unlike those for ^{87}Rb and ^{147}Sm , which are ten and 20 times the age of the Earth. Because of these relatively short half-lives, the isotope ratios plotted against age form strongly curved evolution lines, following the exponential decay equation. However, by plotting the exponential term $e^{\lambda t}$, or $e^{(\lambda t)}$ following Albarède & Juteau (1984), where λ is the decay constant and t is the age,

it is easy to linearize the closed-system growth curves of both $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ perfectly, as can be seen in Figure 2.

Lead isotopes from conformable lead sulphide deposits appear to follow single (closed-system) growth trajectories rather closely. However, if the starting composition of these growth lines is taken to be primordial lead as measured in the Canyon Diablo meteorite (Tatsumoto 1973), then these lines originate at two different ages, both of which are significantly younger than the

meteorite age of 4.56 Ga. For the $^{206}\text{Pb}/^{204}\text{Pb}$ evolution line, this starting age is 4.40 Ga, whereas for $^{207}\text{Pb}/^{204}\text{Pb}$ it is 4.48 Ga. (This result of the analysis of Albarède & Juteau (1984) should formally be modified by adjusting the initial primordial isotopic composition for some amount of radiogenic growth during the time interval of 4.56 to 4.40 Ga ago (Galer & Goldstein 1996).)

There is a debate in the literature whether the combined ^{207}Pb and ^{206}Pb growth can be reconciled with a single, closed-system growth curve, which would define a sort of 'age of the Earth', or whether two-stage or multi-stage models are needed to explain the conformable lead data. What has not been sufficiently considered in this debate is the circumstance that the expectation of a single growth curve for lead isotopes from a truly primitive reservoir is unlikely from a geochemical point of view.

It was shown above that young conformable lead ores are predominantly derived from the continental crust, not the mantle. This is probably also true for ancient ores. However, ancient ores might be derived from crust that was rather 'juvenile' in that it had been separated from the mantle quite recently. In that case, the ancient lead ores might indeed track the isotopic composition of the ancient mantle. We can look for a comparison with isotope data for neodymium from ancient rocks. Unlike U/Pb, the relevant parent/daughter ratio, Sm/Nd, is universally believed to be identical in chondritic meteorites and in the Earth. We therefore assume that we know the evolution of the radiogenic daughter ratio, $^{143}\text{Nd}/^{144}\text{Nd}$, in the primitive mantle quite precisely from measurements on chondritic meteorites. Deviations of $^{143}\text{Nd}/^{144}\text{Nd}$ from the meteoritic value are conventionally expressed in epsilon units, so that $\varepsilon(\text{Nd}) = 1$ represents a deviation of one part in 10 000 from the chondritic value for a given age. A review of the enormous literature on Nd isotopes is beyond the scope of this paper. It is sufficient to note here that the majority of ancient crustal rocks have initial $\varepsilon(\text{Nd})$ values ('initial' meaning at the time of their formation; see also Lewis 2001) that are greater than zero. This means that the mantle from which these ancient crustal rocks were derived was no longer truly primitive but had already been differentiated, and thereby changed its Sm/Nd ratio, by previous geological events. This conclusion has recently been challenged by Nägler & Kramers (1998) who suggested that the difference in $\varepsilon(\text{Nd})$ between ancient crustal rocks and meteoritic values might be caused by uncertainties in chondritic composition, analytical artefacts and interlaboratory bias. However, this issue is not resolved at

present. The search for the elusive truly primitive mantle reservoir will no doubt go on, but at present, we cannot rely on having such a reservoir available for sampling.

The U-Pb coincidence

Why do the time-integrated U/Pb ratios of the average continental crust and the MORB-source reservoirs (indicated on Fig. 1 by the growth curves for $\mu = 9.55$ and 9.26) differ by only about 3%? The reason is neither obvious nor completely understood. If we assume, for the moment, that BSE is actually 4.43 Ga old, then marine sediments and their source rocks, in order for their lead isotopes to coincide approximately with this isochron, must have had U/Pb ratios nearly identical (i.e. within about 3%) to that of BSE, at least on average and in a 'time-integrated' sense. One way or the other, lead and uranium must be enriched in the continental crust (relative to the mantle) by large but very similar factors. This is not at all what one would expect from a conventional geochemical point of view. The geochemically relevant properties of lead, its ionic charge ($Z = +2$) and radius ($r = 1.26 \times 10^{-10}$ m) in silicate structures, are similar to those of strontium ($Z = +2$, $r = 1.21 \times 10^{-10}$ m), and these properties normally govern the degree of compatibility of an element with mantle silicates, the degree of enrichment in mantle-derived melts, and ultimately the enrichment in the continental crust (Taylor & McLennan 1985; Hofmann 1988). Because of its slightly greater ionic radius, one would expect Pb to be only slightly more enriched in the continental crust than Sr. Taylor & McLennan (1985) estimate the enrichment factors of Rb and Sr in the continental crust over BSE to be 53 and 13, respectively; Rudnick & Fountain (1995) estimate enrichment factors of 97 for Rb and 16 for Sr. This means that the average Rb/Sr ratio of the crust is four to six times greater than that of the primitive mantle. Uranium, in spite of its lower ionic radius (1.12×10^{-10} m), is also highly incompatible because of its greater ionic charge (+4). Its enrichment factor in the crust (70) (Rudnick & Fountain 1995) is only slightly lower than that of Rb. These considerations lead to the expectation that continental crust should have much higher U/Pb ratios and much more radiogenic lead than the mantle from which it is made.

To illustrate how far the actual lead isotope data are from what a geochemist might expect, we assume, for the moment, that both U and Pb behave geochemically like ordinary incompatible lithophile elements. Using ionic radius as a

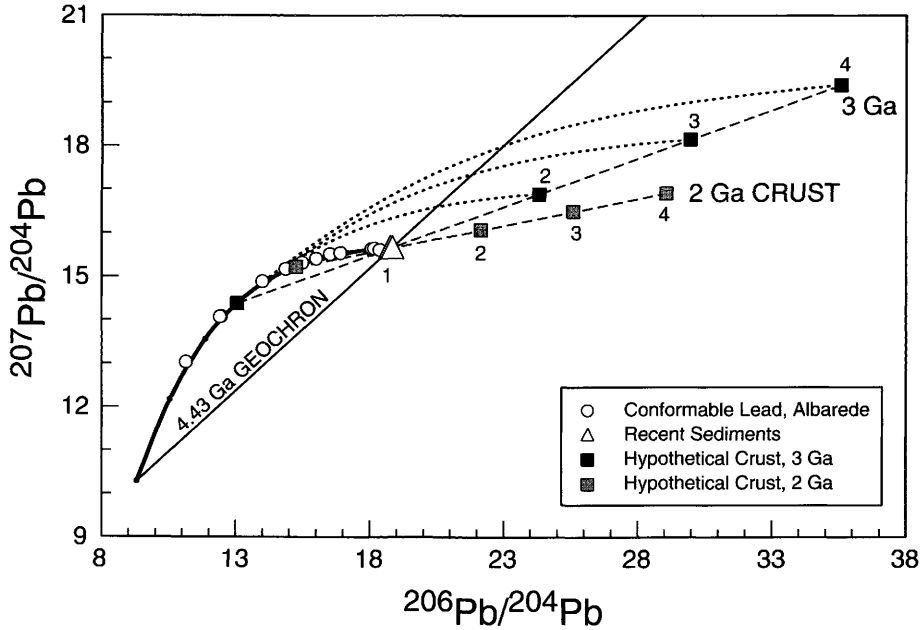


Fig. 3. Geochemically expected evolution of a hypothetical, average continental crust, assuming that U and Pb are partitioned into the crust in a manner similar to Rb and Sr, respectively. Dotted lines are evolution curves assuming U/Pb ratios that are two, three and four times greater than the primitive-mantle value. Black squares represent calculated, hypothetical, present-day compositions of 3 Ga old crust; shaded squares represent 2 Ga old crust. Also shown are conformable lead data (open circles), using the selection of Albarède & Juteau (1984) and recent sediments (open triangles), representing the actual upper continental crust, as in Figure 1.

guide, we further assume that the partitioning behaviour of U and Pb is similar to that of Rb and Sr, respectively, so that the crustal U/Pb ratio (or μ value) should be two to four times higher than the primitive BSE value. Figure 3 shows the hypothetical Pb isotopic compositions of average present-day crust, assuming that the crustal U/Pb ratio is greater than the primitive mantle ratio by factors of two, three and four, and for mean crustal ages of 2 and 3 Ga. This shows that the Pb isotopic composition of such a crust would be expected to be far more radiogenic (with $^{206}\text{Pb}/^{204}\text{Pb}$ values ranging from 22 to 36) than the observed values of recent sediments and conformable lead deposits ($^{206}\text{Pb}/^{204}\text{Pb} < 19$), and also quite far from any present-day geochron.

Therefore, the actual enrichment factor for lead must be three to five times higher than that of strontium. The reasons for this anomalously high enrichment of lead in the continental crust are not completely understood. However, it is quite likely that they are related to 'metasomatic' processes, specifically the hydrothermal transfer of lead from oceanic crust to sediments near ocean ridges (Peucker-Ehrenbrink *et al.* 1994)

and hydrothermal transfer from subducted lithosphere into island-arc magmas and ultimately into the continental crust (Hofmann 1997). Uranium is also mobilized within the continental crust. It is depleted in the lower crust and enriched in the upper crust (Rudnick & Goldstein 1990). Ultimately, a significant portion of the total crustal U inventory is lost by oxidation and dissolution during weathering and erosion. The fortuitous, net result of these different processes is that upper continental crust, average depleted mantle, and probably the primitive mantle all have Pb isotopic compositions that lie close to the 'geochron' shown in Figure 1 rather than far to the right of it as shown on Figure 3.

One might be tempted to explain away the isotopic similarity of continental crust and depleted mantle by invoking mixing processes between the two reservoirs. However, while mixing can reduce the difference between the extreme end members, it will not fundamentally change the slope of a line drawn between these end members in $^{207}\text{Pb}/^{204}\text{Pb}$ – $^{206}\text{Pb}/^{204}\text{Pb}$ space. In other words, extensive mixing might make the two reservoirs more similar to each other, but if the mean differentiation age between these end members is

on the order of 2 Ga, then mixing alone cannot generate an apparent 4.4 or 4.5 Ga isochron. How can such an apparent 'isochron', giving an age clearly in excess of the actual mean differentiation age, be generated from an initially (isotopically) uniform system?

Figure 4 shows an example of a class of possible models for the origin of continental crust, all of which require at least three stages of Pb isotope evolution, including at least one second stage of high μ (U/Pb expressed as $\mu \equiv (^{238}\text{U}/^{204}\text{Pb})_{\text{today}}$) and a third stage of relatively low μ . The earlier, high- μ stage accelerates the growth in $^{207}\text{Pb}/^{204}\text{Pb}$, and the later, low- μ stage retards the growth of $^{206}\text{Pb}/^{204}\text{Pb}$ while preserving the elevated $^{207}\text{Pb}/^{204}\text{Pb}$. Figure 4 shows a highly simplified, three-stage model for generating the Pb isotopic composition of bulk continental crust (Rudnick & Goldstein 1990), produced 2.5 Ga ago from a depleted mantle reservoir. For simplicity, this mantle is assumed to evolve with a single value of $\mu = 9.26$ to the present-day MORB composition, starting with primordial lead 4.43 Ga ago. Juvenile continental crust with a much higher value of $\mu_2 = 14.35$ was formed 2.5 Ga ago. It evolved for 500 Ma until 2.0 Ga ago, when it was differentiated internally and lost

a sufficient amount of uranium (presumably through internal differentiation followed by oxidation, weathering, dissolution and transport of U into the ocean), so that its U/Pb ratio was reduced to $\mu_3 = 7.0$. (This simplified example is intended for illustration purposes only and should not be taken as model for any actual crust-mantle evolution.) Without the low- μ stage 3 this crust would have evolved to present-day Pb isotope ratios of $^{206}\text{Pb}/^{204}\text{Pb} = 21$ and $^{207}\text{Pb}/^{204}\text{Pb} = 5.9$ (end point of the dashed evolution curve in Fig. 4), quite different from any reasonable estimate of the actual composition. Only by reducing μ to a very low value ($\mu_3 = 7$) can the actual isotopic composition of bulk continental crust (as estimated by Rudnick and Goldstein) be reached. This example shows that the evolution of continental crust and MORB mantle, having generally very similar isotopic compositions but slightly different $^{207}\text{Pb}/^{204}\text{Pb}$ ratios, actually requires a very complex geological history. The final position of the continental crust (and of conformable lead ores) at elevated $^{207}\text{Pb}/^{204}\text{Pb}$, but close to the geochron of 4.5 Ga, thus requires a highly fortuitous interplay of growth parameters.

It is this *accidental* geochemical behaviour of the U/Pb ratio which is responsible not only for

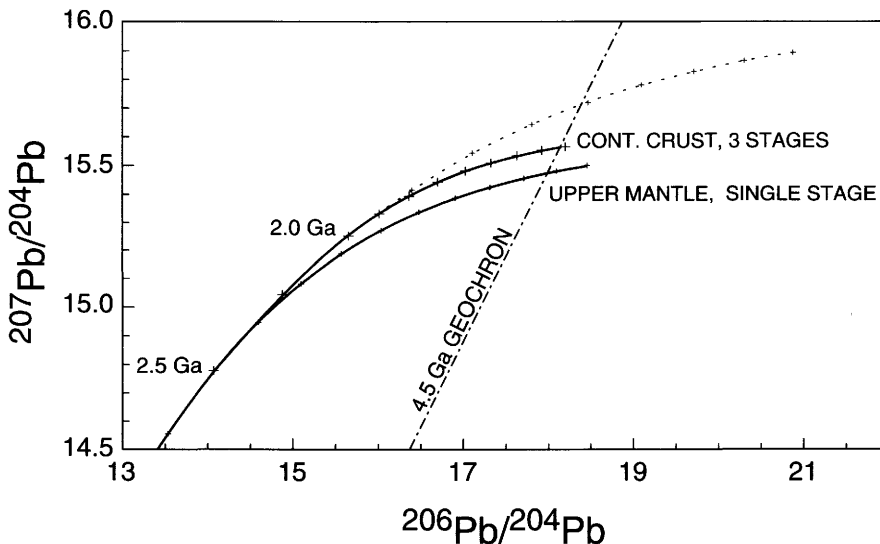


Fig. 4. Three-stage lead evolution model to explain the actual isotopic composition of the bulk continental crust (as estimated by Rudnick & Goldstein 1990). The lowermost curve, (labelled UPPER MANTLE) is a single-stage mantle evolution line which produces average MORB mantle in a 4.43 Ga old Earth with $\mu = 9.26$ (see Fig. 1). The uppermost, dashed curve represents a two-stage model forming a hypothetical crust 2.5 Ga ago with an elevated U/Pb ratio corresponding to $\mu_2 = 14.35$. The intermediate curve (labelled CONT. CRUST) requires three stages, where the third stage departs from the two-stage curve 2.0 Ga ago, when uranium was lost from the crust and U/Pb was reduced to $\mu_3 = 7.0$. This complex, three-stage model with a rather fortuitous sequence of μ values produces a bulk continental crust which lies approximately on a 4.5 Ga geochron (dash-dot line), similar to present-day MORB average which lies on a 4.43 Ga geochron.

Patterson's early perceived success of matching the present-day Earth with the meteorite isochron, but also for a voluminous geochemical literature on plumbology. This includes the concepts of the 'lead paradox' introduced by Allègre (1969), the long-term survival of the hypothesis of a single Pb isotope growth curve for lead deposits, particularly the isotopic evolution of 'conformable' lead deposits (Stanton & Russell 1959), the subsequent multi-stage evolution models (Cumming & Richards 1975; Stacey & Kramers 1975), the 'plumbotectonics' models of Zartman and co-workers (Zartman & Doe 1981), and the efforts of Tera (1980, 1981) to refine the estimate of the age of the Earth. All these concepts and developments are to a significant extent based on, or would not have been possible without, this 'geochemical accident', which produced the approximate equality of time-integrated U/Pb in crust and mantle. This accident probably does provide an approximately correct estimate of the age of the Earth within the broad bounds of uncertainty of about 150 Ma. This rough age estimate might still be in error, if the differentiation of the Earth did produce one or more additional, unsampled (or poorly sampled), isotopically very different reservoirs of lead in some region such as the lower continental crust, the subcontinental lithosphere, the lower mantle or the ocean island basalt source reservoir. In any case, if the reservoirs that we can sample well are not truly primitive, as I have argued above, then we cannot invert the Pb isotope data of terrestrial rocks to refine our estimates of the age of the Earth to closer limits than those given by other, independent information.

Other constraints on the age of the Earth

We have seen that lead isotopes provide only one powerful constraint on the age of the Earth, namely the upper bound of 4.56 Ga, the age of primitive meteorites, which can be measured rather precisely by U-Pb and by Pb-Pb methods. A lower bound is best determined by other methods, because chemical fractionation has obscured the precise record of Pb, Nd and Sr isotopes in the mantle, so that independent confirmation of any precise age derived from a particular selection of lead samples, 'conformable' or otherwise, fails. There are, however, other firm limits on the age of the Earth. A detailed discussion of the current best estimates of these limits is beyond the scope of this paper, and only a brief summary will be given here. For a more in-depth discussion of the early accretion history

of the Earth, the reader is referred to the recent literature (Wetherill 1986; Allègre *et al.* 1995; Galer & Goldstein 1996; Harper & Jacobsen 1996; Halliday & Lee 1999; Ozima & Podosek 1999; Halliday 2000).

The oldest minerals found in the Earth's crust were, until recently, 4.27 Ga-old detrital zircons from western Australia (Compston & Pidgeon 1986). Most recently, further investigation of the same population of zircons yielded a single grain with a concordant U-Pb age of 4.40 Ga (Wilde *et al.* 2001). If confirmed, this will provide a firm lower limit of 4.40 Ga for the age of the Earth. Current theory about the accretion history of terrestrial planets suggests that the accretion process lasted at least several tens of millions of years (Wetherill 1986). Therefore it may be impossible, or in any case not meaningful, to give an 'age of the Earth' with a very much higher precision than, say, 10 to 50 Ma. Given a total timespan between the age of the oldest meteorites and the age of the oldest terrestrial minerals of only about 150 Ma, we may hope to refine the estimate of the 'true' age of the Earth a little further, but probably by less than an order of magnitude. As Claude Allègre once remarked in a lecture, most of us know on which day we were born, some of us know during which hour we were born, but none of us knows the exact second.

One way of determining a reasonable lower limit for the age of the Earth is to accept the widely held view that the Moon was created as a result of a very large impact on Earth at a stage when it was already close to its present size. In this case the oldest lunar rocks provide another lower limit for the age of the Earth. The compilation of ages of the oldest lunar rocks provided by Dalrymple (1991) shows several values ranging in age from 4.0 to 4.51 Ga. Dalrymple concluded from a careful review of the evidence that 'even the most conservative interpretation of the data ... leads to the conclusion that the Moon's age must exceed 4.4 Ga'. His overall conclusion of this review is, however, that 'the Moon is at least 4.5 Ga in age'. This conclusion is consistent (within the quoted uncertainty) with the more recently determined Sm-Nd age of 4.56 ± 0.07 Ga of a lunar anorthosite (Alibert *et al.* 1994) and a combined U-Pb and Pb-Pb age of 4.51 ± 0.01 Ga of another lunar anorthosite (Hanan & Tilton 1987).

The decay products of short-lived, now extinct radioactive nuclides also provide constraints on the formation history of the Earth. These nuclides were produced by nucleosynthesis in stars just prior to the condensation of the solar nebula. They were still 'alive' at the time of

formation of meteorites 4.566 Ga ago, and they can be used to decipher a chronology of the earliest history of the solar system.

One of these short-lived nuclides is ^{182}Hf , which has lithophile affinities and decays to ^{182}W (with siderophile affinities) with a half-life of only 9 Ma. Halliday and co-workers have discovered that terrestrial rocks and carbonaceous chondrites have identical relative abundances of ^{182}W , whereas iron meteorites are deficient in ^{182}W (Halliday & Lee 1999). This deficiency means that tungsten was sequestered into the metal cores of ancient planetesimals before all of the ^{182}Hf had decayed. If the Earth's core had formed at the same time as the iron meteorites, namely within a few million years after the formation of chondritic meteorites 4.566 Ga ago, it would have the same deficiency in ^{182}W as the iron meteorites, and the silicate portion of the Earth would have a complementary relative excess. On the other hand, if the segregation of the core occurred several half-lives later (about 50 Ma or more), after nearly all of the ^{182}Hf had decayed, then the tungsten must have the same isotopic composition in the core and in the mantle. This would be identical to the tungsten isotopic composition of chondritic meteorites, and this is what Halliday and co-workers observed. In principle, this could mean that core formation was delayed relative to the formation of the Earth. However, assuming that current slow Earth accretion models (Wetherill 1986) are correct, it seems more plausible to infer that the protracted accretion process itself caused the delay in core formation (Halliday 2000).

Other evidence for either delayed or slow formation of the Earth comes from xenon isotopes. Ozima & Podosek (1999) have recently reviewed the evidence derived from the differences in the abundances of ^{129}Xe , the decay product of ^{129}I ($t_{1/2} = 16$ Ma), and ^{136}Xe , the decay product of spontaneous fission of ^{244}Pu ($t_{1/2} = 83$ Ma). The Earth's atmosphere is deficient in both ^{129}Xe and ^{136}Xe relative to meteorites, and this can be explained if iodine and plutonium were incorporated into the Earth some 50 to 100 Ma later than the age of meteorite formation and if the Earth's present-day atmosphere was produced by subsequent outgassing of the mantle.

In detail, all the considerations based on extinct radioactivity are somewhat model-dependent and cannot be expected to give highly precise estimates of the age interval between the formation of meteorites and that of the Earth. Nevertheless, all of the different lines of evidence appear to be consistent with the interpretation that the Earth reached a size close to its present value between 4.50 and 4.40 Ga ago. The fact

that this conclusion is not very different from Patterson's original estimate and from the subsequent, more detailed evaluations of conformable lead ores is the result of a 'geochemical accident', namely the amazing similarity of time-integrated U/Pb ratios in averaged mantle and crustal reservoirs. This similarity is all the more remarkable as the compositions of both reservoirs are internally very heterogeneous. It is this stroke of luck which has given us such remarkably close estimates of the age of the Earth from lead isotopes, even though hindsight clearly reveals that the necessary assumption of the Holmes–Houtermans model and the conformable lead model, namely the survival of one or more closed systems of primordial age, has been grossly violated during the Earth's evolution.

I wish to thank G. Wasserburg for drawing my attention to G. B. Dalrymple's admirable book *The Age of the Earth*, Dalrymple for writing it, and C. Lewis for inviting me to help Celebrate the Age of the Earth, and for encouraging me to write this article. G. B. Dalrymple, S. Galer, A. Halliday, C. Hawkesworth, I. Kramers, S. Moorbath and I. Tolstikhin helped by discussing important issues and/or reviewing an earlier version of this manuscript. I thank them all for their efforts and their positive feedback, which, both in spite and because of the great diversity of opinions, helped enormously in preparing the final draft. None of these people should be held responsible for any blunders the reader may still find in this article.

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